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Criteria 3.3.2	**Number of books and chapters in edited volumes/books published and papers published in national/ international conference proceedings per teacher during last five years**
Findings of DVV	Please submit the cover page, table of contents, and the first page of the chosen publication, along with a web link for books.
Response/ Clarification	Scanned copies of cover page and first content pages of all books and chapters in edited books as per data template are attached year wise **(Appendix I)** ***Note :*** *All books are verified with ISBN numbers. Weblink of books are not available as they are published by local publishers.*

Principal
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Appendix I

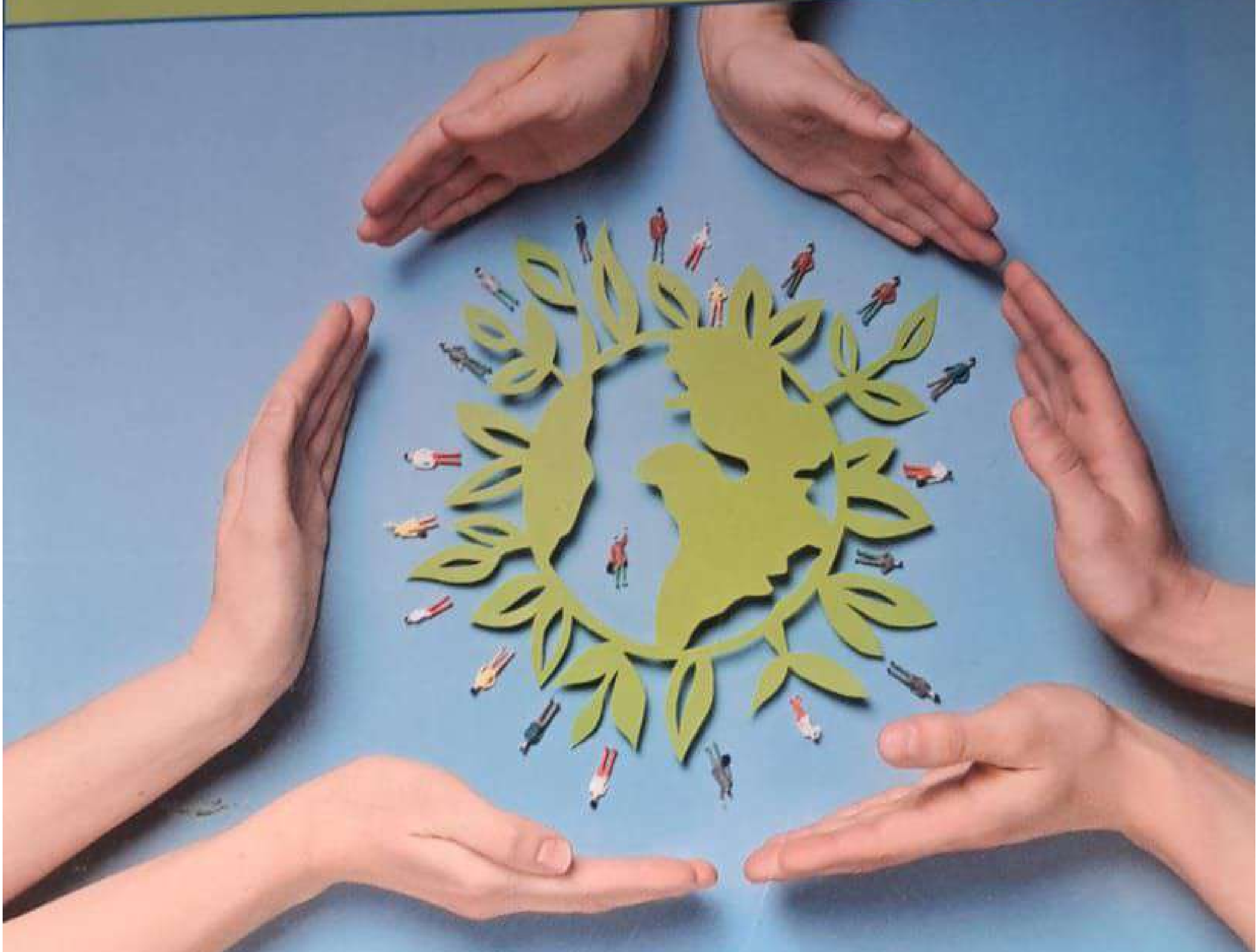
Sem - IV

B.A.- II

मानवी भूगोलाचा परिचय

(Introduction To Human Geography)

डॉ. योगेंद्र शंकरराव नगराळे



Sir Sahitya Kendra

लेखक परिचय

डॉ.योगेंद्र शंकरराव नगराळे

शिक्षण - एम .ए .भूगोल ,नेट ,पीएचडी ,
एम.ए. मराठी ,एम. ए. राज्यशास्त्र ,बी .एड.
अध्यापन -साईबाबा कला व विज्ञान महाविद्यालय
पारशिवनी, तालुका पारशिवनी जिल्हा नागपूर येथे 6
वर्षापासून भूगोल विभाग प्रमुख

संशोधन

पीएच.डी.-"यवतमाळ जिल्ह्यातील वणी कोळसा
क्षेत्रातील खाणकामाचा कृषी व पर्यावरण यावर
होणारा प्रभाव "(कालखंड 2001 ते 2011)

सदस्य

आयुषी इंटरनॅशनल इंटरडिसिप्लिनरी रीसर्च जर्नल
संशोधन लेख- विविध शोध पत्रिकेमधून 5 लेख प्रसिद्ध.
विविध राष्ट्रीय व आंतरराष्ट्रीय कार्यशाळा मधून 4
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  हुडकेश्वर रोड, नागपूर - ३४
  मो. ९५६१८६५०१९, ९८६०२२२९४१

- मानवी भूगोलाचा परिचय भाग - १
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6

Nanoparticles for sustainable agriculture: innovative potential with current and future perspectives

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Chapter outline

6.1 Introduction

The mother earth is in the midpoint of the sixth mass extinction of life. Researchers have estimated that approximately 180–190 birds, amphibians, insects, mammals, and plant species become globally and locally extinct daily. This rate is almost 1000-fold more than that of the natural extinction rate due to global climate change and anthropogenic activities. Taking such burning issues into consideration and to promote strategic action plan, the period 2011–20 was

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declared as the United Nations (UN) Decade on biodiversity; 2020 as the international year of plant health; and 2021–30 as the UN Decade on ecosystem restoration.

In the period of global climate shifting, agriculture sectors are facing several unusual challenges. Very few number of cultivated crop species are available on which global agriculture is heavily dependent, which indicates to optimize productivity within a relatively narrow range of environmental variations (Kukal & Irmak, 2018). Climatic extremities cause a huge loss of crop production. To combat the effects of such extreme events, mitigation strategies are required alongside the global drivers of agricultural production (Dhankher & Foyer, 2018; Nutan et al., 2020; Schewe et al., 2019). The recent ongoing advancements in the field of plant and agri-biosciences have the potential to address these challenges (Bailey-Serres et al., 2019) as far as food and nutritional security is concerned but not the environmental safety.

Recent advancement in nanotechnologies research supports the pathogens, pesticides, and toxins, tracking–tracing–monitoring system that can assure food quality (Sahoo et al., 2021). Nanotechnology will positively lead sustainable agriculture (Prasad et al., 2017), with the formulation and fabrication of more sophisticated nanoagrochemicals, with a lower impact on the environment and human health. Technological innovations in nanoengineering demonstrate multidisciplinary relevance in targeted agrochemical delivery system that is still under progressive development. Moreover, these unique properties and diverse applications of nanomaterials (NMs) prove to be the novel material for the future (Chouke et al., 2022). Thus the cross-pollination of biological ideas and environmental conditions with nanotechnology has significantly increased their potential to identify, develop, and design innovative tools for agricultural uses that possibly help one to satisfy the ever-increasing food demand and environmental sustainability in the age of negative environmental externalities.

6.2 Nanopesticides: agro-based formulations for pest control

Agrochemical technology is classically meant to improve crop health and restrict pests that compromise crop yields. The unscientific and overuses of pesticides to control pests adversely affect crop productivity (Bombo et al., 2019), which leads to pathogen resistance, biodiversity loss, and affect nitrogen fixation, and increasing chances of bioaccumulation of pesticides in agriecosystem. Approximately, half of the applied pesticides saturate in farmlands that contaminate the aquatic bodies. Agrochemicals-based nanoparticles (NPs) enhance overall contact with the crop pest that makes them more competent due to their higher total surface area occupancy (Osorio-Echavarría, 2021; Pérez-Iglesias, 2019; Umekar et al., 2021; Vigneshwaran, 2006). In the modern farming the nanocarrier strategies are significantly used to reduce pesticides application rates and overcome environmental imbalance (Kah & Hofmann, 2014; Kah et al., 2018). Agrochemical-based nanopesticides formulations find wider application over chemical pesticide formulations. Bioinspired NMs formulations with pesticidal activities (nanobiopesticides) are sustainably and effectively used to protect crops against the target pests with improved stability and absorption rate (Borgatta et al., 2018; de Oliveira et al., 2019). It also minimizes adverse environmental consequences and maintains health and integrity of agro-ecosystem.

Nanopesticides are nanoengineered materials are employed in plant protection that increases leaf coverage and stability and reduces the quantities with minimal application losses. In general, nanopesticides formulations can be classified into dendrimers, liposome, metallic and bimetallic NPs (e.g., copper, copper oxide, silver, zinc oxide, silicon dioxide, manganese dioxide, and titanium dioxide), and dynamic encapsulating components such as polymeric NPs, nanoemulsion, lipid NPs, and nanotubes. Several nanosized materials, namely, ceramic, silica, metal, lipids, polymers, copolymers, and carbon, are used to investigate pesticidal efficacies in nanocarrier-mediated formulations (Agostini et al., 2012; Bratovcic, 2020; Chaud et al., 2021; Chaudhary et al., 2019; Chouke et al., 2019; Elmer et al., 2018; Guilger-Casagrande et al., 2019; Lakshmeesha et al., 2020; Shukla et al., 2020). Carbon nanotubes can be used as a biosensor with systemic-release-system for agrochemical pesticide and fertilizer. The carbon nanotubes increase the biomass of the plants, seed germination, and the length of shoot and root (Sarlak et al., 2014), but due to reactive oxygen species (ROS) it leads to cell death (Vithanage et al., 2017). RNAi technologies are designed for gene silencing in insect having multidrug-resistance capacity (Parsons et al., 2018). Due to sequence-specific endogenous RNAi, a novel genetic material delivery—nonencapsulated system is used as pest control strategies (Fletcher et al., 2020).

Recently in agriculture sector, formulation and designing of emulsion-based nanopesticide carriers is a subject of research interest for the systemic release of agrochemicals. The mesoporous silica NPs loaded with azoxystrobin showed more loading content, pH-driven controlled release, and better fungicidal effect in the tomato plant (Xu et al., 2018). Several emulsion-based nanopesticide formulations are designed for pest and weed control (Hazra & Purkait, 2019; Mustafa & Hussein, 2020). The nanoencapsulation of neem and citronella oil biopesticides is used for better efficacy and to improve water solubility using spontaneous emulsification technique. It showed an excellent fungicidal activity (Ali et al., 2017). Adopting the same scientific approach, Hasheminejad et al. (2019) prepared a clove oil encapsulated chitosan-based NPs effective against fungi along with prolonged release of the active ingredient. β-Cyclodextrin encapsulated chitosan NPs, coloaded with linalool, and carvacrol, enhanced insecticidal activity against cotton bollworm and red spider mite (Campos et al., 2018). Liposomes-mediated nanocarriers are designed for easy release of active compound and to preserve it from thermal degradation and photodegradation. Liposome-based nanocarriers can extend the period for the delivery of active agrochemical ingredients, depending on specific properties and types of the compounds used (Bang et al., 2011; Huang et al., 2018; Hwang et al., 2011; Jampílek & Kráľová, 2017).

Synthesis of environmentally safe and cost-effective metallic NPs is generally recognized. Due to a large surface area, metallic NPs have a broad spectrum of action against plants pathogens due to its antimicrobial biochemical behavior and have negligible risk of resistance development (Keller et al., 2017; Malandrakis et al., 2021; Santos et al., 2021). However, pulmonary inflammation (Worthington et al., 2013), immune response, and bioaccumulation on living organisms have been recognized with the exposure copper NPs coating with polysaccharides (Zhang et al., 2012). Silver NPs sulfidate rapidly in the reducing environments that would minimize cytotoxicity and environmental toxicity of AgNPs

(Potbhare et al., 2020a). The nanopesticide formulations can control crop pathogens by increasing their water solubility and bioavailability, and also avoid their environmental degradation (Yadav et al., 2020). The potential of nanopesticides in the pest control in consonance with environmental stimuli can avoid the early complexation and restrain the sulfidation reaction (Agostini et al., 2012; Gao et al., 2021). The effect of nanopesticides formulations in the environment, consumers, workers, and other all associated in the agriculture chain is poorly known (Huang et al., 2015). Depending on the material used, it can produce a toxic effect in plant, human, and other vertebrate classes (Potbhare et al., 2020b).

To understand the toxicity and ability of the NPs to interact with the human biomolecules, more research is being conducted by various researchers. However, enhanced toxicological risk is likely to be associated with nanotechnology-based agrochemicals that can threaten ecosystems and human health (Mustafa & Hussein, 2020; Yadav et al., 2020). Despite lot many advances achieved in nanopesticide formulations for pest control, still direct interactions of NMs between plant products and environment need to be extensively evaluated in terms of bioaccumulation, bioavailability, toxicity, and public health (Chaud et al., 2021; Kah et al., 2019; Lowry et al., 2019; Pascoli et al., 2018; Sanzari et al., 2019; Tiple et al., 2020). The good sides of nanopesticides in crops are understood well, while its negative impacts such as retention time, reactivity, bioaccumulation levels, degradation time, and pollination behavior and food safety are poorly understood. More scientific research on nanopesticides and financial support is needed to understand its linkages and interaction with biochemical pathways. Meanwhile, it is needed to formulate the best possible long-term strategies on the selection of specific nanopesticides materials for synthesis that would get a very negligible genotoxic effect. In that way, nanopesticides usage policy can satisfy the agricultural pest control demand and thereby safeguard agri-workers' health and ecosystems.

6.3 Nanofertilizers: recent trends and prospect in agriculture system

The development of world economy and abundance of victuals for a better living depends predominantly on agriculture. The current global climate change poses great adverse challenges, for agriculture sector, namely, soil contamination/erosion, less production of crops owing to pests (De La Torre-Roche et al., 2020; Kah et al., 2019; Lowry et al., 2019; Pouratashi & Iravani, 2012), incessant use of pesticides and fertilizers, resulting in environmental contamination (Lowry et al., 2019; Sonkusare et al., 2020; Zhao et al., 2020). Sustainable strengthening is a design associated with a production of crop that aims to enhance the yield without adverse ecological impact whilst cultivating the same farming region (Baulcombe et al., 2009). This measure supports an outline to review the finest alternative to farming considering all the relevant factors (Garnett & Godfray, 2012). To hand out these relevant issues, novel techniques and strategies are continuously progressing. NP-based agricultural product introduction is one such step taken for revolutionizing modern agricultural practices. Nanofertilizers contain macro- and microelements required for crop growth and development that are supplied in a controlled manner. NPs (Jeevanandam et al., 2018) and nanoengineering improve crop production and assure sustainability with enhancing the competence of input and minimize significant losses. The engineered NMs act as an exclusive carrier of agrochemicals aid with site-targeted controlled release of nutrients support high-tech agriculture system. Intelligent nanofertilization system finds application in control nutrients discharge in soil that benefits to reduce leaching with an improved uptake of nutrients by crops and extenuating eutrophication (Liu & Lal, 2015) by restricting the nitrogen enrichment to groundwater. NMs reduce nutrient losses and improve utility by rising solubility, increasing resistance against hydrolysis and photodegradation by offering precise and proscribed discharge toward objective organisms (Mishra & Singh, 2015; Nuruzzaman et al., 2016; Sonkusare et al., 2018; Usman et al., 2020), and curtail the expenditure to exploit better output on products for crop fortification.

Innovation in agri-biosciences greatly promotes the research on NPs that plays a diverse role in agricultural system as nutritional supplements and soil monitoring tool, and as nanocapsules to carry slow and constant release of nanofertilizers and nanopesticides, or even uses in genes transfer to plant target sites (Gnanamangai et al., 2017; Kamle et al., 2020; Ma et al., 2018) (Fig. 6–1). Nanofertilizers have been proposed as a sustainable agricultural tool for the next 30 years due to the feasibility of slow-release means of nitrogen and phosphorus that results in rise of crop production by up to 30% with minimal inputs (Kah et al., 2018; Kalia et al., 2019) (Fig. 6–1). Nanofertilizers are applied in smaller quantities compared to traditional fertilizers that could be crucial development in the environment protection (Adisa et al., 2019), in terms of reducing runoff, leaching, and gas emissions (Manjunatha et al., 2016). Nanosized ammonia, urea, ammonium humate, plant wastes, and peat particles are being employed to prepare nanosized fertilizers (Taiz & Zeiger, 2010; Wan et al., 2010) (Fig. 6–1). Applications of P, Zn, Fe, and Mg NPs remarkably improve (three to four times) nutrient use efficiency by facilitating a slow-release nutrients thus help crops for required nutrient uptake (Jyothi & Hebsur, 2017; Kalia & Sharma, 2019; Manjunatha et al., 2016). Incredible boost was observed in organic acid and phosphorous uptake in the rhizospheric zone of plants after an application of nanophosphorous (Tarafdar & Adhikari, 2015). Similarly, it is observed that nanostructured 2D clays can enhance nutrients uptake efficiency (Lazaratou et al., 2020).

Foliar NPs improved seed germination (Zhao et al., 2020), increased shelf life of agricultural produce, improved absorption and assimilation of foliar fertilizer (García-López et al., 2019), and reduced damage by abiotic stresses (Elsheery et al., 2020). Foliar application of one or many NPs collectively accelerates the activity of antioxidative enzymes and improves resistance against stress (Ei et al., 2020; Faizan et al., 2021; Gao et al., 2020; Ogunkunle et al., 2020). It is demonstrated in growth chamber experiments that the ability of the amorphous-calcium–phosphate nanofertilizer to enhance quality and yields of the wheat grains (Ramírez-Rodríguez et al., 2020a, 2020b). N-doped nanofertilizers may open a bright future for urban and vertical farming in soilless (hydroponic) conditions (Beacham et al., 2019) (Fig. 6–1), and a new way to enhance output, mainly in arid and densely populated areas with limited lands (Sambo et al., 2019). In brief, fertilizers encapsulated with NPs have broad outlook for preparing plant-nutrient supplements with more use efficacy.

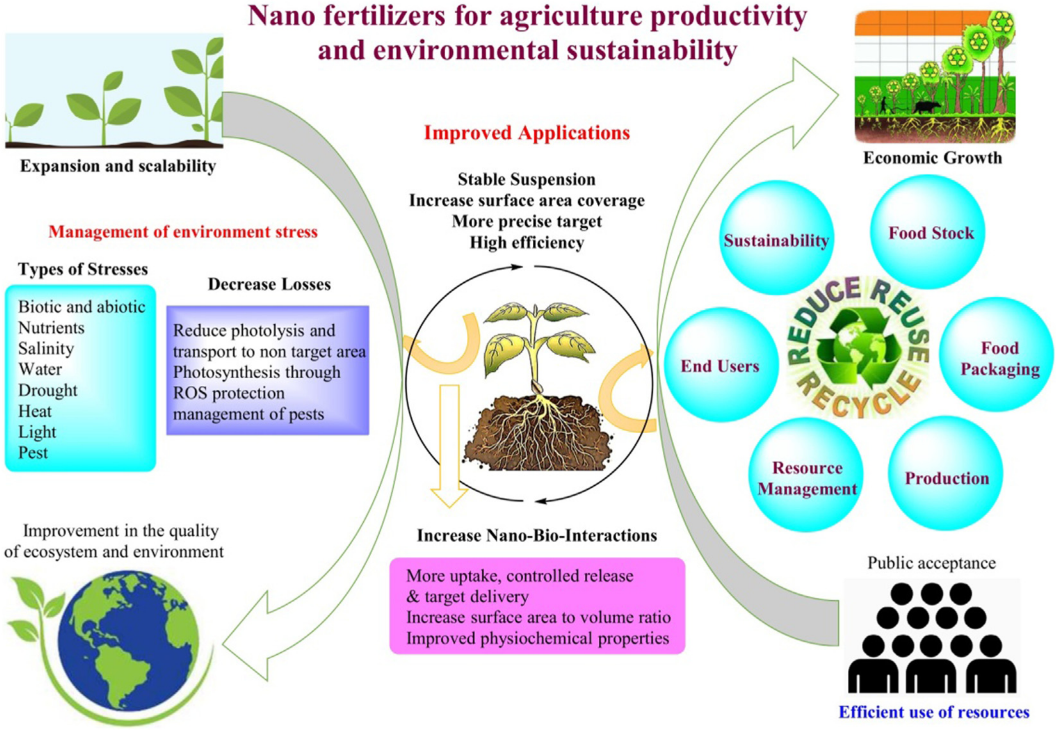

FIGURE 6–1 Schematic representation of efficient use of nanofertilizers for agriculture productivity and environmental sustainability.

6.4 Nanoparticles: uptake, translocations, and plant growth

It is evident that the use of NPs influences the growth and development of plant that comprises seedling vigor, photosynthesis process, and growth of plant parts such as roots and shoots. Lv et al. (2015) and Su et al. (2019) comprehensively reviewed and explained the uptake, transport, and fate of NMs. Physiological and structural variations in plants show variations in uptake patterns of various classes of NMs, such as TiO_2 and carbon-coated Au (Gandhare et al., 2016; Larue et al., 2012). Uptake of NMs depends upon the mode of exposure and the ability of plants (Schwab et al., 2016). Soil organic matter, humic acid, mycorrhizal fungi, and bacteria enhances the uptake and access of NPs to plants (Feng et al., 2013; Navarro et al., 2012). NMs change the confirmation of cell membrane proteins with the help of their energy and surface charge (Juárez-Maldonado et al., 2019; Pérez-de-Luque, 2017). Usually, plasmodesma develops cytoplasmic connections to assist the movement of NPs between adjacent cells during translocation (Dietz & Herth, 2011). Wang et al. (2012) reported the translocation of CuO NPs from roots to shoots and wise versa through vascular tissues. The negatively charged plant cell-walls component act as the surface for positively charged NPs (Meychik et al., 2005; Santiago et al., 2013; Zeng et al., 2017).

Related to the previous observation, surface charge-dependent uptake of Au NPs in roots and its translocation from roots to shoots was investigated (Milewska-Hendel et al., 2019). They also observed that negatively charged NPs support both transport pathways (symplastic and apoplastic) into the vascular system. More root surface areas in tomato and lettuce plants were observed when treated with positively charged cerium oxide NPs, while improved root to shoot movements were observed with neutral and negatively charged cerium oxide NPs (Spielman-Sun et al., 2019). NPs are mostly deposited on the cell wall of the guard cells or subsidiary cells of stomata or stomatal opening when entering through the stomata that was proved by Fe_3O_4 NPs, through transmission electron microscopy studies (Cai et al., 2020). In the view of above context, Li et al. (2020) also observed a biotransformation of Ag NO_3 applied with AgNPs (24.8–38.6 nm) within *Lactuca sativa* leaves. Su et al. (2020) observed that NPs (ZnO and Cu) affect seed germination in Mung bean plant (Raja et al., 2019). Rahman et al. (2020) examine the seed germination and growth-enhancement effect in a pea plant with the polyvinyl–pyrrolidone-protected platinum NPs treatment. Chitosan-based NPs show positive effect on seed germination and growth of wheat even at a very lower concentration (Li et al., 2019).

Govea-Alcaide et al. (2016) tracked Fe_3O_4 NPs in plant tissues by applying magnetic properties. Raliya et al. (2016) quantified the AuNPs by using inductively coupled plasma mass spectrometry (ICP-MS) to observe the uptake pathway and saturation in *Citrullus lanatus* plants. When garlic leaves were treated with TiO_2 NPs, it is observed that of chlorophyll content and photosynthetic rate were enhanced (Bharti et al., 2018). Mozhayeva and Engelhard (2020) suggested that single-particle ICP-MS (SP-ICP-MS) analysis serves as a promising and reliable method for the detection, characterization, and quantification of NMs. Earlier, with the help of single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) technique, Keller et al. (2018) quantified the uptake of CuONPs in various edible plants, while Wojcieszek et al. (2019) used SP-ICP-MS and electrospray ionization (ESI) tandem MS to confirm the fate of ZnO NPs inside the edible plant lettuce. Nath et al. (2018) used SP-ICP-MS, scanning electron microscopy, and energy-dispersive x-ray spectroscopy (EDS) to study simultaneous uptake, retention, and distribution of Cu, Ag, and ZnO NPs in *Arabidopsis thaliana*, while Deng et al. (2017) utilized the SP-ICP-MS, electron microscopy, and ICP-optical emission spectroscopy (OES) techniques to understand the size, distribution, and uptake of TiO_2 NPs in rice. NPs caused injury to the plant when applied with higher dose. Yuan et al. (2018) observed the increased plant growth and extra gain of chloroplast content in *Capsicum annuum* when treated with lower concentrations of Fe NPs.

6.5 Recent advances in nanoparticles for plant protection

Plant grows ubiquitously in nature in diverse habitat; therefore they tolerate environmental extremities. Plant shows various kinds of stress responses against biotic and abiotic stresses. Depending on the stress, it modifies stress-responsive gene regulation and produces antioxidative enzymes that play a significant role in protecting the plants from stresses (Rejeb et al., 2014; Sharifi et al., 2020). SiO_2 NPs improve the water use efficacy, enhance transpiration rate, accelerate carbonic anhydrase activity, and increase chlorophyll content in the *Cucurbita pepo* against abiotic stress (Siddiqui & Al-Whaibi, 2014).

Abiotic stress minimizes the photosynthetic efficacy of the plant that led to influence the additional ROS production with an oxidation of biomolecules (Wakeel et al., 2020). Nanoceria (CeO NPs) showed extensive linkages with positive and negative plant health and growth conditions (Milenković et al., 2019). Nano-Ce acts as an antioxidative agent that regulates ROS by scavenging pathways (Chaudhary et al., 2020; Collin et al., 2014) (Fig. 6–2) and improves the resistance against a range of abiotic plant stresses. Si NPs can interact with plants directly or indirectly by conferring morphological and physiological changes (Babajani et al., 2019) (Fig. 6–2) to afford tolerance against drought stress (Ashkavand et al., 2015) and under saline environment at various concentrations by maintaining osmotic and ionic balance that enhance the antioxidant system, along with increased levels of various phytopropanoids (Soleymanzadeh et al., 2020). Interestingly, it is observed that the application of SiNPs in strawberry plants leads advance structure and thickness of epicuticular wax as compared to salt-stressed plants (Avestan et al., 2019) (Fig. 6–2).

The enzymatic and nonenzymatic defense mechanism can be triggered by the TiO_2 NPs against stress in plants. Karamian et al. explained that methyl jasmonate, salicylic acid, and TiO_2 NPs reduce drought stress in medicinal plants. TiO_2 NPs-treated plants show higher chlorophyll content and biomass by maintaining the osmotic balance and antioxidant enzymes pathways (Karamian et al., 2020). TiO_2 NPs regulate the synthesis of glutamate dehydrogenase and glutamine synthase thereby accumulates more nutrients and essential oil content in plants (Ahmad et al., 2018) under normal conditions. This concludes that aromatic plants can be protected against the stress by changing essential oil synthesis profile and composition (Gohari et al., 2020). TiO_2 NPs enhances the accumulation of osmolytes by recovering the hydration status of the plant. It can increase the activity of the nitrate reductase enzyme that induces proline and glycine betaine synthesis that leads to nitric oxide production (Khan et al., 2020).

6.6 Nanomaterials as agents to smart monitoring

Agro-nanotechnology is an emerging field where the reduction of biotic stress is a novel sustainable approach employed for improving plant growth (Khan et al., 2021) and overall health. Khot et al. (2012) stated that Au, SiO_2, ZnO, and TiO_2 carbon nanotubes and NPs can accelerate the nutrients and elemental uptake and improve the plant development. Nanosensors may be connected with self-directed sprinkling controllers for estimating soil–water tension in real time. This attribute offers management of sustainable irrigation on the basis of drying soil (de Medeiros et al., 2001). Nanosensors are sensitive and cost-effective, which perform quick operation in detecting various targets related to food qualities. Moreover, nanosensors are amongst one of the emerging technologies that might challenge the estimation of food safety and quality, being capable of providing a smart monitoring of food ingredients and impurities. A nanosensor plays a significant role in intelligent packaging along with monitoring the food and checking of the integrity of the packages during transport, storage, and display in markets (Vanderroost et al., 2014). Furthermore, nanosensors can be employed in monitoring physical parameters of agri-produce such as freshness, decomposition, and to trace out pathogens and toxins.

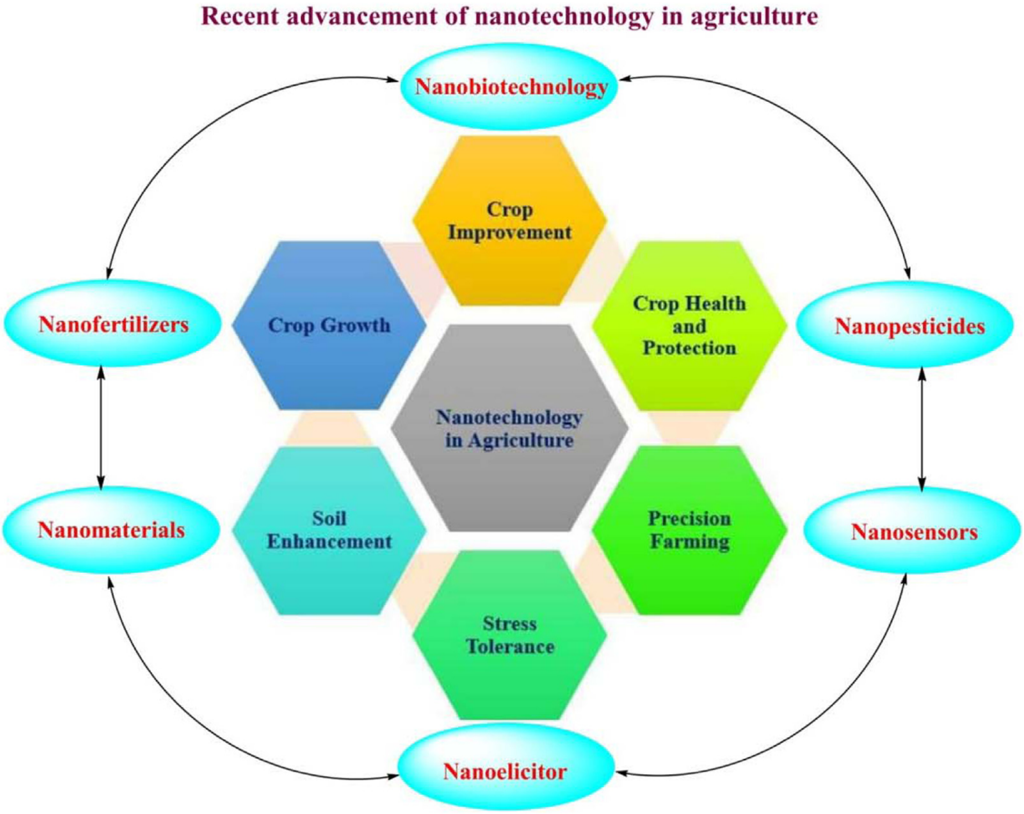

FIGURE 6–2 Application of nanotechnology-based nanofertilizers and nanopesticides to improve crop growth, protection, yield, and productivity. Nanosensors can greatly contribute to precision farming. Nanomaterial-mediated gene transfer to organelles/cell can be used for crop improvement.

6.7 Nanoparticles for managing the agricultural postharvest waste

Recent literature has highlighted that nanotechnology offers a variety of applications in the agricultural postharvest waste management. The aerogel is a very hydrophilic nanoscale cellulosic material that has diverse applications in postharvest management. Agricultural waste has more amount of lignocellulose that can be used to prepare nanocomposites (Othman, 2014), nanocellulose (Shahabi-Ghahafarrokhi et al., 2015), nanohemicellulose, nanolignin, nanopectin, and nanoxylan. A cellulose biopolymer is the most abundant component of cell wall of the tree. Nano- and holocellulose aerogels are employed widely as adsorption materials owing to the nanofibrillar structure with some unique properties (Dai & Fan, 2013; Muñoz-García et al., 2015). Rice and wheat husks waste can be used to produce value-added nanoproducts to tackle the agricultural disposal problem (Kaur et al., 2016) by utilizing electrospinning technique (Ramakrishna et al., 2006). The rice husk is an excellent material for nano- and microsilica that can be utilized to extract silica. The nanosilica in conjugation with valid amycin has been effectively used to control the delivery of water-soluble pesticides (Liu et al., 2006). Huang et al. (2015) reported that the nanosilica conjugates promote plant growth and act against mildew diseases.

6.8 Future perspective

Nanotechnology has diverse and promising applications in different domains of the agriculture practices and agriculture-based processing industries. However, most of the information is gathered mainly from laboratory experiments performed by various researchers. The application and practical relevance of NPs-based agrochemicals need to be investigated in details with basic understanding by their impact on socioenvironment-related toxicity. Hence, there is a prerequisite to execute bulky trials of novel NP-based agrochemicals to encourage further investigations for understanding long-term food security and environment safety. Furthermore, it is very essential to prepare specific regulatory guidelines and a list of eco-friendly NP-based novel agrochemicals available for sale to get approval and support from consumers.

6.9 Conclusion

Recently, prodigious challenges we are facing due to a growing global population, climate sifting, and outbreak of plant pathogens. The introduction of NPs can significantly contribute to addressing these burning issues. To enhance crop production, unscientific use of chemical pesticides and fertilizers, causing a desertification of agri-soil, affects natural environment and leads to biodiversity loss. As nanotechnology is a promising research field in the current times when broad spectrum research is being conducted in terms of optimizing efficiency of nanofertilizers, nanocarriers, nanosensors, fuel additives, and NMs-mediated genetic engineering. Likewise, eco-sustainable innovations in agri-biosciences are also essential to explore and promote agriculture-based industry and socioenvironment safety. The scientific use of NPs-based agrochemicals provides better application that can result in a system safer for farmers as well as consumers for future environmental sustainability. A nanotechnology contributes in waste reduction and improves efficiency, while nanocarriers and nanosensors technology encourages the precision agriculture. Furthermore, cutting edge research is needed on efficient use of agriculture waste to convert that waste into value-added nanoproducts.

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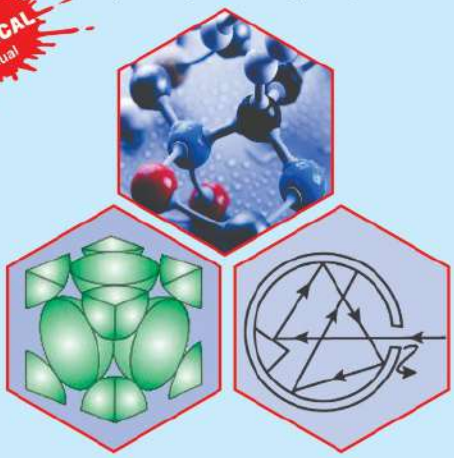

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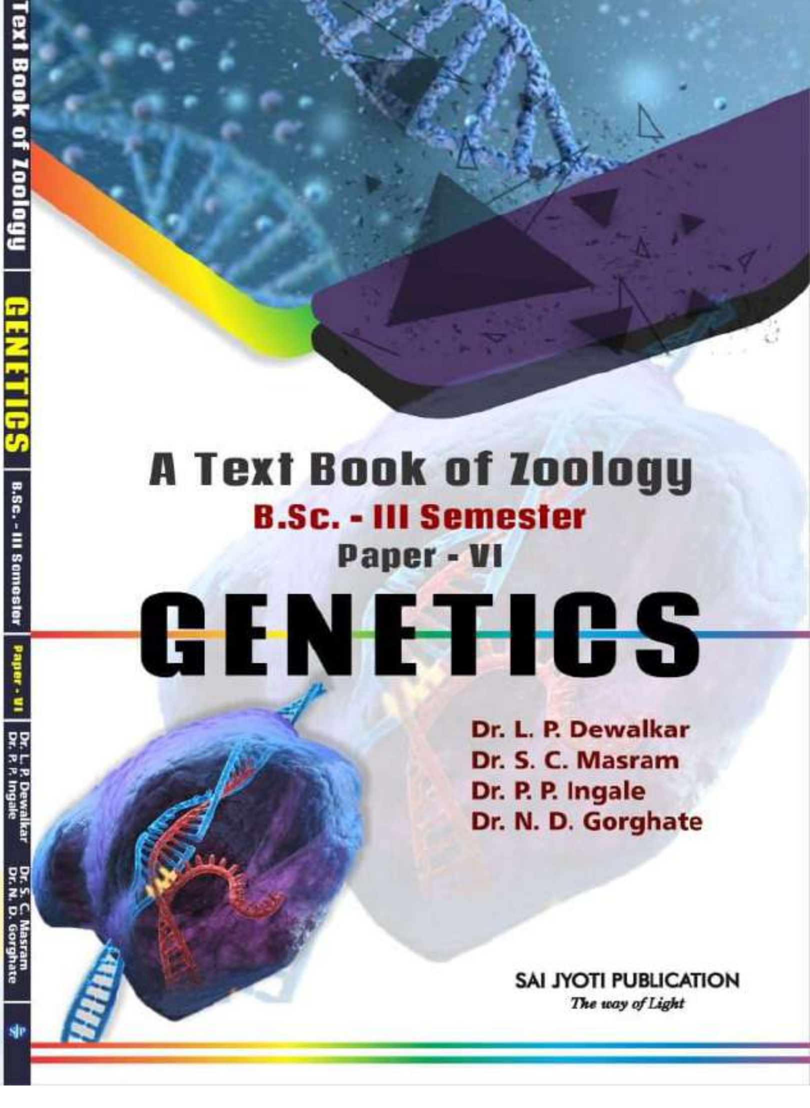

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ABOUT THE BOOK

An extensive examination of the chemistry underlying nanotechnology may be found in the fundamental classic Introduction to Nano Chemistry. This book is a vital resource for learning about the production, characterisation, and multidisciplinary applications of nanomaterials. It gives readers a thorough grasp of the fundamentals of nanochemistry, covering everything from the creation of nanomaterials to their special qualities and uses.

The arrangement of the book is meant to accommodate both chemical novices and experts. It starts with a thorough explanation of the basic ideas, covering the many kinds of nanomaterials and how they are synthesised. After that, it looks at how nanomaterials are used in industries including electronics, health, and environmental research. The characterisation methods for studying nanomaterials and their behaviour at the nanoscale are given particular attention.

Introduction to Nano Chemistry attempts to provide readers with the information necessary to comprehend and interact with the most recent advancements in nanotechnology by providing a well-balanced blend of theory and real-world insights. For researchers, professionals, and students who want to learn more about nanochemistry and how it affects contemporary science and technology, this book is a priceless tool.

PREFACE

The study of altering matter at the atomic and molecular size, or nanotechnology, has had a significant impact on a number of sectors, including materials science and medicine. Introduction to Nano Chemistry focusses on the basic principles, applications, and consequences of nanotechnology in an effort to demystify the field. For professionals, researchers, and students alike, a grasp of the fundamental chemistry of nanotechnology is crucial as it continues to transform businesses and research. We explore the synthesis, characterisation, and applications of nanomaterials as we dig into the fundamental ideas of nanochemistry in the next chapters. We discuss a wide variety of subjects, such as the fundamentals of creating nanomaterials, the special qualities that emerge at the nanoscale, and the many uses of nanomaterials in industries including environmental research, electronics, and medicine. This book bridges the gap between basic chemistry and cutting-edge nanotechnology by offering a thorough introduction to the topic by fusing theoretical understanding with real-world experiences.

This book offers depth for readers who want to comprehend the most recent developments in nanochemistry, but it is also meant to be understandable to readers with a foundation in fundamental chemistry. We hope it proves to be a useful tool and stimulates further research in this fascinating and quickly developing area.

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CHAPTER 1

Introduction to Nanoscience and Nanotechnology

Learning Objective

This chapter will examine the meaning and application of nanoscience, as well as the field's development throughout time and historical context. It will also look at the significance and range of uses of nanotechnology.

1.1. Definition and Scope of Nanoscience

1. Definition

Nanoscience is the study of phenomena and material manipulation at the nanoscale, typically ranging from 1 to 100 nanometers. At this scale, materials exhibit unique chemical, biological, and physical properties that differ significantly from those observed at larger scales. This field encompasses both the exploration and understanding of these nanoscale characteristics and the development and application of technologies based on these principles.

2. Scope

Nanoscience encompasses a wide range of multidisciplinary fields, including physics, chemistry, biology, materials science, & engineering. It includes:

Nanomaterials: The production and investigation of materials of nanoscale dimensions. Nanoparticles, nanotubes, nanowires, & nanocomposites are examples of this. Nanomaterials are useful for a variety of applications because they often have improved mechanical, electrical, optical, & chemical capabilities.

Nanostructures: The creation and modification of nanoscale objects, including quantum dots, nanorods, & nanoplates. These frameworks are used in the investigation of basic science concepts and the creation of new technologies.

Nanotechnology: Nanotechnology is the process of developing new goods and technologies by using the concepts of nanoscience. This covers the creation of materials with enhanced functionality or novel features, drug delivery systems, sensors, and nanoscale devices.

Applications: Numerous sectors, including health (targeted medication administration, imaging), electronics (smaller, more efficient devices), energy (better batteries, solar cells), & environmental science (pollution management, water purification), might be revolutionised by nanoscience.

Ethical and Societal Implications: Being aware of the possible hazards and moral issues related to nanotechnology. This entails assessing the safety, regulatory, and environmental effects of nanomaterials and devices.

1.2. Historical Background and Evolution

The development of nanotechnology was catalyzed by the 1959 symposium "There's Plenty of Room at the Bottom," delivered by American physicist and Nobel laureate Richard Feynman. During this seminar, Feynman explored the potential of manipulating molecules at the atomic level. In 1974, Japanese professor Norio Taniguchi coined the term "nanotechnology" to describe advancements in semiconductor technology and its applications. The creation of the scanning tunnelling microscope in 1981 by scientists Binnig and Rohrer, who were awarded the Nobel Prize in 1986, stemmed from this emerging field.

Nanotechnology involves manipulating matter at a scale of 10^-9 meters. Before Feynman's lecture, this scale had not received significant attention, but early experiments managed to produce atomic-level molecules with properties similar to those seen in modern nanotechnology. The development of graphene sheets and nanotubes is a notable example of such advancements.

Interest in nanotechnology grew following the publication of several works discussing its potential. Feynman's iconic phrase, *"There's plenty of room at the bottom,"* established him as a pivotal figure in the field and inspired many scientists. In the late 1980s and early 1990s, scientist Eric Drexler introduced innovative concepts for building complex machinery and materials from individual atoms. These ideas have since motivated numerous scientists to explore the vast possibilities of nanotechnology.

1.2.1. Evolution

1. Early Concepts and Theoretical Foundations (1950s-1960s)

Physicist Richard Feynman, winner of the 1959 Nobel Prize, delivered a lecture titled "There's Plenty of Room at Bottom." He described the potential for a brand-new scientific discipline that we now refer to as "nanotechnology". Nanotechnology is a general word for any substance or device with at least a single dimension on the nanoscale, or between 1-100 nm, which is equal to the size difference between a centimetre and a metre but 10 million times smaller. This includes electrical, medicinal, and magical devices. Nanodevices can have a size of up to one million times smaller than a single grain of sand.

While it is often accepted that Feynman's presentation served as the inspiration for the whole discipline, this is not entirely accurate: The scientific world didn't take notice of it until the 1990s, by which time nanotechnology research was well advanced. Feynman nonetheless has the title of *"Spiritual Grandfather"* of nanotechnology, and he offered some fascinating predictions about the future of the field.

a. Small Size, Huge Memory

Computers of the 1950s required several square meters of space and could only have a few megabytes of internal memory. This is the same as having a computer that takes up your whole living room—or, if you're a student, maybe your whole apartment—but having just enough space to save one song. You can see how far technology has come when you compare this to today when you can fit your whole music library into your pocket.

This is because transistors, the primary building blocks of computer circuits, have shrunk in size. Currently, over a billion of them are crammed into chips that are as tiny as a fingernail. They have dropped from 0.00001m to 0.000000014m since 1971. Though it may not seem like much, this drop is around 1000 times smaller—roughly equivalent to the difference in size between a person and a midge. These tiny transistors, which enable the creation of smaller computers with greater memory, are the result of advancements in nanofabrication techniques.

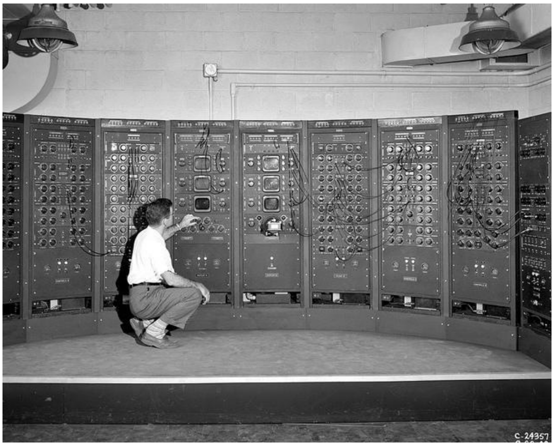

Figure 1.1 An early Computer, in the days before semiconductors.[*]

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[*] https://the-gist.org/wp-content/uploads/2015/03/Early-computer.jpg

Before transistors were employed in computers, Richard Feynman, in his lecture, addressed the necessity of shrinking computers and expanding their memory capacities. He also explored potential applications of enhanced computing power, such as facial recognition—a technology widely used today. Feynman remarked, "No machine with such speed can currently take a picture of a face and even determine that it is a human; much less recognize if it is the same individual shown previously." He further noted that, given the technological constraints of his time, a computer capable of such tasks would need to be significantly larger than a typical smartphone, potentially as large as the Pentagon.

2. Development of Nanoscience and Technology (1980s-1990s)

Owing to developments in imaging and manufacturing methods, nanoscience and technology saw tremendous strides in the 1980s and 1990s. Scientists were able to see and work with individual atoms in 1981 when Gerd Binnig & Heinrich Rohrer created the scanning Tunnelling Microscope (STM). This breakthrough was crucial because it made it possible to see events at the nanoscale and to manipulate matter at the atomic level.

After that, in 1985, Richard Smalley, Robert Curl, & Harold Kroto discovered buckyballs, or fullerenes, which led to the discovery of a new class of carbon molecules with special characteristics. The creation of these instruments and materials created new opportunities for study and development while laying the foundation for useful applications of nanotechnology.

3. **Expansion into Nanomaterials and Nanodevices (2000s)**

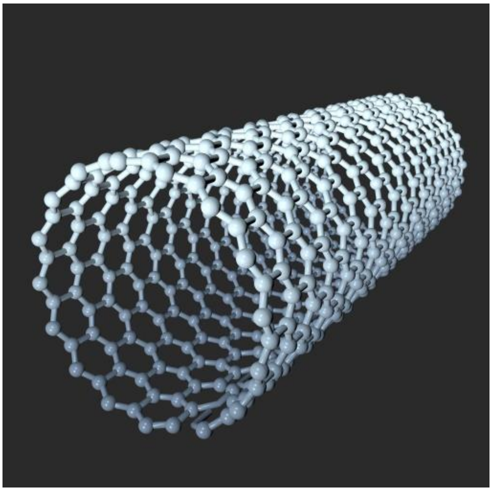

Figure 1.2 Carbon nanotubes[*]

The synthesis & application of nanomaterials experienced significant progress in the 2000s. Researchers have created a variety of nanoscale materials, such as carbon nanotubes, quantum dots, as well as nanoparticles, each of which possesses unique properties and potential applications. Carbon nanotubes, which were identified in the 1990s, exhibited exceptional electrical conductivity and mechanical strength, rendering them advantageous for a

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[*] https://cdn.britannica.com/29/193229-050-ACB6E78D/Illustration-carbon-nanotube.jpg

variety of applications in nanomedicine, materials science, and electronics. Quantum dots, semiconductor nanoparticles, exhibited distinctive optical properties and were employed in biological imaging as well as display technologies. The discipline experienced substantial growth during this period, with a heightened emphasis on the commercialisation and practical applications of nanotechnology.

4. Integration and Regulation (2010s-Present)

Nanotechnology has undergone a continuous evolution in recent years, with a focus on the integration of extant technologies and the resolution of regulatory as well as ethical concerns. Innovative medical applications, including targeted drug delivery systems, advanced imaging techniques, as well as nanorobots for medical procedures, have been facilitated by recent advancements in nanotechnology.

Simultaneously, there has been heightened scrutiny of the safety, environmental impact, as well as ethical considerations associated with nanomaterials. In order to guarantee the responsible development and utilisation of nanotechnology, regulatory bodies have been developing safety standards and guidelines. This period signifies the field's maturation, as it maintains a balance between technological advancement and public and environmental health concerns, while also emphasising practical implementations.

1.3. Importance and Applications of Nanotechnology

In the near future, it is anticipated that nanotechnology will provide a valuable collection of clinically beneficial devices and research instruments. The pharmaceutical industry is anticipated to develop new commercial applications, such as advanced drug delivery systems, novel therapies, and in vivo imaging, according to the National Nanotechnology Initiative.

Current research objectives include the development of neuro-electronic interfaces along with additional nanoelectronic-based sensors. Cell regeneration devices are believed to have the potential to further revolutionise the field of medicine in the speculative field of molecular nanotechnology. Nanotechnology is intended to offer a new and enhanced method of identifying and treating cancer. Large biological molecules can interact with nanoscale devices on the surface and within cancer-related cells. Nanotechnology provides numerous instruments due to the fact that biological processes, such as those that contribute to the development of cancer, transpire on a nanoscale within and on the surface of cells.

Materials and Processes

Nanotechnology has the potential to enhance the functionality and durability of numerous everyday materials. Nanomaterials are present in numerous commercial products. These consist of:

- For health monitoring, environmental monitoring within industries such as mining, and kinetic energy harvesting for self-power, durable, washable smart fabrics alongside embedded flexible nanosensors and electronics are proposed.
- To enhance self-cleaning capabilities, increase electrical conductivity, protect against UV radiation, and improve waterproofing, clear nanoscale films are used for displays, spectacles, and windows.
- Nanoscale additives over lightweight ballistic armour.
- Nanoscale materials are utilised in automotive components, including thin-film smart solar panels, battery systems, and low-rolling resistance tyres.
- Catalysts on a nanoscale to accelerate chemical reactions.
- Nanomaterials are utilised in the development of enhanced household and personal care products.
- Nanoscale sensors are integrated into smart packaging for the food industry to identify spoilage-related issues.

IT and Electronics

Numerous applications in the fields of information technology and electronics are currently employing nanomaterials. Additionally, there is a significant amount of effort being conducted to capitalise on the materials' exceptional electrical conductivity and other advantageous characteristics to revolutionise the electronics industry, thereby enabling the development of atomic electronics and quantum computing.

- Nanoscale transistors.
- Magnetic random access memory systems that employ magnetic tunnel junctions on a nanometre scale.
- Quantum dots are integrated into ultra-high-definition displays.
- Electronics that are mechanically flexible and capable of withstanding mechanical deformation are intended for use in smartphones, IoT devices, medical applications, and wearable electronics.
- Conductive coatings are utilised in the production of printed electronics.
- Enhanced flash memory processors for smartphones and portable devices.
- Paper that is stored electronically.
- Light-Emitting Diodes (LEDs).
- Lasers.
- Batteries.

Biomedicine and Healthcare

Nanotechnology has the potential to revolutionise the disciplines of healthcare and medicine by offering advantages such as improved medication delivery, improved diagnostic as well as prevention capabilities, and innovative therapies. Nanomedicine is a developing discipline that draws inspiration from biological phenomena. Nanomaterials were particularly noteworthy in the development of SARS-CoV-2 (COVID-19) vaccines. Its applications encompass:

- Probes based on gold nanoparticles for the detection of the targeted gene therapies.
- Gold nanoparticle-based therapies for cancer and other ailments.
- Enhanced diagnostic and imaging instruments.
- Novel gene sequencing technologies and low-cost, high-throughput single-molecule detection are made possible by advanced solid-state nanopore materials.
- Utilising nanocapsules for targeted drug delivery, the treatment of diseases that include cancer can be enhanced with minimal adverse effects.
- Neural as well as bone tissue engineering and regenerative medicine.
- Graphene nanoribbons for the treatment and regeneration of spinal injuries.
- mRNA carriers within vaccines.
- Vaccine delivery without the use of needles.
- Drug transporters.

Energy

In order to satisfy the global demand for renewable energy, nanotechnology is being implemented in the production and harvesting of alternative energy sources. Numerous scientists are currently researching the utilisation of nanoscale devices and materials to mitigate environmental toxicity, reduce energy consumption, and create cost-effective, sustainable energy sources. Examples of applications include:

- Nanoscale catalysts for enhanced fuel production efficiency.
- Optimising combustion efficiency and reducing friction through the use of nanomaterials to decrease fuel consumption in vehicles and power facilities.
- Improved offshore oil and gas extraction through the use of nanotechnology-enabled gas lift valves.
- Scrubbers and carbon nanotube membranes for CO_2 filtering as well as carbon capture in power facilities.
- The utilisation of carbon nanotube conductors to mitigate transmission power loss in electric circuits.
- New generations of energy storage devices and batteries that are based on nanomaterials.
- Wind turbine blades that are longer, lighter, and more durable are produced by carbon nanotube epoxies.
- Enhanced solar harvesting through the use of thin-film photovoltaic solar panels.

Environmental Remediation

Environmental remediation applications include:

- **Water purification:** Long-lasting, self-cleaning "graphene-based water filtration membranes" that are capable of removing environmental contaminants, including heavy metals, from industrial effluent.

- Nanoparticles are utilised to remove pollutants from industrial effluent in groundwater.
- MoS_2 membranes with a thin-film nanoporous structure for enhanced energy efficiency in desalination.
- A nano fabric "paper towel" based on potassium manganese oxide nanowires for the cleanup of oil spills.
- Sensors that are facilitated by nanotechnology to monitor environmental contamination and air quality.

Transportation

By creating energy-efficient, lightweight multifunctional materials for a variety of applications and components in infrastructure, space exploration, ships, aeroplanes, and automobiles, nanotechnology offers advantages to the transportation industry. These consist of:

- Structural components made from polymer nanocomposites.
- Rechargeable batteries with exceptional capacity.
- Thermoelectric materials for temperature regulation.
- High-efficiency nanoscale sensors and low-cost electronics.

- Enhanced durability and longevity of transportation infrastructure materials, such as concrete, cementitious materials, steel, and polymer composites, through nanoengineering.
- Lightweight, high-strength materials for the aerospace industry, facilitated by nanotechnology.

Chapter Summary

This chapter explored the fundamentals of nanoscience and nanotechnology, starting with definitions and the scope of the field. It traced the historical development from early theoretical foundations in the 1950s and 1960s, through significant advancements in the 1980s and 1990s, to the expansion of nanomaterials and nanodevices in the 2000s.

The chapter also highlighted the integration and regulatory aspects that have emerged since the 2010s. The importance and diverse applications of nanotechnology were examined, including its impact on materials and processes, information technology and electronics, biomedicine and healthcare, energy solutions, environmental remediation, and transportation. This overview underscores the transformative potential of nanoscience in addressing complex challenges and advancing technological innovation across various sectors.

Assessment Questions

1. In his 1959 lecture, what was Richard Feynman's prediction regarding the future of nanotechnology?
2. What effects did the transistor size decrease from the 1970s to the present have on computer memory and size?
3. In the 1980s, what discovery made it possible for scientists to see and interact with individual atoms?
4. What are quantum dots and carbon nanotubes, and what special qualities and uses do they offer?
5. Which areas of nanotechnology are now of interest, and what legal issues are raised by its advancement?
6. How can the performance of environmental monitoring systems and smart textiles be improved by the usage of nanoscale materials?
7. What are some of the ways that nanotechnology is being used in the IT and electronics industries to improve memory and display technologies?
8. In what ways can nanotechnology aid in the progress of biomedicine and healthcare, specifically with regard to medication delivery and diagnostics?
9. What part does nanotechnology play in the creation of sustainable environmental practices and renewable energy sources?
10. How is nanotechnology advancing materials and transportation infrastructure, including advances in battery and structural component technology?

CHAPTER 2

Basic Concepts in Nano Chemistry

Learning Objective

This chapter will investigate the physical, chemical, optical, as well as electrical properties of nanomaterials, as well as their classifications and types. It will also examine the quantum effects that are observed in nanomaterials.

2.1. Nanomaterials: Types and Classifications

Nanomaterials are materials with structures or properties at the nanoscale, typically ranging from 1 to 100 nanometers. They are classified based on many factors and unique characteristics that differ from bulk materials.

1. Classification of nanomaterials based on origin

Nanomaterials are classified into two categories based on their origin: natural and artificial nanoparticles.

a. Natural nanomaterials

Natural colloids (like milk and blood), viruses, protein molecules, minerals like clay, fog, gelatin, mineralised natural materials, insect wings and opals, lotus leaves, gecko feet, spider silk, volcanic ash, and ocean spray are just a few examples of the diverse forms that natural nanomaterials can be found in.

b. Artificial nanomaterials

Manufactured nanomaterials, such as carbon nanotubes and semiconductor nanoparticles like Quantum Dots (QDs), are materials that are purposefully created using precise mechanical and manufacturing techniques. Based on their structural makeup, nanomaterials are categorised as composites, metal-based materials, or dendrimers.

2. Classification of nanomaterials based on the structural configuration/composition

Nanoparticles can be broadly classified into four categories based on their structural composition: organic/dendrimers, inorganic, carbon-based, as well as composite.

a. Organic nanomaterials

At the nanoscale, organic molecules are converted into organic nanomaterials. Among the organic nanoparticles or polymers are liposomes, dendrimers, micelles, and ferritin. Non-toxic biodegradable nanoparticles with hollow interiors, such as liposomes and nanocapsule micelles, may absorb light, heat, and electromagnetic radiation.

Many chain endings covering a dendrimer's surface allow it to participate in certain chemical processes. molecular recognition, optoelectrochemical systems, light harvesting, and nanosensing. Dendrimers are used for these kinds of uses. Furthermore, since three-dimensional (3D) dendrimers include interior holes that may hold extra molecules, they may be useful for the delivery of drugs.

b. Inorganic nanomaterials

Inorganic nanoparticles are materials that do not contain carbon atoms. They are generally classified into two main categories: metal-based and metal oxide-based nanomaterials.

Metal-based nanoparticles: Metal-based nanoparticles may be produced by destructive or even constructive techniques. Metal elements such as copper (Cu), gold (Au), iron (Fe), aluminium (Al), cadmium (Cd), cobalt (Co), lead (Pb), silver (Ag), and zinc (Zn) are often used in the production of nanoparticles. Due to their quantum effects and high surface-to-volume ratio, metal nanoparticles have remarkable electrical, catalytic, thermal, and antibacterial properties in addition to their remarkable UV-visible sensitivity. Since metal nanoparticles have such remarkable optical qualities, they are used in many different types of study.

Metal oxide nanoparticles: Positive metallic ions and negative oxygen ions make up metal oxide nanoparticles, also known as metal oxide nanomaterials. Metal oxide nanoparticles that are often synthesised include silicon dioxide (SiO_2), titanium oxide (TiO_2), zinc oxide (ZnO), and aluminium oxide (Al_2O_3). Compared to their metal counterparts, these nanoparticles exhibit remarkable properties.

c. Carbon-based nanomaterials

Graphene, fullerenes, carbon nanotubes, carbon nanofibers, and carbon black are the five primary materials that comprise carbon-based nanomaterials. Fullerenes, which are carbon nanomaterials with spherical and ellipsoidal configurations, are often referred to as Bucky spheres. The spherical structure of fullerenes is characterized by diameters of up to 8.2 nm for a single layer and 4 to 36 nm for multi-layered fullerenes. These structures are composed of 28 to 1500 carbon atoms.

Graphene is the name for the two-dimensional (2D) planar surface honeycomb lattice network made up of carbon atoms arranged in a hexagonal pattern. About one nanometre is the thickness of the sheet, and cylindrical ones are called nanotubes. Nanotubes with lengths ranging from a few micrometres to several millimetres are made using hollow cylinders with diameters as low as 0.7 nm for a single-layered carbon nanotube and 100 nm for a multi-layered carbon nanotube.

The same graphene nano fossils have been used to produce carbon nanofiber. Carbon black is an amorphous material composed of carbon, typically spherical in shape, with diameters ranging from 20 to 70 nm. Structural reinforcement is the primary application of carbon-based nanomaterials, as they are occasionally more durable than steel. Thermally conductive nanomaterials that are carbon-based are non-conductive across the tube and thermally conductive along the length.

d. Composites nanomaterials

Composite nanomaterials are created by combining nanoparticles with other nanoparticles, larger-scale materials, or bulk materials. These composites are increasingly used in a variety of applications, including packaging materials and vehicle components, to enhance their mechanical, thermal, and flame-retardant properties.

3. Classification of nanomaterials according to the number of dimensions

Nanomaterials are categorized into four categories according to their physical size dimensions: 0D, 1D, 2D, and 3D.

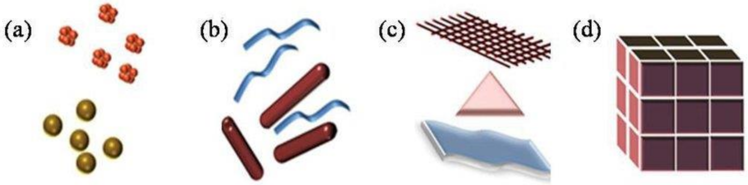

Figure 2.1 Classification of nanomaterials according to dimension: A, zero-dimensional; B, one-dimensional; C, two-dimensional; D, three-dimensional[*]

a. Zero-dimensional nanomaterials

0D nanomaterials: These nanomaterials have all 3 dimensions (x, y, and z) inside the nanoscale range, or they are non-dimensional beyond the nanometric range

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[*] https://www.researchgate.net/publication/321905166/figure/fig1/AS:573188377907200@1513670166042/Classification-of-Nanomaterials-a-0D-spheres-and-clusters-b-1D-nanofibres-wires.png

(>10nm). Quantum dots, fullerenes, and nanoparticles are examples of 0D nanomaterials. They may take on a variety of shapes and structures, be amorphous or crystalline, single crystalline or polycrystalline, and be metallic or ceramic.

b. One-dimensional nanomaterials

One dimension of the nanostructure is beyond the non-metric range (>10 nm), however, the other two dimensions (x, y) of the nanomaterials in this category fall within the nanoscale range. 1D nanomaterials, such as nanofibers, nanohorns, nanorods, nanotubes, thin coatings, and nanowires, are examples of needle-shaped nanomaterials. These materials may be freestanding or immersed in another media, such as metallic, ceramic, or polymeric. They can also be amorphous or just crystalline, single crystalline or just polycrystalline, chemically pure or polluted. One-dimensional nanoparticles might be polymeric, metallic, or ceramic.

c. Two-dimensional nanomaterials

While 2D nanomaterials feature plate-like structures having two dimensions that are beyond the nanometre range, 1D (x) is at the nanoscale. Coatings and thin-film multilayers, nanosheets or simply nanowalls, tubes, fibres, ultrafine-grained overlaps, free particles, wires, and platelets are a few examples of 2D nanomaterials. Two-dimensional nanomaterials may be crystalline or amorphous, made of different kinds of chemicals, placed on a substrate, or combined with a metallic or polymeric matrix material.

d. Three-dimensional nanomaterials

Three-dimensional nanomaterials, often known as bulk materials, are nanomaterials that are not limited to the nanoscale in terms of dimensions or other attributes. 3D nanomaterials possess three arbitrary dimensions above 100 nm since the bulk material is made up of discrete units that are in the nanometre scale (1–100 nm). Nonetheless, every dimension of a three-dimensional substance is either larger than 100 nm or is beyond the nanometre range. It is made up of many nanolayers joined by bundles of nanowires and nanotubes, dispersed nanoparticles, and close contact between the 0D, 1D, & 2D structural elements. 3D nanomaterials include colloids, unbound nanoparticles with a range of morphologies, and thin films with atomic-scale porosity.

2.2. Properties of Nanomaterials

The size, structure, as well as surface area of nanomaterials, are substantially different from those of their bulk counterparts, which is why they exhibit distinctive properties. It is essential to comprehend these properties to effectively apply them in a variety of domains.

2.2.1. Physical Properties

The nanoscale dimensions and substantial surface-to-volume ratio of nanomaterials have an impact on their physical properties. These properties frequently differ from those of mass materials and can be customized to suit specific applications.

1. Size and Shape

The properties of nanomaterials can vary considerably depending on their size and shape, with dimensions that can range from 1 to 100 nanometers. For instance, the behaviour and applications of a material can be influenced by the shape of the nanoparticles, which may be spherical, cylindrical, or tubular.

2. Surface Area

The surface area-to-volume ratio of nanomaterials is high as a result of their diminutive size. The interaction with the surrounding environment is improved by the increased surface area, which influences properties such as adhesion and reactivity.

3. Mechanical Properties

Nanomaterials frequently demonstrate improved mechanical properties, including increased elasticity, rigidity, and strength. This is the result of the unique interactions at the nanoscale and the reduced number of defects.

2.2.2. Chemical Properties

Size, shape, and surface characteristics are all factors that influence the chemical properties of nanomaterials. These properties may be distinct from those of bulk materials, resulting in distinctive chemical reactivity and interactions.

1. Reactivity

In contrast to their bulk counterparts, nanomaterials frequently demonstrate elevated chemical reactivity. This is a result of the high surface area as well as the presence of active sites and surface defects. The high reactivity of silver nanoparticles results in their enhanced antibacterial properties, which are employed in medical as well as consumer products to control infection.

2. Stability

In contrast to bulk materials, nanomaterials may exhibit varying degrees of chemical stability. Their stability in a variety of environments can be influenced by factors such as the presence of stabilizers and surface coating. In order to prevent aggregation and guarantee the controlled release of therapeutic agents, nanoparticles utilized in drug delivery must be stabilized.

3. Surface Functionalization

Chemical modification of the surface of nanomaterials may be employed to improve their properties or facilitate specific interactions. Surface functionalization enables the customization of nanomaterials for specific applications. The targeting capability of gold nanoparticles in medical imaging as well as therapy can be improved by functionalizing them with specific ligands.

2.2.3. Optical Properties

Nanomaterials possess distinctive optical properties as a result of their diminutive size and the quantum effects which transpire at the nanoscale. Imaging, sensing, as well as display technologies are among the numerous applications that can benefit from these properties.

1. Quantum Dots

Quantum dots have semiconductor nanoparticles that possess optical properties that are dependent on their size. Their size and composition enable them to emanate a variety of colours, rendering them advantageous for fluorescence imaging as well as display technologies. Quantum dots are employed in bioimaging to monitor and visualize cellular processes via high resolution and specificity.

2. Surface Plasmon Resonance

Gold and silver nanoparticles are examples of nanomaterials that exhibit surface plasmon resonance. This phenomenon is characterized by the resonance of free electrons on the metal surface with incident light. This phenomenon leads to the significant absorption and diffraction of light at particular wavelengths. Biological interactions are detected in biosensing applications by measuring variations in light absorption through the use of SPR.

3. Size-Dependent Optical Properties

The size and shape of nanomaterials can influence their optical properties, including colour and absorption. The interaction of light via nanoscale structures and quantum confinement effects are the causes of this size dependence. As the size of gold nanoparticles decreases, their colour undergoes a transformation from red to blue, which can be utilized in colourimetric assays.

2.2.4. Electrical Properties

The size, structure, as well as surface characteristics of nanomaterials all contribute to their electrical properties. The development of sensors and electronic devices is contingent upon these properties.

1. Conductivity

In comparison to their bulk counterparts, nanomaterials can demonstrate improved electrical conductivity. For example, graphene and carbon nanotubes are suitable for a variety of electronic applications due to their exceptional electrical conductivity. In nanoelectronics, carbon nanotubes are employed to fabricate conductive coatings and high-performance transistors.

2. Semiconducting Properties

The size and composition of numerous nanomaterials, including quantum dots as well as nanowires, can be adjusted to optimize their semiconducting properties. This tunability enables the creation of innovative optoelectronic and electronic devices. Silicon nanowires are employed in field-effect transistors and sensors as a result of their high surface area and tunable electronic properties.

3. Tunnelling Effects

Quantum tunnelling phenomena may affect a material's electrical activity at the nanoscale. This phenomenon arises when electrons traverse energy barriers that might prove insurmountable on a larger scale. Tunnelling effects in nanometer-sized transistors can result in leakage currents and affect device performance, necessitating meticulous management during the design of nanoscale electronics.

2.3. Quantum Effects in Nanomaterials

Nanoparticles are particles that are infinitesimal in size, measuring between 1 and 100 nanometers in one dimension. The characteristics of particles at the lower end of this distribution are frequently influenced by intriguing quantum effects, which render them entirely distinct from their macroscale counterparts. Behaviours such as their chemical reactivity, electrical conductivity, and fluorescence are affected by their dimensions.

1. The Quantum Confinement Effect

The properties of any substance are essentially the average of the quantum effects that act on its atoms. This averaging is no longer effective in describing the physical properties of the material as the particle size decreases, ultimately reaching the nanoscale. Rather, we must examine the quantum behaviour of each atom and how they communicate with one another. This phenomenon, which is also referred to as the quantum size effect, is more prevalent in nanoparticles that are 10 nm or smaller and is caused by confinement. It is widely recognized that particles may be characterized as either a wave or a particle.

In a bulk material, electrons are typically regarded as wave-like entities that are "free" to traverse between atoms. The spatial extent of the electron wave function is equivalent to the particle's size as the particle's size decreases. Consequently, the electron begins to "feel" the presence of particle limits and adjusts its energy accordingly. Electrons are now "confined" in quantized energy levels, and they are no longer free to move between them.

a. Energy Quantization

The energy levels of electrons are quantized in quantum-confined structures. For example, within quantum dots, electrons inhabit specific energy states, resulting in discrete emission and absorption spectra. When agitated, quantum dots of varying sizes emanate a variety of colours of light, a characteristic that is utilized in biological imaging as well as display technologies.

b. Size-Dependent Properties

Quantum-confined nanomaterials exhibit a range of optical and electronic properties that are dependent on their size. The energy gaps of smaller quantum dots are greater, resulting in the emission of higher-energy (bluer) light. Conversely, larger dots emanate lower-energy (redder) light. Researchers can customize their emission spectra for particular applications, including solar cells and LED displays, by adjusting the size of quantum dots.

2. Tunnelling Effects

Quantum tunnelling is a phenomenon in which particles traverse potential barriers that they are normally incapable of surmounting from a classical perspective. Tunnelling effects can affect the mechanical and electrical characteristics of nanomaterials.

a. Electrical Tunneling

Electrons can tunnel through narrow insulating barriers in nanoscale electronic devices, like transistors. This can result in leakage currents and compromise the functionality of the device. Data storage and retrieval are facilitated by the use of tunnelling in nanoscale flash memory devices, which facilitates the movement of charge between various layers.

b. Tunnel Junctions

Tunnel junctions, which are formed by positioning two conductive materials in close proximity, utilize tunnelling to facilitate high-speed electronic switching. In comparison to conventional transistors, tunnel field-effect transistors employ tunnelling to accomplish quicker switching rates.

3. Quantum Dots

The notion of "tunability" is a captivating and potent consequence of quantum effects on the nanoscale. A material's characteristic of interest, such as its fluorescence hue, may be precisely adjusted by varying the size of the particles. These modified particles can then be identified and marked with markers for a variety of uses.

Quantum dots are among the most significant advancements that capitalize on this quantum tunability. They are semiconductor nanoparticles that possess fluorescent properties and are less than 10 nm in size. Size and shape are closely correlated with their properties, which are intermediate between those of discrete molecules and bulk semiconductors.

a. Size-Tunable Emission

Quantum dots' electronic bandgap is contingent upon their dimension, which enables them to emit light with a precise wavelength. Fluorescent imaging and labelling employ this size-dependent emission. Quantum dots of varying diameters can be employed in biological imaging to designate a variety of cell components, thereby enabling the creation of multi-colour and detailed images.

b. Photonic Applications

Quantum dots are employed in photonic devices, including lasers as well as Light-Emitting Diodes (LEDs), as a result of their adjustable emission characteristics. In comparison to conventional LEDs, quantum dot-based LEDs provide enhanced efficiency and colour purity, rendering them appropriate for high-definition displays.

4. Surface Plasmon Resonance

The concept of Surface Plasmon Resonance (SPR) is the phenomenon of free electrons on the surface of a metal nanoparticle resonating with incident light. This effect is especially potent in nanomaterials such as silver and gold nanoparticles.

a. Localized Surface Plasmon Resonance (LSPR)

As a result of surface plasmon resonance, nanoparticles display high light absorption and scattering at certain wavelengths, a phenomenon known as LSPR. This effect is contingent upon the shape and magnitude of the object. This property is advantageous in imaging and sensing applications, as gold nanoparticles can be adjusted to absorb and deflect specific wavelengths of light.

b. Sensing Applications

SPR is employed in a variety of sensing technologies, such as biosensors, to detect the presence of particular biological molecules from variations in the resonance wavelength. SPR-based biosensors are advantageous for environmental monitoring and medical diagnostics due to their capacity to identify minute fluctuations in biomolecule binding.

Chapter Summary

This chapter explored the fundamental concepts in nanochemistry, focusing on the types and classifications of nanomaterials. It covered their classification based on origin, structural configuration, and dimensionality. The chapter further examined the various properties of nanomaterials, including physical attributes such as size, shape, surface area, and mechanical properties; chemical characteristics like reactivity, stability, and surface functionalization; and optical properties including quantum dots, surface plasmon resonance, and size-dependent effects.

Additionally, it addressed the electrical properties of nanomaterials, such as conductivity, semiconducting traits, and tunnelling effects. The chapter concluded with an overview of quantum effects in nanomaterials, highlighting quantum confinement, tunnelling effects, quantum dots, and surface plasmon resonance. This comprehensive overview underscores the diverse and unique properties of nanomaterials, which are pivotal in their applications across various scientific and technological fields.

Assessment Questions

1. How are origin-based nanomaterials categorized?
2. Which structural compositions or combinations are utilized to categorize nanomaterials?
3. In what way are nanomaterials categorized based on the number of dimensions?
4. Which mechanical characteristics are often connected to nanomaterials?
5. What effects does surface functionalization have on a nanomaterial's characteristics?
6. What are the optical characteristics of nanomaterials that vary with size?
7. What influence do quantum processes like tunnelling have on nanomaterials?
8. Why is localized surface plasmon resonance (LSPR) important for quantum dots?
9. What makes one-dimensional and three-dimensional nanomaterials different from one another?
10. What functions do metal-based nanoparticles serve in the study and use of nanomaterials?

CHAPTER 3

Synthesis and Characterization of Nanomaterials

Learning Objective

This chapter will investigate the use of both top-down and bottom-up methods to synthesize nanomaterials. It will encompass the characterization of various synthesis methods, including the Sol-Gel process, Chemical Vapour Deposition (CVD), and others.

3.1. Top-Down vs. Bottom-Up Approaches

Two primary methods can be employed to synthesize nanomaterials: top-down and bottom-up. The selection of the most suitable method is contingent upon the desired properties and uses of the nanomaterials, as each method has its own unique techniques, advantages, and applications.

3.1.1. Top-Down Approach

The top-down approach entails the initial deconstruction of bulk materials into nanoscale structures. This approach typically entails the use of physical or chemical processes that decrease the material's dimension and generate nanostructures.

1. Techniques

The techniques that fall under the top-down approach are as follows:

a. Mechanical milling method

The top-down approach that is most often used to produce different types of nanoparticles is mechanical milling. It is used to create a wide range of nanocomposite materials, such as wear-resistant spray coatings, oxide- and carbide- and nickel-based nanoalloys, and aluminium alloys enhanced by oxides and carbides.

b. Nanolithography method

It is the technique of selectively removing material to get the required form and structure, as well as printing the appropriate shape or structure onto a light-sensitive material. One workable method for creating nanoarchitectures using a focused electron or plain light beam is lithography.

One main advantage of nanolithography is the ability to build a cluster from a single nanoparticle of a desired size and shape. The disadvantages include expensive related costs and complex equipment.

c. Laser ablation method

Nanoparticles are produced through laser ablation synthesis, which involves the application of a powerful laser beam to the target material. In a laser ablation experiment, metal atoms vaporize and are promptly solvated by surfactant molecules, resulting in the formation of nanoparticles in the solution.

d. Sputtering method

The process by which discharged particles are hit with ions to generate nanoparticles is known as sputtering. The technique of depositing a thin coating of nanoparticles and then annealing them is known as sputtering.

e. Thermal decomposition method

The breakdown occurred due to heat. It is an endothermic reaction. Chemical bonds fracture and disintegrate into smaller pieces when heated. When the metal breaks down at a certain temperature, a chemical reaction produces the nanoparticles.

f. The arc discharge method

A diverse array of nanostructured materials can be generated using this method. Carbon nanotubes, carbon nanohorns (CNHs), amorphous spherical carbon nanoparticles, few-layer graphene (FLG), and fullerenes are among the carbon-based materials that are manufactured.

This approach is of paramount significance in the development of fullerene nanomaterials.

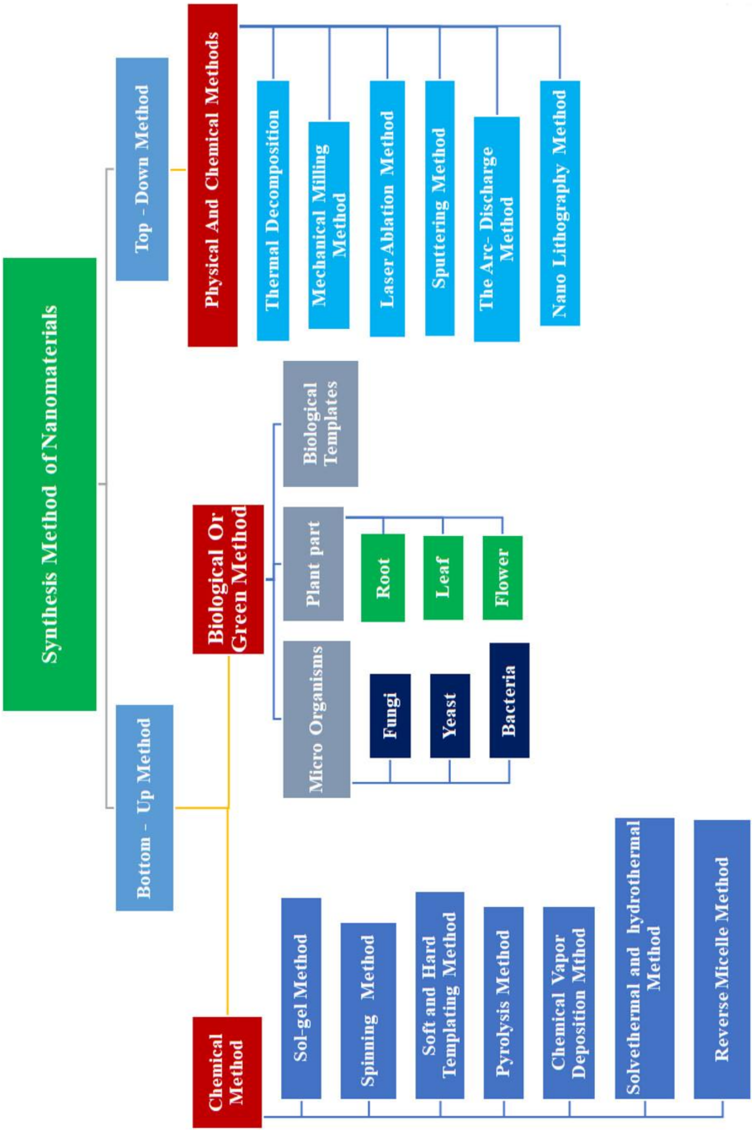

*Figure 3.1 Synthesis methods of nanomaterials**

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*https://onlinelibrary.wiley.com/cms/asset/08691409-a1cf-4faf-ad4e-e8bae663d3ce/nano450-fig-0009-m.jpg

3.1.2. Bottom-Up Approach

By constructing nanomaterials from smaller building components, such as atoms, molecules, or nanoparticles, the bottom-up technique is implemented. In order to produce nanostructures, this approach primarily involves chemical synthesis and self-assembly.

1. Techniques

The following are the techniques:

a. Sol-gel method

It's the process by which a chemical solution supplies an appropriate precursor. The sol-gel technique often uses metal oxide & chloride as precursors. Metal oxides and chlorides are the most probable precursors for sol-gel.

b. Spinning method

Nanoparticles are produced by spinning in a Spinning Disc Reactor (SDR). It consists of a rotating disc contained in a reactor or other container that has physically adjustable parameters like temperature. Several factors affect it, including feed location, liquid flow rate, disc rotation speed, liquid/precursor ratio, and disc surface. Magnetic nanoparticles were created by spinning disc processing.

c. Chemical vapour deposition (CVD) method

Gaseous reactants are thin-film deposited on a substrate during the CVD process. When a mixed gas and heated substrate come into contact, a chemical reaction occurs. This reaction produces a thin coating of product on the substrate surface that may be recovered & reused. The disadvantages of CVD include the necessity for specialised equipment and the very dangerous nature of gaseous byproducts.

d. Pyrolysis method

Pyrolysis is the most often used process in industry to produce nanoparticles on a large scale. The advantages of pyrolysis are its continuous nature, high yield, affordability, and simplicity of usage.

e. Solvothermal and hydrothermal methods

This procedure carries out a heterogeneous reaction which yields nanostructured materials using an aqueous hydrothermal method. Hydrothermal and solvothermal methods are often used in closed systems. Hydrothermal and solvothermal methods may make it easier to produce various nanogeometries of materials, such as nanowires, nanorods, nanosheets, & nanospheres.

f. Soft and hard templating methods

In order to produce nanoporous materials, both flexible and rigid template methods are heavily used. The soft template approach is a simple conventional method for producing nanostructured materials. This method produces nanoporous materials by using a range of soft templates, such as block copolymers, flexible organic molecules, and anionic, cationic, & non-ionic surfactants.

g. Reverse micelle method

To create nanomaterials with the required sizes and shapes, the reverse micelle approach is also helpful. When an emulsion of water and oil forms in nature, reversible micelles are created, with the hydrophilic heads facing in the direction of the water-containing core.

h. Biosynthesis/biological method

An eco-friendly and sustainable method for creating biological, non-toxic nanoparticles is called biosynthesis. Green synthesis nanoparticles are well suited for biological applications due to their unique and improved characteristics. Biosynthesis uses a variety of plant components, biological templates, and microorganisms (fungi, algae, and bacteria).

Biosynthesis method using microorganisms: Different kinds of nanomaterials may be made from aqueous solutions containing metal salts by using algae, fungi, and bacteria. For instance, on the ocean floor, photosynthetic bacteria like Rhodopseudomonas capsulate produce 10–20 nm-sized gold nanoparticles extracellularly; the fungus Fusarium oxysporum is utilized to produce extracellular silver nanoparticles; and Sargassum wightii algae is utilized to prepare extracellular gold nanoparticles. This procedure has the drawback that care has to be taken since certain bacteria, fungi, and algae are harmful.

Biosynthesis method using biological templates: Nanostructures are made of complex and one-of-a-kind materials thanks to biological templates like DNA and proteins. These nanoparticles may be used in the development of bioelectronic systems, biosensors, and bioNEMS. The main components of nanocomposite materials are proteins. For instance, in prokaryotes and eukaryotes, ferritin is the internal iron store protein. It retains it as iron oxide and then releases it gradually. In humans, it functions as a buffer to control iron excess and deficiency.

Biosynthesis method using different plant parts: Plants & plant extracts have also been used in the synthesis of nanoparticles. Phytochemicals found in plants aid in the reduction of metal nanoparticles. Organic acids, quinones, and flavones are effective organic reducing agents for the synthesis of nanoparticles. Gold nanoparticles in a range of forms are produced from the biomass of the plants Medicago sativa (alfalfa) and Pelargonium graveolens (geranium). Azadirachta indica (neem) leaves are utilised to produce bimetallic Au, Ag, and bimetallic Au core-Ag shell nanoparticles.

3.2. Techniques for Synthesis

There are many ways to synthesize nanomaterials, and each one has benefits and differing ways of producing materials with special qualities.

3.2.1. Chemical Vapour Deposition (CVD)

One popular coating technique for creating very high-quality thin films and coatings is chemical vapour deposition. In this procedure, gaseous reactants are often used. Several volatile precursors are transported to the reaction chamber during chemical vapour deposition. In the reaction chamber, the volatile precursors typically disintegrate on a heated substrate surface. Along with the volatile precursors that have not yet reacted, several chemical byproducts produced by this process are released from the reaction chamber. The chemical vapour deposition process is used to deposit a wide range of compounds, such as silicides, metal oxides, sulfides, & arsenides.

1. Chemical Vapor Deposition Reactors

CVD reactors come in two varieties, each with unique uses, benefits, and drawbacks.

a. Hot Wall Reactors

Compared to other varieties, hot wall reactors are not as often utilized. They entail heating the reactor walls as well as the substrates.

Advantages

- Substrates may be created in large quantities at once.
- Operating hot wall reactors is simple.
- The temperature of the substrate is constant. As a result, the coating thickness is consistent.
- A wide variety of pressures and temperatures may be used to run hot wall reactors.

Disadvantages

- It needs energy and a very high temperature.
- Coating happens on the reactor walls in addition to the substrate. The reactor is challenging to clean as a result.
- It's conceivable that gas-phase reactions will happen.

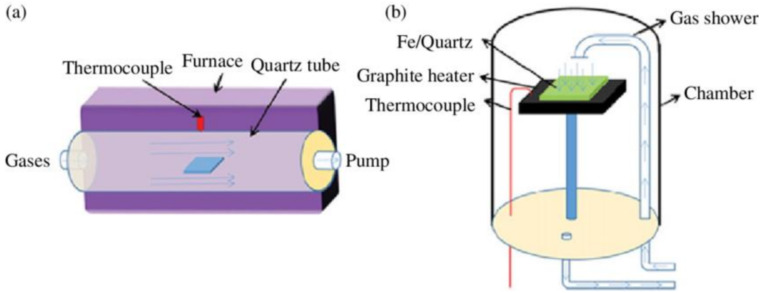

Figure 3.2 Schematic illustration of (a) the hot-wall CVD furnace, and (b) the cold-wall CVD chamber.[*]

b. Cold Wall Reactors

The most popular kind of CVD reactor is the cold wall reactor. They cool the reactor walls while heating the substrate. As a result, the ground experiences a greater temperature than the walls. Cold wall reactors are very well suited for CVD operations using compound semiconductors.

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[*] https://www.sputtertargets.net/wp-content/uploads/2022/08/Schematic-illustration-of-a-the-hot-wall-CVD-furnace-and-b-the-cold-wall-CVD-chamber.png

Advantages

- The walls have less coatings, which facilitates easy cleaning.
- Reactors with cold walls use less energy and temperature.
- Plasma-based chemical vapour deposition methods are supported by cold wall reactors.
- Depositions happen more quickly.
- Reactions in the gas phase are less common.

Disadvantages

- They are more challenging to use.
- One can work on fewer substrates at once.
- There is variation in the substrate temperature. As a result, coating thickness is often uneven.

2. Types of Chemical Vapour Deposition Processes

Following is the chemical vapour deposition process:

a. Plasma-enhanced Chemical Vapour Deposition (PECVD)

Chemical vapour deposition in a specific form is called PECVD. This approach uses a mix of radio frequency and direct current discharge to ionize the reactive gases into plasma. The area between two electrodes is where the ionization process takes place, where gasses are injected and converted into plasma. In comparison to conventional CVD procedures, this technology improves the deposition process by enabling the films to be produced at lower temperatures.

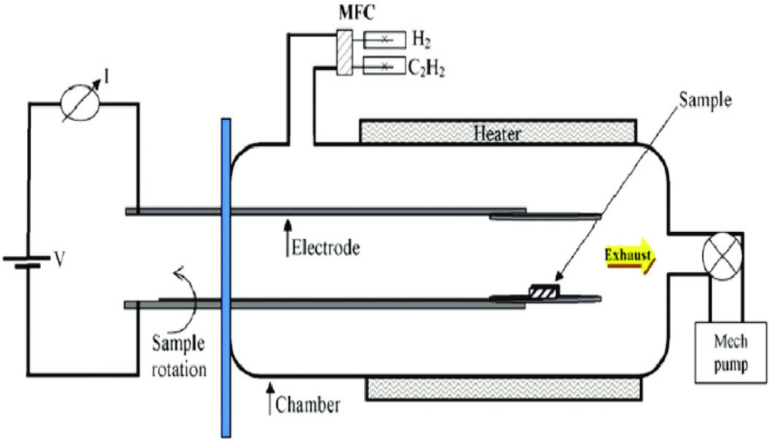

Figure 3.3 Schematic diagram of the plasma-enhanced chemical vapour deposition (PECVD)[*]

3. Thermal Chemical Vapour Deposition

Coatings are readily deposited on surfaces in an open environment during Thermal CVD. The precursor material is introduced to burning gas during this process, which increases the precursor's reactivity. With the help of the heat from the burning gas, this process makes it possible to deposit thin films directly onto surfaces at atmospheric pressure, maximizing the reactivity of precursors to produce homogeneous and effective coatings.

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[*] https://www.sputtertargets.net/wp-content/uploads/2022/08/Schematic-diagram-of-the-plasma-enhanced-chemical-vapor-deposition-PECVD..png

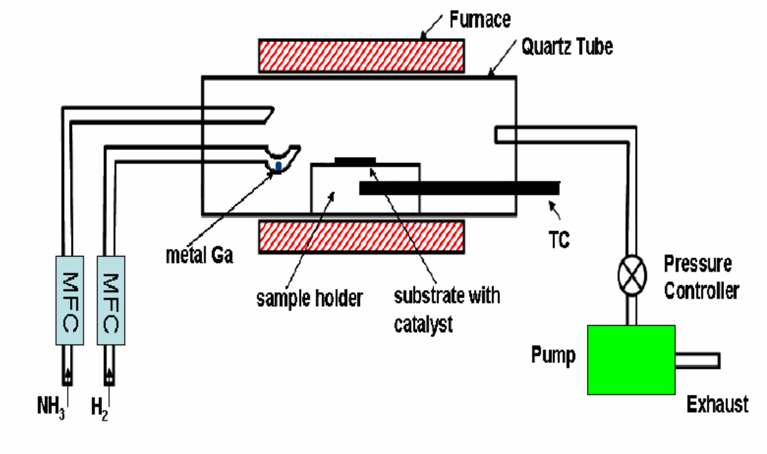

Figure 3.4 Schematic diagram of the thermal chemical vapor deposition (CVD) reactor.[*]

4. Hot-filament Chemical Vapour Deposition (HFCVD)

"Catalytic chemical vapour deposition", or HFCVD, breaks down precursor gases using a heated filament. The heated filament acts as a catalyst in this process, greatly accelerating the decomposition of the gasses. This technique guarantees effective material deposition onto the substrate by placing the device above it, which is kept at a lower temperature than the filament. A regulated deposition environment is made possible by the temperature difference between the hot filament and the cooled substrate, producing coatings that are consistent and of excellent quality.

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[*] https://www.sputtertargets.net/wp-content/uploads/2022/08/Schematic-diagram-of-the-thermal-chemical-vapor-deposition-CVD-reactor..png

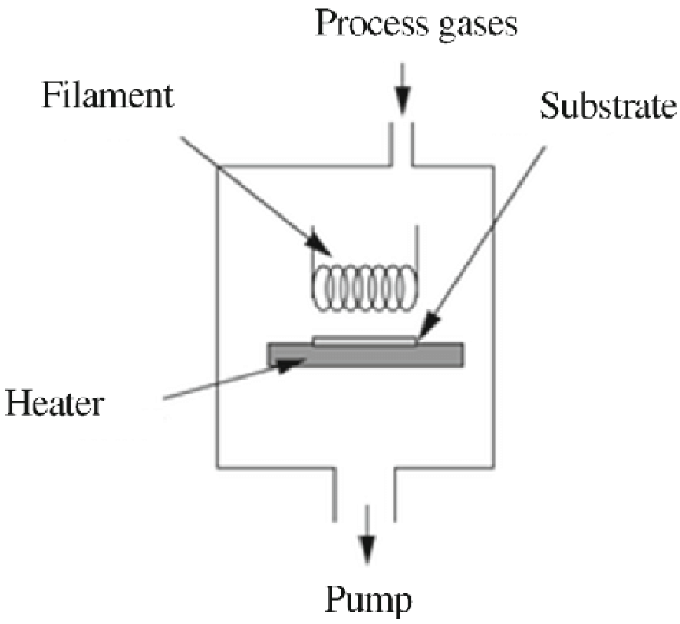

Figure 3.5 Schematic of hot filament chemical vapour deposition setup.[*]

5. Metalorganic Chemical Vapour Deposition (MOCVD)

A specific method for producing single or polycrystalline film thickness is called MOCVD. MOCVD uses chemical processes to create crystals, as opposed to molecular beam epitaxy, which employs physical deposition. Precursors including germane, phosphine, & ammonia are often utilized in this procedure. Thin film materials are formed on substrates as a result of the controlled breakdown of

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[*] https://www.sputtertargets.net/wp-content/uploads/2022/08/Schematic-of-hot-filament-chemical-vapour-deposition-setup..png

certain chemical components. This differentiation highlights the function of MOCVD in enabling intricate chemical reactions necessary for the creation of sophisticated material coatings.

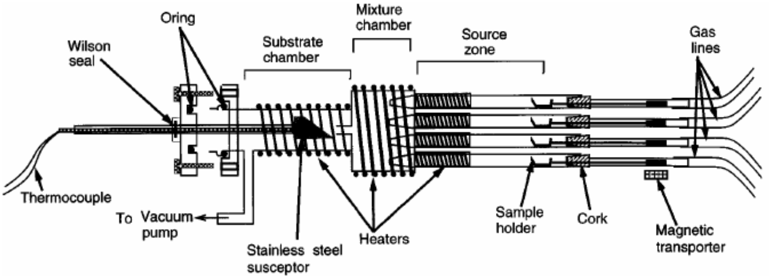

Figure 3.6 Schematic of metalorganic chemical vapour deposition system.[*]

6. Laser Chemical Vapour Deposition (LCVD)

For spot coating applications, LCVD is a precise technique that is often used, particularly in the semiconductor sector. Using a concentrated laser beam, this method heats certain regions of a substrate. The quick and controlled development of material coatings is made possible by the laser's targeted heating, which speeds up the deposition process within the heated regions. LCVD is perfect for applications requiring careful material deposition on intricate substrate geometries because of its focused approach, which guarantees great accuracy in coating location and thickness.

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[*] https://www.sputtertargets.net/wp-content/uploads/2022/08/Schematic-of-metalorganic-chemical-vapor-deposition-system.png

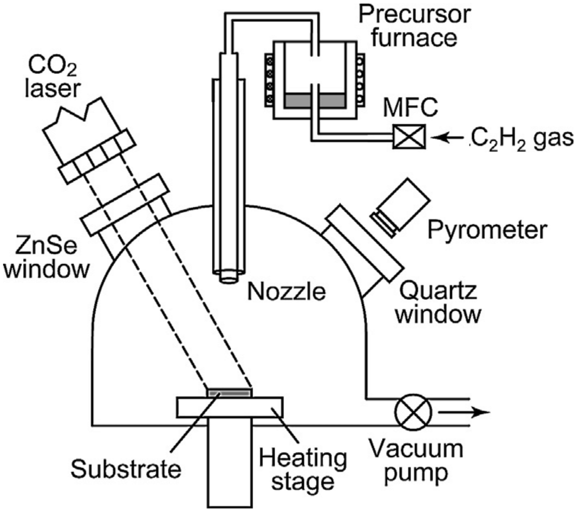

Figure 3.7 Schematic representation of the laser chemical vapour deposition apparatus used in this study.[*]

7. Benefits of Chemical Vapour Deposition

Chemical Vapour Deposition (CVD) is a common technique for depositing thin films to surfaces because it has numerous important benefits that make it appropriate for a broad range of industrial uses. Here are some more details on the advantages of utilizing CVD:

Affordability: When compared to other deposition procedures, CVD is acknowledged as a more economical coating technology. It is a financially feasible choice for high-volume production as well as specialized applications where cost reduction is essential because of its

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[*] https://www.sputtertargets.net/wp-content/uploads/2022/08/Schematic-representation-of-the-laser-chemical-vapor-deposition-apparatus-used-in-this-study..png

efficiency and capacity for large-scale operations, which lower total manufacturing costs.

Versatility: The adaptability of CVD is one of its most notable qualities. Numerous materials, such as metals, ceramics, or polymers, may be deposited onto almost any substrate using this technique. Due to its versatility, it is used to deposit conductive layers and protective coatings in a wide range of sectors, from electronics to aerospace.

High Deposition Rate: High deposition rates in CVD methods are especially noteworthy because they allow substrates to be coated quickly, which is very advantageous in mass-production situations. Large batches of components may be handled swiftly thanks to its efficiency, increasing throughput and cutting down on turnaround times.

Uniform Coating: Another advantage of CVD is its capacity to provide a uniform, constant coating throughout a substrate's whole surface, including intricate geometries and different scales. This consistency is essential in industries like semiconductor production and protective coatings for aircraft components, where the exact thickness of a coating affects the final product's performance or longevity.

High Purity: Since the technique includes the deposition of vapour-phase precursors that can be precisely regulated and purified before use, chemical vapour-deposited compounds are usually exceedingly pure. This produces coatings devoid of contaminants that could jeopardize their structural soundness or efficacy.

Non-Line of Sight Deposition: CVD can cover intricate structures and interior surfaces that are not in direct contact with the deposition material source, in contrast to line-of-sight methods. This feature is especially crucial for parts used in complicated electrical devices or fluid flow systems that have elaborate designs or internal chambers that need to be covered consistently.

8. Applications of Chemical Vapour Deposition

Following are the applications

a. Electronics

In the field of electronics, CVD is crucial to the production of semiconductors since it is used to deposit thin films which are necessary for the production of transistors and integrated circuits. These thin films comprise the gate dielectrics and active layers that are essential to the operation of electronic devices. Since CVD can produce uniform, flawless layers with great accuracy, it is essential for manufacturing the ever-tinier components needed for sophisticated electronics.

b. Cutting Tools

In the tool sector, chemical vapour deposition is widely used to coat cutting instruments, such as milling cutters and drills. The materials used to create CVD coatings, such as diamond-like carbon or titanium nitride, greatly improve the performance, longevity, and efficiency of these instruments. These coatings lessen wear and corrosion on the tool and increase lubrication to lower friction while offering a thermal barrier that aids in preserving the tool's integrity in situations when temperatures are high. Longer tool life, increased machining accuracy, and less downtime for tool change are the results of this.

c. Solar Cells

Another well-known use of CVD is in the production of thin-film solar cells. In this method, photovoltaic materials are deposited onto a substrate in one or more layers. These materials may have varying properties and efficiency, such as silicon, cadmium telluride, as well as copper indium gallium selenide. In this case, CVD is essential because it provides exact control over the composition and thickness of the deposited layers, which is necessary to maximize the efficiency and performance of the solar cells. The importance of CVD in allowing affordable and high-efficiency solar panels becomes increasingly crucial as the need for renewable energy alternatives rises.

3.2.2. Sol-Gel Process

In nanotechnology, the sol-gel process is a flexible and popular method for producing sophisticated materials with particular characteristics and synthesizing nanomaterials. Through chemical processes, a liquid precursor is transformed into a solid gel network and ultimately into a solid substance. The capacity of this process to create materials with exact compositions and architectures at comparatively low temperatures makes it valuable.

1. Steps

An initial sol, or colloidal suspension of the nanoparticles in a liquid, is the basis of the sol-gel process. This sol becomes a gel-like network by chemical reactions, which are followed by drying and heat treatment to turn the substance into a solid.

a. Preparation of Sol

To make a sol, precursor compounds—typically metal alkoxides or salts—are dissolved in a solvent. The ultimate substance that is sought determines the choice of precursor and solvent. Tetraethyl orthosilicate (TEOS), dissolved in ethanol, is a common precursor used to make silica sol.

b. Gelation

The process of gelation causes the sol to change into a network that resembles gel. Through the processes of hydrolysis and condensation, the precursor molecules join forces to create a three-dimensional network. When TEOS is hydrolyzed with water, silanol groups are formed, which subsequently condense to form silica networks.

c. Drying

To create an aerogel or xerogel, the gel is dried to eliminate the solvent. Carefully regulated drying conditions prevent shrinkage or cracking. Aerogels with low density and substantial porosity may be created by either supercritically drying the gel or allowing it to dry at room temperature.

d. Heat Treatment (Sintering)

To get the appropriate material qualities, the dried gel is heated (calcined). This stage improves the material's crystallinity and gets rid of any last bits of organic residue. High-temperature sintering of silica enhances its mechanical and density characteristics, hence enabling its use in coatings and ceramics.

2. Types of Sol-Gel Processes

Following are the types of Sol-Gel Processes:

Different sol-gel techniques may be used, based on the intended material and usage. These consist of dip-coating with sol-gel, template-assisted sol-gel, and the conventional sol-gel method.

a. Traditional Sol-Gel Process

Involves easily preparing gels and sols without the need for extra templates. Coatings, thin films, and bulk ceramics are all made using this technique. In order to produce titanium dioxide (TiO_2) thin films for photocatalysis, a sol must be prepared, applied to a substrate, and heat-treated to create a TiO_2 coating.

b. Template-Assisted Sol-Gel

Uses moulds or templates to direct the creation of certain nanostructures. After gelation & drying, the template is removed, leaving the desired nanostructure in place. To build pores in mesoporous silica materials, surfactants are used as templates and then removed to form a porous structure.

c. Sol-Gel Dip-Coating

Involves covering a substrate with a sol by immersing it in it, letting it dry, and then heating it to solidify the coating. This technique is used in intricate geometries to produce homogeneous coatings. Applying thin, homogeneous coatings of materials produced from sol-gel onto glass or metal surfaces for protective and optical coatings is known as dip-coating.

Chapter Summary

This chapter explored the synthesis and characterization of nanomaterials, focusing on the top-down and bottom-up approaches. The top-down approach involves breaking down larger materials into nanoscale particles using various techniques, while the bottom-up approach builds nanomaterials from atomic or molecular components.

It reviewed several synthesis techniques, including Chemical Vapour Deposition (CVD), which involves processes such as Thermal Chemical Vapour Deposition, Hot-filament CVD, Metalorganic CVD, and Laser CVD. Each CVD method is discussed with its benefits and applications. Additionally, the chapter examined the Sol-Gel process, detailing its steps and different types. This overview highlights the diverse methodologies for nanomaterial synthesis and their significance in advancing nanotechnology.

Assessment Questions

1. What is the fundamental idea behind the top-down methodology in nanofabrication?
2. What role does nanolithography play in the top-down method of producing nanomaterials?
3. In nanotechnology, what sets apart the top-down and bottom-up approaches?
4. How does the bottom-up approach's chemical vapour deposition (CVD) process operate?
5. What are the main advantages of fabricating nanomaterials by chemical vapour deposition (CVD)?
6. How is the sol-gel technique used in the creation of nanomaterials?
7. Which kind of sol-gel techniques are used in nanotechnology?
8. What distinguishes conventional chemical vapour deposition (CVD) from plasma-enhanced CVD?
9. What functions do reactors serve when it comes to chemical vapour deposition, and which kinds are utilized?
10. How are biological templates used in biosynthesis to create nanomaterials?

CHAPTER 4

Introduction to Nanomaterials

Learning Objective

The fundamentals of inorganic materials chemistry & nanochemistry will be covered in this chapter, along with an overview of nanomaterials and their importance in a range of applications.

4.1. Inorganic Materials Chemistry and Nanochemistry

Inorganic materials chemistry focuses on the study of inorganic compounds and their properties, synthesis, and applications. Nanochemistry, a subset of this field, investigates the unique characteristics and behaviours of inorganic nanomaterials at the nanoscale. Together, they explore how nanoscale inorganic materials can be engineered to achieve advanced functionalities and applications.

4.1.1. Inorganic Chemistry

The term "organic" describes substances that have carbon atoms in them. Therefore, "Inorganic Chemistry" refers to the area of chemistry that studies molecules devoid of carbon-hydrogen atoms.

1. Concepts under Inorganic Chemistry

The following are the concepts:

a. Organometallic Chemistry

Over the last three to four decades, the multidisciplinary field of organometallic chemistry within inorganic chemistry has expanded at an astounding rate. Academically, attempts to clarify the nature of bonds in the growing number of fascinating organometallic compounds have improved our knowledge of the types and characteristics of chemical bonds. In industries, organometallic compounds are mostly used as homogenous catalysis agents.

The study of organometallic compounds is known as organometallic chemistry. Compounds having mostly covalent metallic connections may be an option since many compounds lacking these bonds are chemically similar. Organic and inorganic chemical elements are combined in organometallic chemistry.

b. Transition Elements

One may characterize a transition element as having partly filled d-orbitals within its penultimate shell. We can identify a transition element only by seeing its electrical configuration thanks to this helpful conceptual characterization. According to this definition, the transition elements do not include zinc, cadmium, or mercury since they lack a partly filled d-orbital. Since their characteristics extend those of transition elements within inorganic chemistry, they are also regarded as transition elements. The representative elements and the transition elements are connected by the zinc group.

The fact that all 24 of the elements in question are metals, that the majority of them are hard, solid, and lustrous, that they have high melting or boiling temperatures, and that they are effective heat and electrical conductors are among their most noteworthy commonalities. Since there is a large range of these attributes, the statements may be compared to the generic attributes of every other element.

c. Coordination Chemistry

Applications for coordination compounds were known even before inorganic chemistry was developed. With Tassaert's curiosity, a methodical study of structure and bonding within coordination chemistry got underway. Until the end of the nineteenth century, notable chemists like Wilhelm Blomstrand, Jorgensen, and Alfred Werner continued this work. As a result, Werner's theory of coordination served as the foundation for contemporary coordination chemistry.

d. P-Block Elements

The p-block is made up of the elements listed in groups 13 through 18 of the periodic table. Like other block elements, the inorganic chemistry p block elements' atomic size, electron gain enthalpy, ionization enthalpy, and electronegativity all have a significant impact on their characteristics. Heavy p-block elements are distinct from their lighter congeners due to the existence of d-or f-orbitals in heavier elements and the lack of d-orbitals in second-period elements, which have a substantial impact on the elements' characteristics.

2. Classification of Inorganic Compounds

The Inorganic compounds are classified as:

Acids: Compounds classified as acids are those that dissolve within water and release H+ ions or hydrogen ions. Acids include things like vinegar, citric acid, sulfuric acid, and hydrochloric acid. The following is an acidic reaction example: $HCl + water \rightarrow H^+ + Cl$

Bases: A base is a kind of material or chemical that, in water, yields hydroxyl ions. When bases including potassium hydroxide, calcium hydroxide, sodium hydroxide, and ammonia are dissolved in water, OH- ions are produced. Hydrogen peroxide + $H_2O \rightarrow K^+ + OH^-$

Salts: The term "salt," as one may know, is rather common. Salts are materials that are produced when an acid and a base react with one another. One of the common examples of salt is sodium hydroxide table salt.

Oxides: Oxides are compounds made up of a single oxygen atom.

3. Applications of Inorganic Chemistry

There are several uses for inorganic chemistry in a variety of sectors, including chemical, biological, engineering, etc.

- It is used in medical settings as well as in healthcare institutions.
- The most popular usage is in our everyday life, where we utilize ordinary salt or the chemical sodium hydroxide.
- Cakes and other baked goods are made with the aid of baking soda.
- The ceramic industries use a lot of inorganic chemicals.
- It is used in the electrical sector in silicon circuits found in computers, etc.

4.1.2. Nanochemistry

The chemical uses of nanoparticles in nanotechnology are the focus of the discipline of nanochemistry. It comprises studying the physical and chemical characteristics of materials as well as their creation and manipulation at the molecular and atomic levels.

The study of chemistry at nanoscale is known as nanochemistry. One nanometre is equivalent to one billionth of a metre. Considering that human hair possesses a thickness of 100,000 nanometres, this minuscule length makes sense. In order to be categorised as a nanomaterial, a substance has to have at least one dimension that falls between 1 and 100 nm.

In the last several years, there has been significant advancement in nanotechnology and science. In particular, nanochemistry offers a novel approach to precisely building devices at the molecular level. Since nanochemistry can build objects atom by atom, nanodevices may find use in scientific research, electronics, computing, and medicine. Understanding novel behavioural principles is the largest barrier to fully using nanochemistry as nanoscale systems sit at the boundary between classical and quantum behaviour and exhibit properties not seen in larger devices.

While the concept of nanochemical control dates back many decades, many of the instruments needed to investigate the nanoworld are relatively new. These include innovative techniques for nanofabrication and lithography, high-resolution scanning & transmission electron microscopies, Atomic Force Microscopes (AFMs), and STMs.

Research on nanochemical systems covers a broad spectrum of subjects, from the manipulation of individual atom interactions to the study of larger molecule assemblies including polymers, dendrimers, and clusters. As a consequence, assembly studies have produced important novel structures such as nanotubes, nanowires, three-dimensional molecular assemblies, & lab-on-a-chip devices for biological research and separations.

1. Nanoparticle Size

The term "nano" comes from the Greek word "nanos," which denotes the billionth part of a unit.

One nanometer, for instance, is equivalent to 1/1,000,000,000 meter.

One nanometer (nm) is equivalent to 0.000000,001 meters or 10^{-9}.

The following instances might aid in illustrating how tiny the nanoscale is:

- The size difference between a nanometer and a metre is equivalent to that between an Earth and a golf ball.
- Twenty-five thousandths of a human hair's diameter equals one nanometer.
- The width of the cell membrane is around 9 nm.
- The diameter of the DNA double helix is 2 nm.
- The diameter of one hydrogen atom is around 0.2 nm.

2. Applications of Nanochemistry

Chemical, physical, & materials science, biology, medicine, and engineering all make use of nanochemistry. Utilizing single atoms as building blocks opens up new possibilities for investigating quantum computing, enabling the creation of the tiniest features feasible in integrated circuits, and providing new approaches to produce novel materials.

a. Catalysis: Nano-enzymes (or Nanozymes)

Nano-enzymes, also known as nanozymes, are very tiny (1–100 nm) and possess special optical, magnetic, electrical, and catalytic capabilities.

Moreover, these tiny enzymes' predictable nanostructure and capacity to regulate the activity of nanoparticle surfaces have enabled them to develop a complex surface structure tailored to particular applications.

b. Cosmetics

Nanochemistry may be useful in the production of deodorant, moisturizer, and sunscreen-containing cosmetic materials. Manufacturers are attempting to use oil nanoemulsion to increase the effectiveness of different cosmetics. When it comes to treating dryness, inelasticity, and wrinkles in aged skin, these particles are pushing the envelope. In sunscreen, zinc oxide and titanium dioxide nanoparticles work well as UV filters, but they may also seep into the skin. By reflecting or absorbing UV light, these substances shield the skin from damaging UV rays and stop the skin from suffering full-thickness damage from the photoexcitation of electrons within nanoparticles.

c. Drug Delivery

Nanotechnology-based new medication delivery techniques may be advantageous because they enhance the body's reaction, target particular areas, and promote non-toxic metabolism. It is possible to functionalize several nanotechnological techniques and materials for medication delivery. Ideal materials employ a controlled-activation nanomaterial to deliver a drug payload into the body. Mesoporous silica nanoparticles, or MSNs, are becoming more and more popular in research because of their vast surface area and ability to be modified individually while still performing well in high-resolution imaging.

Due to its non-toxicity, ability to pass the blood-brain barrier, and spontaneous absorption via the skin, nanodiamonds have lately shown promise in medication administration.

Numerous inventive medical procedure advancements are also inspired by the unusual structure of carbon nanotubes. As more medication is created at the nanoscale to transform how people identify and cure illnesses, they are emerging as a more viable option for novel detection techniques as well as treatment approaches. Specifically, carbon nanotubes may be converted into complex biomolecules and identified by modifications in their fluorescence spectra. These nanotubes may also be made to resemble tiny drugs, which would allow a target cell to endocytose them and use them as a delivery system.

d. Tissue Engineering

Cells are very dependent on nanotopographical characteristics, which has led to a drive toward implantation in tissue engineering by surface optimization. Under the correct circumstances, a precisely designed three-dimensional scaffold is utilized to guide cell seeds toward the creation of artificial organs. The 3-D scaffold integrates many nanoscale environment-controlling elements for optimum and suitable performance. By providing the necessary, intricate biological components, the scaffold—an in vitro equivalent of the extracellular matrix found in living organisms—enables the effective development of artificial organs.

e. Wound Healing

Applications of nanochemistry have been shown to speed up the healing of wounds and abrasions. In addition to tissue engineering, electrospinning serves as a polymerization technique that may be used in medication administration and wound dressing. This creates nanofibers in a controlled setting that are both antimicrobial and encourage cell division. These characteristics are apparent at the macroscale, but the nanotopographical aspects may make the nanoscale versions more effective. Targeted nanofiber-wound interfaces in vivo have increased surface area interactions. Additionally, there is evidence that certain viruses and bacteria may be inhibited by specific silver nanoparticles.

4.2. Basics of Nanomaterials

Materials having at least 1 dimension on nanometric scales, ranging in size from 1 to 100 nm, are referred to as nanomaterials. The human eye is unable to detect these chemicals. Methods from materials science of nanotechnology are taken into consideration while discussing nanomaterials. Despite their activity at the molecular scale, these materials have distinct optical, electrical, mechanical, & quantum-mechanical properties at this scale.

Materials with nano-objects or nano-structures are referred to as nanomaterials. Nano-objects are discrete pieces of material as opposed to nanostructured materials, whose internal or surface structure is within the nano range. Nanomaterials may be created purposefully, accidentally, or organically. Scientific progress has led to the production and commercialization of nanomaterials.

Since they may be created in a precise method to fulfil a specified purpose, nanomaterials are employed in a broad variety of sectors, from air purification & environmental preservation to healthcare & cosmetics. For example, the delivery of medications is one of the primary uses of nanoparticles in the healthcare sector. The creation of nanoparticles to aid in the delivery of chemotherapeutic treatments to malignant growths and to deliver therapeutics to damaged areas of arteries to treat cardiovascular disease is one example of this process. By fusing nanotubes with antibodies, carbon nanotubes may also be used to create bacteria sensors.

In the aerospace industry, carbon nanotubes may be used to modify the form of an airplane's wings. When an electric voltage is applied, the composite shape of the nanotubes is used to create bending. Additionally, other methods of environmental preservation also make use of nanomaterials, in this instance, nanowires. Two current applications under investigation include the usage of zinc oxide nanowires: the filtration of polluted water and flexible solar panels.

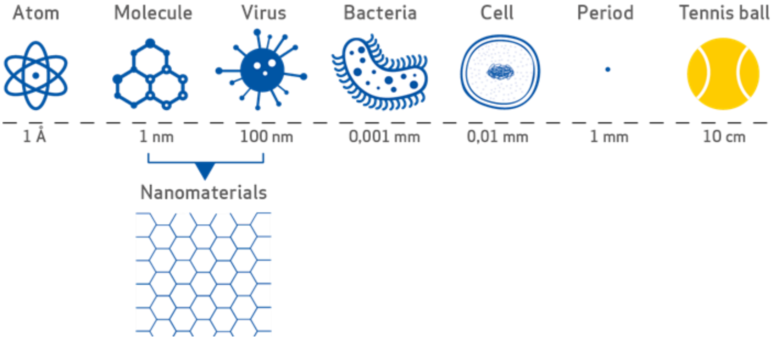

Figure 4.1 Scale size of nanomaterials[*]

1. Properties of nanomaterials

Materials at the nanoscale exhibit noticeable changes in their characteristics as they break down. Materials' electronic characteristics vary from the molecular to nanoscale level due to quantum size effects. As the surface surface-to-volume ratio rises at the nanoscale, materials' mechanical, thermal, & catalytic characteristics may alter. Many insulator materials start to act like conductors at nanoscale levels. This also holds true at nanoscale levels, where a wide range of intriguing surface and quantum phenomena are seen.

The size, shape, stability, chemical composition, crystal structure, surface area, surface energy, and other characteristics of nanomaterials are among their physical and chemical composition. As the surface-to-volume ratio rises, the surfaces of nanomaterials react with one another and with other systems.

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[*] https://ion2.upm.edu.my/summer-uploads/20220830154907blobid0.png

The size of a nanomaterial has a big impact on its pharmacological properties. When nanomaterials come into contact with water or another dispersion medium, they might alter their crystal structure. The size, composition, & surface charge of nanoparticles determines how they aggregate. Surface coatings influence the physicochemical, psychokinetic, and magnetic characteristics of these materials. Particle contact at the nanoscale is caused by Van Der Waals forces or strong polar or covalent interactions. The surface properties of nanomaterials & their interactions with other materials and environments may be changed with the use of polyelectrolytes.

2. Uses of Nanomaterials

Nanomaterials are used in a wide range of sectors, from air purification and environmental preservation to healthcare and cosmetics, since they may be produced in a precise fashion to fulfil a specific purpose.

For instance, the delivery of drugs is one of the main applications of nanoparticles in the healthcare industry. As an illustration of this process, consider the development of nanoparticles to help carry chemotherapy medications to malignant growths directly and to damaged artery sections in the battle against cardiovascular disease. Additionally, carbon nanotubes are being created for use in procedures like incorporating antibodies into the nanotubes to produce bacteria sensors.

Carbon nanotubes may be utilized in aerospace to change the shape of an aircraft's wings. When an electric voltage is applied, the composite shape of the nanotubes is exploited to bend. In other instances, nanomaterials—in this example, nanowires—are also used in environmental preservation procedures. Applications for zinc oxide nanowires, which may be used in flexible solar panels and help remediate contaminated water, are currently being researched.

3. Applications of Nanomaterials

Due to their special qualities, nanomaterials have a broad variety of applications in several disciplines. Their uses include anything from electronics and health to environmental research and energy.

a. Medicine

Drug delivery techniques, imaging agents, & diagnostics all employ nanomaterials. Their diminutive dimensions facilitate precise administration and enhanced imaging proficiencies. Gold nanoparticles are utilized in targeted cancer therapy, whereas quantum dots are used as fluorescent markers during biological imaging.

b. Electronics

Nanomaterials are used in nanoelectronics to make transistors, sensors, & memory devices, among other electronic components, quicker, smaller, and more efficient. Conductive films and high-performance transistors are made using carbon nanotubes.

c. Energy

Solar cells, fuel cells, batteries, and other energy-storage and conversion technologies are improved by nanomaterials. Their qualities improve performance and efficiency. Lithium-ion batteries with nanostructured electrodes have higher capacity & charge/discharge rates.

d. Environmental Science

Environmental uses of nanomaterials include cleanup, contaminant detection, and water purification. They work well in these capacities because of their large surface area and responsiveness. Utilizing titanium dioxide nanoparticles as photocatalysts, organic contaminants in wastewater are broken down.

4. Challenges and Safety Concerns

The use of nanoparticles presents unique difficulties and safety issues, including possible harm to the environment and human health. Resolving these concerns is essential to the ethical development and use of nanotechnology.

a. Environmental Impact

There might be unidentified ecological consequences from the possible discharge of nanomaterials onto the environment. Evaluating their behaviour and effects on ecosystems is crucial. Research is required to comprehend the possible impacts of nanomaterials on animals as well as how they interact with soil and water systems.

b. Health Risks

Due to their microscopic size and potential for ingestion or inhalation, nanomaterials may be hazardous to one's health. To ascertain their safety and provide handling instructions, research is still in progress. Since breathing in nanoparticles might cause respiratory problems, industrial facilities need to include safety procedures and precautions.

c. Regulation and Standardization

Creating rules and guidelines for nanomaterials is essential to guarantee their quality, safety, and uniformity across sectors. In order to address possible dangers, regulatory authorities are striving to set criteria for the testing & labelling of nanomaterials.

Chapter Summary

This chapter explored the introduction to nanomaterials, focusing on inorganic materials chemistry and nanochemistry. It covered the fundamental concepts of inorganic chemistry, including the classification and applications of inorganic compounds. The chapter then transitioned to nanochemistry, discussing the size of nanoparticles and their various applications.

It also addressed the basics of nanomaterials, outlining their properties, uses, and applications across different fields. Finally, it highlighted the challenges and safety concerns associated with nanomaterials. This comprehensive overview provides a foundational understanding of nanomaterials and their significance in both scientific and practical contexts.

Assessment Questions

1. What fundamental concepts underpin inorganic chemistry?
2. In chemistry, how are inorganic substances categorized?
3. What is the connection between inorganic and nanochemistry?
4. What are the most important uses of nanochemistry in contemporary science?
5. Which characteristics are often linked to nanomaterials?
6. How are nanomaterials used in different sectors and fields?
7. How do nano-enzymes, or nanozymes, function in catalysis?
8. What effects does a particle's size have on its characteristics and uses?
9. What are some noteworthy uses of inorganic chemistry across different sectors?
10. How can inorganic compound applications be enhanced and integrated with nanochemistry?

CHAPTER 5

Types of Nanoparticles

Learning Objective

The many kinds of nanoparticles that will be discussed in this chapter include semiconductor nanocrystals, metal nanocrystals, organic nanoparticles (latexes), porous inorganic nanoparticles, and carbon-based nanoparticles like graphene and carbon nanotubes.

5.1. Metal Nanocrystals

Metal nanocrystals were nanoparticles composed of metals with nanoscale crystalline formations, usually between 1 and 100 nanometers. Metal nanocrystals vary from their bulk counterparts in their physical, chemical, & optical properties due to their size, shape, and surface features. They are useful in a variety of applications, including catalysis, electronics, sensing, & medicine, because of their qualities.

1. Characteristics of Metal Nanocrystals

Due to its high surface-to-volume ratio and nanoscale size, metal nanocrystals have unique properties. These features include distinct chemical, visual, and electrical qualities.

Size and Shape: The size and form of metal nanocrystals greatly influence their characteristics. Cubes, triangles, rods, and spheres are typical shapes. Since gold nanorods and gold nanospheres have distinct surface plasmon resonance characteristics, the two display different optical qualities.

Surface Effects: Metal nanocrystals' large surface area increases their surface energy and reactivity. In contrast to bulk metals, this may lead to distinct catalytic activities & chemical reactivity. Since platinum nanocubes have more surface area and distinct surface facets than bulk platinum, they exhibit better catalytic activity during hydrogenation processes.

Quantum Effects: Quantum effects become important at the nanoscale, affecting the electrical and optical properties of metal nanocrystals. Size-dependent characteristics like changed band gaps and SPR may result from this. Size-dependent Surface Plasmon Resonance (SPR) in silver nanocrystals may be controlled to produce colour shifts by varying the particle's size or shape.

2. Synthesis of Metal Nanocrystals

Metal nanocrystals may be created in a variety of ways, with each approach offering a degree of control over the final product's dimensions, form, and quality. The intended use and the characteristics of the material determine the procedure to be used.

Chemical Reduction: Chemical reducing agents are used to decrease metal ions into metal nanocrystals in solution. This is a typical process used to create metal nanoparticles. Reducing gold chloride ($HAuCl_4$) using sodium citrate/sodium borohydride may produce gold nanocrystals.

Physical Vapour Deposition (PVD): A substrate is coated with metal vapour, which condenses into nanocrystals. Thin films & nanostructures are produced using this technique. One may deposit metal films by sputtering or evaporating them, and then refine them into nanocrystals.

Colloidal Synthesis: Metal precursors dissolve in a solvent, and in the presence of stabilizing chemicals that regulate particle development, the precursors nucleate into nanocrystals. In the process of creating colloidal silver nanoparticles, stabilizers such as polyvinyl alcohol (PVA) are used to reduce silver salts within an aqueous solution.

Template-Assisted Methods: The size and form of metal nanocrystals are determined by the templates they develop inside or on. Afterwards, the template is eliminated, leaving the nanocrystals in place. Anodic Aluminium Oxide (AAO) is one kind of template that may be used to develop metal within its pores, and then the template is removed to create nanorods.

3. Applications of Metal Nanocrystals

Due to their special qualities, metal nanocrystals offer a broad variety of applications in several sectors.

Catalysis: Because of their large surface area and strong catalytic activity, metal nanocrystals serve as catalysts in chemical processes. They are used in both environmental and industrial operations. Catalytic converters employ platinum nanocubes to lower vehicle emissions.

Medicine: Drug delivery, cancer treatment, and medical imaging all make use of metal nanocrystals. Their surface characteristics and size allow for improved imaging and targeted delivery. In photothermal treatment, gold nanoparticles are applied to cancer cells and heated using infrared light to cause the cells to rupture.

Electronics: Because of their electrical characteristics and nanoscale size, metal nanocrystals are used throughout electronic devices as sensors, transistors, and memory systems. Conductive inks for printed and flexible electronics both employ silver nanoparticles.

Environmental Applications: Metal nanocrystals have applications in pollution prevention, water purification, and environmental sensing. They are efficient in identifying and eliminating pollutants due to their large surface area and reactivity. Utilizing titanium dioxide nanocrystals as photocatalysts, organic contaminants in wastewater are broken down.

5.2. Semiconductor Nanocrystals

Semiconductor nanocrystals, often called quantum dots, are tiny semiconductor particles that are usually between one and ten nanometers in size. When the size of these nanocrystals reaches the exciton Bohr radius, quantum confinement phenomena occur, giving birth to unique electrical and optical features. They are useful in a variety of applications, including electronics, optoelectronics, & biomedical imaging, due to their unique qualities.

1. Characteristics of Semiconductor Nanocrystals

Due to their small size, semiconductor nanocrystals have special qualities that set them apart from bulk semiconductors in terms of their electrical and optical characteristics.

Quantum Confinement: Quantum confinement effects, in which the size of the nanocrystals affects the electrical and optical characteristics, are shown by semiconductor nanocrystals because of their tiny size. In quantum dots, size-tunable fluorescence emission results from a rise in the bandgap as the nanocrystal's size decreases.

Size-Dependent Optical Properties: The optical characteristics of semiconductor nanocrystals, such as their emission and absorption spectra, are influenced by their size. Emission colour tweaking is possible because of this size dependency. Depending on its size, cadmium selenide (CdSe) quantum dots produce a range of hues from red to blue that are used in a variety of imaging and display technologies.

High Surface-to-Volume Ratio: Semiconductor nanocrystals' high surface-to-volume ratio increases surface effects, which may affect how they behave electrically and optically. Enhancing the solubility and stability of quantum dots in many solvents and media may be achieved by surface modification using ligands.

2. Synthesis of Semiconductor Nanocrystals

Several techniques are available for the synthesis of semiconductor nanocrystals, which provide exact control over their dimensions, form, and surface characteristics.

Colloidal Synthesis: Involves reducing metal precursors chemically in a solution to create nanocrystals. Because of its ease of use and capacity to provide high-quality nanocrystals, this approach is often used. Usually, stabilizing ligands are present when cadmium & selenium precursors react to create CdSe quantum dots.

Chemical Vapour Deposition (CVD): A method that creates nanocrystals by depositing gaseous precursors on a substrate and allowing them to condense. Nanowires and thin films are produced using this technique. For electrical and optoelectronic applications, CVD is used to produce semiconductor nanostructures such as silicon nanowires on substrates.

Hydrothermal and Solvothermal Methods: Involves creating nanocrystals in an organic or aqueous solution at high pressure and temperature. These techniques can yield nanocrystals with precise sizes and shapes. Hydrothermal techniques may be used to create ZnO nanocrystals, which are well-defined hexagonal or just spherical particles.

Template-Assisted Synthesis: Use moulds or templates to regulate the size and form of the nanocrystals. Once the nanocrystals have formed, the template is removed. Semiconductor materials, such as Anodic Aluminium Oxide (AAO), may be grown within the pores of a template to create nanowires or nanorods.

3. Properties of Semiconductor Nanocrystals

Since semiconductor nanocrystals have nanoscale dimensions & quantum effects, they display a variety of features different from those of their bulk counterparts.

Photoluminescence: Strong photoluminescence is a common feature of semiconductor nanocrystals, and their emission may be controlled by varying their size. Technologies related to images and displays make extensive use of this feature. Since they can be made to emit certain hues of light, quantum dots are helpful for biological imaging and colour displays.

Electro-optical Properties: The bandgap and charge transport characteristics of semiconductor nanocrystals may be modified by adjusting their size. Applications in electrical devices and sensors should take note of this. Field-effect transistors (FETs) made of quantum dots may exhibit size-dependent electrical properties that affect how well the transistors function in electronic circuits.

Stability and Surface Chemistry: The stability and interactions of semiconductor nanocrystals with other materials may be influenced by their surface chemistry.

Often, surface passivation is needed to improve their functioning and stability. To increase quantum dots' stability and stop oxidation or aggregation, coat them with inorganic shells or organic ligands.

5.3. Porous Inorganic Nanoparticles

Porous inorganic nanoparticles are inorganic materials with a porous structure arranged in nanometer-sized particles. These nanoparticles' structure is made up of a network of linked voids or pores and a large surface area. These particles' porous characteristic increases their usefulness in several applications, such as medication administration, environmental cleanup, and catalysis.

1. Synthesis of Porous Inorganic Nanoparticles

Porous inorganic nanoparticles are made using a variety of synthesis techniques, all of which provide control over the size, distribution, and shape of the pores.

Sol-Gel Method: A method of chemical synthesis in which metal salts or alkoxides are transformed into a gel and then treated to create porous nanoparticles. Pore size and placement may be precisely controlled using this technology. The sol-gel process may be used to create silica nanoparticles, which can then be used to create mesoporous silica with adjustable pore sizes.

Template-Assisted Synthesis: Entails giving the nanoparticles a porous structure by employing a template. The porous substance is then removed by removing the template. Porous silica nanoparticles may be made using polystyrene spheres as templates. After the removal of the spheres, a porous silica structure is seen.

Hydrothermal Synthesis: A process that creates porous nanoparticles by reacting inorganic precursors in an aqueous solution under high pressure and temperature. Porous titanium dioxide (TiO_2) nanoparticles with large surface areas and regulated pore diameters may be created using hydrothermal synthesis.

Physical Vapour Deposition (PVD): Involves vapour-phase depositing of inorganic materials onto a substrate such that porous nanoparticles may be produced by processing the substrate. Zinc oxide (Z_nO) and other porous metal oxide nanoparticles with regulated porosity may be produced using PVD and employed in photocatalysis and sensors.

2. Properties of Porous Inorganic Nanoparticles

These nanoparticles' porous nature gives them certain special qualities that are helpful in a variety of applications.

Enhanced Adsorption Capacity: Increased molecular adsorption capacity is made possible by the wide surface area and pore structure, which is beneficial for applications in separation & purification. Activated carbon nanoparticles are useful for cleaning up the environment because of their high adsorption capabilities for contaminants.

Catalytic Activity: These nanoparticles are efficient catalysts for chemical reactions because of their large surface area and the porous structure's availability of active sites. Because of their large surface area and catalytic sites, porous silica-supported metal nanoparticles serve as catalysts in processes like hydrogenation and oxidation.

Controlled Release: The porous nature of the drug delivery applications enables controlled drug release that may be adjusted to obtain desired release patterns. Drugs may be encapsulated in mesoporous silica nanoparticles and released in a regulated way, increasing the effectiveness of treatments.

Structural Flexibility: Nanoparticles may be tailored for specialized uses, such as filters and sensors, by adjusting their pore size and shape. Molecules may be separated according to size using selective filters made of porous nanoparticles with controllable pore diameters.

3. Applications of Porous Inorganic Nanoparticles

Due to their special qualities, such as their large surface area and adjustable pore structure, porous inorganic nanoparticles are employed in many different applications.

Catalysis: These nanoparticles are efficient catalysts in a variety of chemical reactions, notably industrial operations and environmental cleanup, due to their large surface area and active sites inside their porous structure. Catalytic metals are supported by porous silica and alumina nanoparticles in procedures like pollution control and petroleum refining.

Drug Delivery: Drugs can be delivered more precisely and with fewer adverse effects when they are delivered via porous nanoparticles. Anticancer medications are delivered to specific tumour cells using mesoporous silica nanoparticles.

Environmental Remediation: Due to their great adsorption capacity, porous nanoparticles may effectively remove contaminants from soil, water, and the air. Heavy metals & organic pollutants are among the contaminants that are adsorbently removed from wastewater by the use of porous carbon-based nanoparticles.

Sensors: The large surface area or pore structure makes it possible to create sensitive sensors that can identify vapours, gasses, and biomolecules. Gas sensors utilize porous metal oxide nanoparticles to identify dangerous gasses even at low concentrations.

5.4. Organic Nanoparticles (Latexes)

Often called latexes, organic nanoparticles are nanoscale particles made of copolymers or organic polymers. Because of these nanoparticles' adaptability, biocompatibility, and simplicity in functionalization, they are extensively employed in many different sectors. The main uses of latex nanoparticles are in coatings, medication administration, environmental cleanup, and diagnostics. The unique characteristics of organic nanoparticles stem from their nanoscale size and polymeric composition. These qualities are essential to their performance in a variety of applications.

Size and Shape: Synthetic organic nanoparticles may take on a variety of forms and dimensions, usually falling between 10 and 1000 nanometers. These nanoparticles' size and shape may affect how they behave and function in many applications. Since they are the ideal size for interacting with biological molecules, spherical latex nanoparticles, typically measuring around 100 nm, are often used in diagnostic tests.

Surface Chemistry: Organic nanoparticles' surfaces may be readily functionalized to improve their interactions with target molecules or as surfaces. This makes modification possible depending on certain application requirements. To increase the stability or facilitate certain binding interactions, latex nanoparticles may have functional groups added to them, such as amino, carboxyl, as well as thiol groups.

Biocompatibility: Since many organic nanoparticles remain biocompatible, they may be used in biological and medical research. As they are organic, they are often less harmful and more compatible with biological systems. Because polystyrene nanoparticles are biocompatible and readily customizable for individual purposes, they are frequently employed in medication administration and cell imaging.

5.5. Carbon-Based Nanoparticles

Carbon-based nanoparticles are materials composed primarily of carbon atoms arranged in various nanostructures, such as fullerenes, carbon nanotubes, and graphene. These nanoparticles exhibit remarkable mechanical, electrical, and thermal properties due to their unique carbon arrangements. They are widely used in diverse applications, including electronics, materials science, and medicine.

5.5.1. Carbon Nanotubes

Carbon nanotubes are hollow tubes made of carbon atoms at the nanoscale. The cylindrical carbon molecules have diameters ranging from a few nanometers to tens of nanometers, lengths up to millimetres, and high aspect ratios usually over 103. Carbon nanotubes have a particular character due to their unique one-dimensional structure and accompanying features, which gives them limitless potential in applications related to nanotechnology. One member of the fullerene family is the carbon nanotube. Even though the initial fullerene molecules were found in 1985, the public did not become aware of carbon nanotubes until Sumio Iijima published his research on needle-like carbon tubes in Nature in 1991.

Since then, several shaped carbon nanotubes have been found. They are primarily divided into two groups according to the quantity of graphic shells: single-walled (SWNTs) & multi-walled carbon nanotubes (MWNTs).

Iijima reported on carbon nanotubes that were made using arc discharge techniques, or MWNTs. Two years later, utilizing transition-metal catalyzed arc discharge, two separate research teams—Iijima and Toshinari Ichihashi—as well as Donald S. Bethune and his IBM colleagues—synthesised SWNTs.

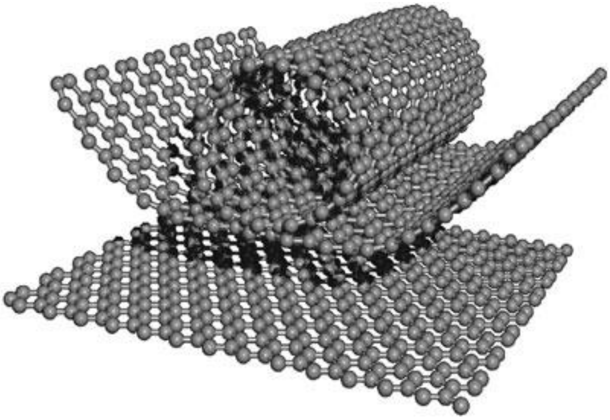

Figure 5.1 Schematic of how graphene could roll up to form a carbon nanotube.[*]

1. Carbon allotropes

The element carbon, which is the fourth most prevalent in the universe, may exist in a broad range of configurations known as allotropes, depending on how its atoms are arranged. Allotropes of carbon have unique electrical conductivity and strength characteristics.

Diamond and graphite are the two traditional morphologies of solid carbon at room temperature. A

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[*] https://www.nanowerk.com/images/cnt-from-graphene.jpg

significant advance in the science of carbon nanochemistry was made in 1985 with the identification of a third and new carbon allotrope, known as C60, fullerene, or buckyballs, that included sixty precisely symmetrically distributed carbon atoms. Subsequently, graphene was found in 2004 and carbon nanotubes in 1991.

2. Electrical properties of carbon nanotubes

The electrical characteristics of the nanotubes are determined by the rolling-up direction (also known as the chiral vector) of graphene layers. The hexagonal carbon-atom lattice angle of a nanotube is characterized by its chirality.

Armchair nanotubes – Known for their armchair-like edges, these materials possess identical chiral indices & are highly sought-after for their flawless conductivity. In contrast to them, zigzag nanotubes could be semiconductors. A graphene sheet may be turned only thirty degrees to convert it from an armchair to a zigzag nanotube, or vice versa.

SWCNTs' conductivity is dependent on their chiral vector; unlike MWCNTs, which are always conducting and reach at least the same degree of conductivity as metals, SWCNTs may exhibit the characteristics of a semi-conductor, behave like a metal, or exhibit no conductivity at all. For instance, a little alteration in the helicity's pitch may convert a metal tube into a large-gap semiconductor.

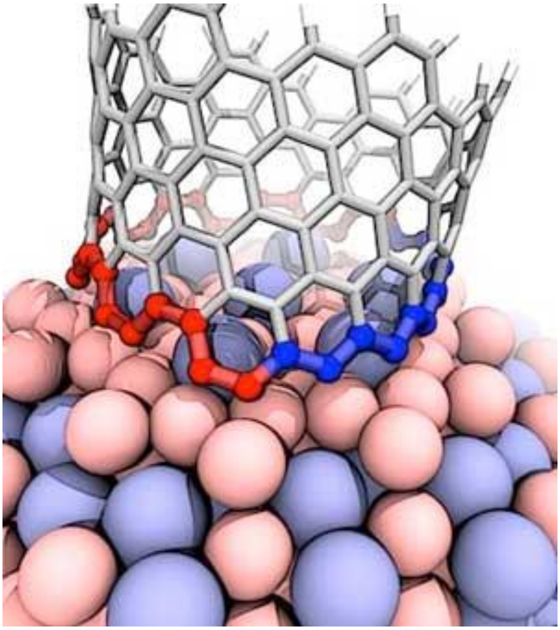

Figure 5.2 This illustration shows the interface between a growing carbon nanotube and a cobalt-tungsten catalyst. The atomic arrangement of the catalyst forces the nanotube to quickly transition from zigzag (blue) to armchair (red), which ultimately grows a nanotube.*

3. Properties of carbon nanotubes

In addition to their electrical characteristics, which they share with graphene, carbon nanotubes (CNTs) have special mechanical and thermal characteristics that make them interesting for the creation of novel materials:

- They are very light, with a density of just one-sixth that of steel, and their mechanical tensile strength may reach 400 times that of steel.

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*https://www.nanowerk.com/nanotechnology-news2/id50764.jpg

- They possess a very high aspect ratio—more than 1000—meaning that they are very thin in comparison to their length, and their heat conductivity is superior to that of diamonds.
- A tip-surface area close to the theoretical limit; the field enhancement factor increases with a smaller tip-surface area and a more concentrated electric field.
- They are exceedingly resistant to corrosion and, like graphite, are highly chemically stable. They can withstand almost any chemical assault unless they are concurrently subjected to high temperatures & oxygen.
- Their hollow interior may be packed with different nanomaterials to isolate and protect them from the outside world; this is a very valuable feature for applications in nanomedicine, such as medication delivery.

4. Making of carbon nanotubes

There are three primary techniques for producing CNTs: Chemical Vapour Deposition (CVD), laser ablation of graphite, & arc discharge.

In the first two steps, the CNTs that are forming in the gaseous phase are separated from the graphite using electrical or laser combustion. All three techniques need to make use of metal catalysts, such as nickel, cobalt, and iron.

a. CVD process

Right now, the CVD method shows the most promise since it makes it possible to produce CNTs in bigger numbers at a cheaper cost and under more readily controlled circumstances. Carbon nanotubes may be formed on a catalyst in a high-temperature furnace by combining a metal catalyst (like iron) with carbon-containing reaction gasses (like hydrogen or carbon monoxide) in the CVD process.

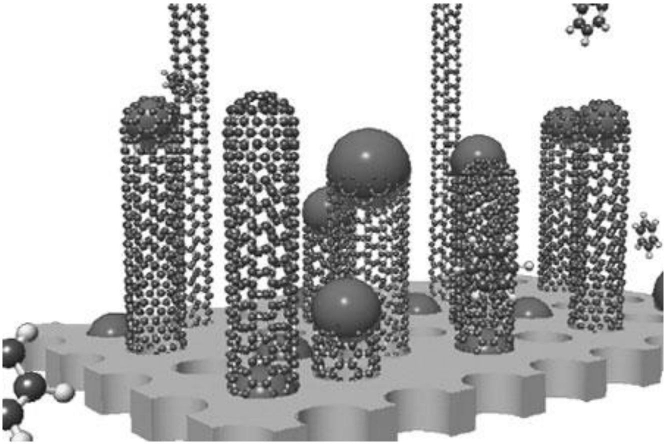

Figure 5.3 Schematic view of CNT growth on catalyst particles during CVD. First, small secondary catalyst particles of the size of a CNT diameter develop, on which the nanotubes start growing. The catalyst particle is either at the top or at the bottom of the emerging nanotube. Growth will stop if the catalyst particle is deactivated through the development of a carbon envelope[*]

There are two types of CVD processes: plasma-supported and pure catalytic. With the latter, 'lawn-like' CNT growth

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[*] https://www.nanowerk.com/images/cntgrowth.jpg

is intended to be produced at temperatures that are somewhat lower (200–500°C) than those required by the catalytic method (up to 750°C).

b. Purification

Improved synthetic methods have been able to produce high-purity carbon nanotubes, but because metal nanoparticles are necessary for the growth of the nanotubes, it has been inevitable for byproducts containing impurities to form, including metal encapsulated nanoparticles, metal particles within the tip of a carbon nanotube, as well as amorphous carbon. The unpleasant result of these alien nanoparticles and structural flaws during synthesis is that they alter the physico-chemical characteristics of the carbon nanotubes that are formed. For this reason, at the conclusion of the manufacturing process, carbon nanotubes must be purified using a variety of techniques, such as acid treatment or ultrasonic.

5. Applications of carbon nanotubes and their uses

Compared to traditional materials, carbon nanotubes (CNTs) provide superior strength, durability, electrical conductivity, thermal conductivity, and lightweight characteristics for almost any application. At the moment, CNTs are mostly added to synthetic materials. Commercially, CNTs are sold as a powder, which is to say, in a highly aggregated and tangled state. CNTs must be dispersed equally across the substrate and untangled to exhibit their unique qualities.

CNTs must also form a chemical bond with the substrate, such as a plastic substance, according to other criteria. To do this, CNTs are functionalized, or have their surface chemically altered for the best possible integration into various materials and for the intended use. It is possible to spin carbon nanotubes into fibres, which might lead to the realization of a particularly fantastical project: the space elevator, in addition to offering intriguing possibilities for specialized fabrics.

a. Materials

A lot of attention has been paid to carbon nanotube-enabled nanocomposites as a very appealing substitute for traditional composite materials because of their mechanical, electrical, thermal, barrier, and chemical characteristics, like electrical conductivity, enhanced tensile strength, better heat deflection temperature, or just flame retardancy.

These materials claim to provide improved breaking strength and wear resistance, antistatic qualities, and weight savings. Advanced carbon nanotube composites, for example, are thought to be able to lower the weight of spaceships and airplanes by as much as 30%.

These hybrid materials are now used in:

- Sporting goods (sports arrows, skis, kayaks, golf clubs and balls, tennis rackets, sticks for hockey, and bicycle frames).

- Yachting (hulls, masts, and other sailboat components).
- Textiles (such as water-resistant, flame-retardant, and antistatic/electrically conducting fabrics, or "smart textiles"); bulletproof vests.
- Aerospace, automotive, and space (high-strength, lightweight structural composites).
- Industrial engineering (e.g., industrial robot arms, coating of wind turbine rotor blades).

Figure 5.4 CNT fabric stopped a 9MM, jacketed round in controlled ballistics testing. This material shown is roughly the same thickness as six stacked business cards.[*]

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[*] https://www.nanowerk.com/spotlight/id15742_2.jpg

b. Catalysis

Carbon nanotubes are highly valued for catalysis due to their exceptional surface area and ability to bind a wide range of chemical species through their sidewalls. While carbon nanotubes (CNTs) have been used effectively as catalysts in various chemical reactions, controlling their catalytic activity remains challenging.

Initially, CNTs were linked to molecules through strong covalent bonds, resulting in highly stable compounds. However, this strong bond often alters the nanotube's structure and properties. This can be likened to using a thumbtack to attach an advertisement to a post—while the bond is strong, it can damage the advertisement and the post.

In contrast, non-covalent interactions, which are weaker, maintain the nanotube's structure without causing significant damage. This is analogous to taping the advertisement to the post, where neither the post nor the advertisement is harmed.

To address these challenges, researchers are developing methods to chemically modify carbon nanotubes using mechanical bonding techniques. This approach aims to create mechanically interlocked carbon nanotubes (MINTs) that preserve the original structure of the nanotubes while combining the benefits of both covalent and non-covalent interactions.

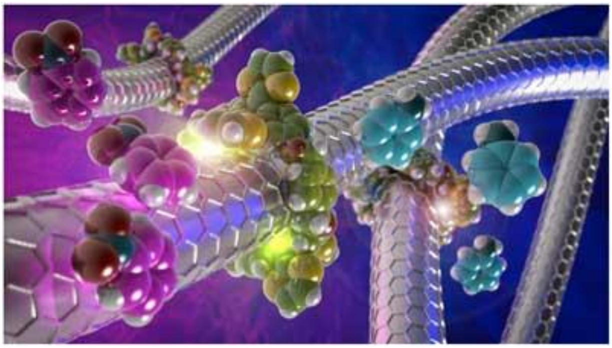

Figure 5.5 Positive and negative regulation of carbon nanotube catalysts through encapsulation within macrocycles*

c. Transistors

Semiconducting carbon nanotubes with single walls are still seen as strong contenders for the next generation of ultra-scaled, high-performance thin-film transistors and optoelectronic devices that will replace silicon electronics, even in light of the emergence of graphene and other two-dimensional (2D) materials. Whether CNT transistors at sub-10 nm widths can provide performance benefits over silicon is one of the key issues.

Regarding the question of whether CNT transistors will continue to exhibit remarkable performance at extraordinarily scaled lengths, the nanoelectronics community has been divided on the subject. The few theoretical studies that examined nanotube devices at such dimensions confirmed the view that the relatively tiny effective mass of the carriers could add to a tunnelling

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*https://www.nanowerk.com/nanotechnology-news2/id50632.jpg phenomenon that would lead the devices to break down at around 15 nm.

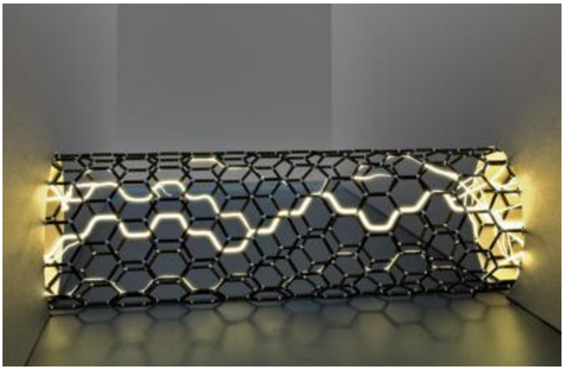

Figure 5.6 Schematic of a sub-10 nm carbon nanotube transistor configuration.[*]

Conversely, some individuals persisted in their belief that the very thin single-walled carbon nanotube body, measuring only 1 nm in diameter, would enable superior transistor performance even in the sub-10 nm region.

d. Sensors

By showcasing the potential of SWCNTs as quantum wires and their efficiency in the creation of field-effect transistors, the Cees Dekker group cleared the path for the development of CNT-based electrochemical nanosensors. Numerous investigations have shown that although carbon nanotubes (CNTs) have strong, inert structures, their electrical characteristics are very susceptible to the effects of charge transfer & chemical doping from different substances.

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[*] https://www.nanowerk.com/spotlight/id24224.jpg

The majority of CNT-based sensors are field effect transistors (FETs); although CNT structures are strong and inert, charge transfer & chemical doping by different molecules have a significant impact on their electrical characteristics. In environmental applications, CNTs-FETs have been extensively employed to detect chemicals, including greenhouse gasses. CNTs must be functionalized for them to be selective for the intended analyte. The molecular recognition relationships among functionalism CNT & target analytes are the basis for several kinds of sensors. For instance, using single-walled carbon nanotubes embellished with palladium nanoparticles, researchers have created flexible hydrogen sensors.

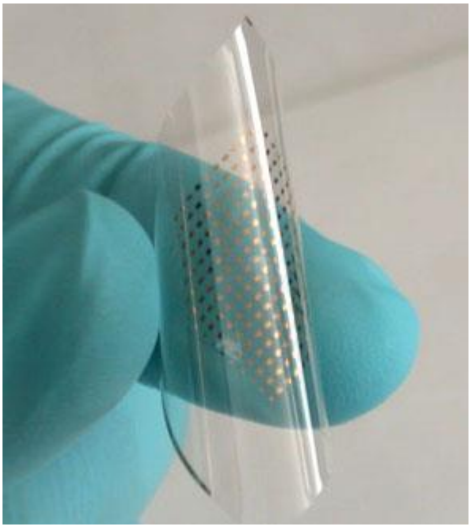

Figure 5.7 Example of a flexible hydrogen sensor fabricated with single-walled carbon nanotubes.[*]

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[*] https://www.nanowerk.com/spotlight/id2887.jpg

5.5.2. Graphene

Graphene is a two-dimensional variant of crystalline carbon that is either a single layer of carbon atoms that create a hexagonal honeycomb lattice or several coupled layers for this honeycomb structure. Generally, single-layer graphene is meant when the term "graphene" is used without defining its shape (e.g., bilayer graphene, layered graphene). All graphitic structures of carbon have their parent form in graphene: buckyballs, which are spherical molecules made of graphene with some hexagonal rings substituted with pentagonal rings; nanotubes, which can be thought of as scrolls of graphene; and graphite, a three-dimensional crystal made up of relatively barely coupled graphene layers.

1. **The properties of graphene**

Even though graphene is a very thin layer of carbon atoms, it has exceptional qualities that make it a desirable material for a variety of uses.

The world's thinnest substance is graphene, which is one million times thinner than human hair and just one atom thick. But it is very strong—stronger than both diamond and steel. This opens up a wide range of uses for composite materials that have exceptional durability and rigidity. Additionally, graphene is very flexible, which inspires ideas for wearable technology and foldable electronics. Additionally translucent, it would be a perfect match for bending displays.

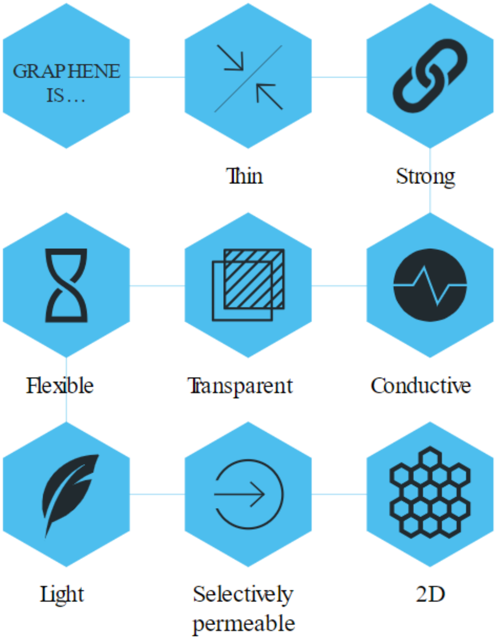

Figure 5.8 Properties of graphene[*]

Moreover, graphene is an excellent heat and electrical conductor. These two ideas have been used by certain manufacturers to create heat-dissipating gels and conductive paints and inks for electrical circuits. Even longer-lasting batteries may be possible because of graphene's conductive qualities. Since graphene is only a sheet of carbon atoms, it is naturally light. Graphene is being researched by the automotive and aviation sectors to lighten vehicles and aircraft, hence lowering fuel consumption & carbon emissions.

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[*] https://graphene-flagship.eu/media/caub45sv/graphene-is.svg?width=597&height=597&mode=max

2. The electronic structure of graphene

Graphene's fundamental electrical structure and thus its electric characteristics are quite unusual. Similar to the conductivity established in semiconductors, one may create an electron or hole (an area where an electron is absent and behaves as a positive electric charge) conductivity within graphene by providing a gate voltage or chemically doping with adsorbed atoms and molecules. But in most semiconductors, there are energy levels where holes and electrons are not permitted to exist in quantum states. As a result, for certain gate voltages and chemical doping types, the semiconductor functions as an insulator.

Conversely, graphene lacks an insulator state and its conductivity is limited at all doping levels, even at zero doping. One notable distinction between graphene and other semiconductors is the existence of this low conductivity in the undoped scenario. The states of the ultra-relativistic quantum particles, or quantum particles travelling at the speed of light (the highest velocity in nature, according to relativity theory), are comparable to the electron and hole states in graphene that are pertinent to charge-carrier transport.

In reality, the graphene honeycomb lattice is made up of two sublattices, A and B, whereby three atoms from sublattice B surround each atom from sublattice A and vice versa. Due to this straightforward geometric configuration, graphene's electrons and holes seem to have an exceptional amount of internal flexibility, which is known as pseudospin. Pseudospin resembles the spin, or internal directional momentum of subatomic particles, which completes the connection. According to this comparison, graphene's electrons and holes function similarly to quantum electrodynamics particles and antiparticles (such as electrons and positrons). However, the electron and hole velocities are only about 1/300 the speed of light at the same moment.

This makes graphene an ideal platform for high-energy physics: due to the electrons' and holes' slower velocities, graphene's electron and hole physics reflects some of the same quantum relativistic effects that are hard to achieve in subatomic particle experiments with particle accelerators. One such is the Klein paradox, which shows that, in contrast to what one would expect, ultra-relativistic quantum particles may pass through very high and wide energy barriers with ease. Thus, graphene serves as a link between several branches of basic physics, including relativistic quantum mechanics, and materials science.

3. Graphene as a two-dimensional material

Graphene is also of particular significance to fundamental science since it is the earliest and most basic example of a two-dimensional crystal or a solid composed of just one layer of atoms organized in an orderly pattern. Surfaces, membranes, and interfaces—two-dimensional systems—are very important to the natural sciences of biology, chemistry, physics, and other fields.

For instance, lipid molecules are fundamentally arranged in sheets with proteins attached; these membranes are necessary to life. Two-dimensional and three-dimensional systems vary greatly from one another in numerous ways. In particular, long-range crystalline organization is not possible in two dimensions because of very significant thermal fluctuations of atomic locations that persist over extended distances. Rather, when graphene is referred to as a two-dimensional "crystal," one should take notice of the fact that only short-range order exists and that it only does so on a limited scale of characteristic length.

Due to this, two-dimensional systems are never flat and are constantly rippling or corrugated. They are intrinsically "flexural," exhibiting substantial bending fluctuations. Due to its relative simplicity, graphene may be used as a model system for a broad study of two-dimensional chemistry and physics. In addition to graphene, alternative two-dimensional crystals may be produced chemically (graphane, hydrogenated graphene, or fluorinated graphene) or by exfoliation from other multilayer crystals.

Modern electronics mostly exploit the surface of semiconducting materials, making them two-dimensional devices. Consequently, for many of these applications, graphene along with other two-dimensional materials is seen to be particularly promising. For instance, it should be able to create transistors and other electrical devices using graphene that are much thinner than those constructed of conventional materials. Numerous more uses have been suggested.

For instance, graphene, which is strong, flexible, transparent, and electrically conducting, might one day be used as a material for touch displays. Due to its very high thermal conductivity, graphene may also be used to take heat out of electrical circuits. Its exceptional mechanical strength makes it a potential scaffold for the study of biological molecules & materials.

Chapter Summary

This chapter explored various types of nanoparticles, including metal nanocrystals, semiconductor nanocrystals, porous inorganic nanoparticles, organic nanoparticles (latexes), and carbon-based nanoparticles. It began with metal nanocrystals, detailing their characteristics, synthesis methods, and applications. The discussion then moved to semiconductor nanocrystals, covering their unique properties and synthesis techniques. Porous inorganic nanoparticles were examined next, focusing on their synthesis, properties, and diverse applications.

The chapter also addressed organic nanoparticles, highlighting their roles and uses. In-depth sections on carbon-based nanoparticles included carbon nanotubes, with a focus on their allotropes, electrical properties, and manufacturing processes. Finally, the chapter covered graphene, emphasizing its properties, electronic structure, and significance as a two-dimensional material. This comprehensive overview provides a foundational understanding of the different types of nanoparticles and their significance in various applications.

Assessment Questions

1. Which qualities make up metal nanocrystals?
2. Which typical uses do metal nanocrystals have?
3. In what ways do the properties of metal and semiconductor nanocrystals vary from one another?
4. What characteristics of semiconductor nanocrystals are typical?
5. What distinguishing characteristics do porous inorganic nanoparticles have?
6. What special qualities do carbon nanotubes possess?
7. In what ways does the method of Chemical Vapour Deposition (CVD) aid in the creation of carbon nanotubes?
8. What are some of the uses and applications of carbon nanotubes?
9. What is the graphene's electrical structure?
10. As a two-dimensional material, how does graphene function and what are its implications?

CHAPTER 6

Basic Synthesis and Fabrication Methods

Learning Objective

The basic techniques for creating and synthesizing nanoparticles will be covered in this chapter. These techniques include hydrothermal synthesis, microemulsion techniques, template techniques, Sol-Gel synthesis, and Chemical Vapour Deposition (CVD).

6.1. Microemulsion Method

A microemulsion is a transparent, translucent, isotropic liquid combination of water, oil, & surfactant that is thermodynamically stable and often contains a co-surfactant. Under certain circumstances, it occurs spontaneously and is usually composed of the nanoscale droplets of one liquid scattered in another.

1. Components

The following are the components of microemulsion:

a. Oil Phase

The continuous phase of a microemulsion is called the oil phase, and it is made of organic solvent or oil. It is usually selected based on its capacity to dissolve reactants or hydrophobic materials. Alkanes, esters, & aromatic hydrocarbons are typical examples. The size & stability of microemulsion droplets may be strongly influenced by the kind of oil that is utilized.

b. Water Phase

In water-in-oil microemulsions or oil-in-water microemulsions, the water phase, which possesses aqueous components, is distributed as droplets inside the oil phase. It could also include tiny molecules that can take part in chemical processes or dissolved ions.

c. Surfactant

The chemicals known as surfactants lessen the interfacial tension that separates the water and oil phases. Their hydrophilic head attracts water, while their hydrophobic tail attracts oil. This combination enables them to stabilize droplets by encircling them in a monolayer. To create and maintain microemulsions and make sure that the droplets stay scattered and don't coalesce, surfactants are essential.

d. Co-surfactant (optional)

In order to improve the stability of microemulsion, a co-surfactant is often added in addition to the main surfactant. It helps to enhance the packing of surfactant molecules at the interface and further lowers the interfacial tension. Alcohols, amines, and other tiny compounds that help generate a more durable microemulsion may be considered co-surfactants.

2. Steps in the Microemulsion Method

Following are the steps of microemulsion methods:

Step-1 Preparation of Microemulsion

The oil, water, surfactant, & co-surfactant are combined in exact amounts to create a microemulsion. Since it controls the size and stability of droplets, the microemulsion's composition is essential. To ensure that components are well combined, the mixture is usually produced by vigorous mixing or by utilizing techniques like sonication or high-shear mixing. Depending on its composition, the resultant microemulsion is stable and often has a clear or nearly opaque appearance.

Step-2 Incorporation of Precursor

The production of the nanoparticles is started by adding metal precursors or just other reactants into the microemulsion. The precursor dissolves in the water phase of an oil-in-water microemulsion and the oil phase of a water-in-oil microemulsion. Since the precursor is limited to the nanoscale droplets, the microemulsion droplets' contained environment for regulated reactions and uniform nanoparticle creation.

Step-3 Nanoparticle Formation

Within the microemulsion droplets, the precursor initiates a chemical reaction upon addition. Usually, this reaction results in the creation of nanoparticles by reduction or precipitation processes. The confinement of the nanoparticles inside the microemulsion helps regulate their development by preventing them from aggregating or expanding over the target size. The homogeneous size and shape of the generated nanoparticles are guaranteed by the stability of the microemulsion system.

Step-4 Separation and Purification

The nanoparticles and microemulsion must be separated after the process is finished. This may be accomplished by techniques like filtering or centrifugation, which separates the nanoparticles according to their size and density. The nanoparticles are purified after separation to get rid of any leftover surfactants, co-surfactants, as well as unreacted precursors. The process of purification might include dialysis or solvent washing of the nanoparticles.

Step-5 Characterization

Characterizing the produced nanoparticles to ascertain their size, shape, and various other characteristics is the last stage. The morphology of the nanoparticles may be seen in great detail thanks to methods like transmission electron microscopy and Scanning Electron Microscopy (SEM). While dynamic light scattering assesses the particle size distribution, X-ray diffraction (XRD) aids in determining the crystalline structure. By characterizing the nanoparticles, one can make sure they fit the intended uses and satisfy the necessary requirements.

3. Advantages

Size Control: Through manipulation of the microemulsion's composition and circumstances, the microemulsion process provides accurate control over nanoparticle size. For applications that need homogenous particles, the ability to tailor the size of nanoparticles to a tight range is essential.

Uniformity: The process yields very homogenous nanoparticles in terms of size and shape, which is advantageous for guaranteeing reliable performance in a range of applications, including medication administration and catalysis.

Scalability: Scaling up the microemulsion process from the laboratory to the industrial level is possible. It is feasible to create vast amounts of nanoparticles while preserving uniformity and quality by adjusting the formulation and manufacturing parameters.

4. Applications

Catalysis: Microemulsion-synthesised nanoparticles have a large surface area and are homogenous, making them useful catalysts. They may be used in a variety of catalytic processes, such as those in environmental remediation and chemical synthesis.

Drug Delivery: Nanoparticles may be developed for targeted medication delivery in the pharmaceutical industry. They are the best at delivering medications to precise locations throughout the body, increasing therapeutic effectiveness, and minimizing adverse effects because of their tiny size and controlled release characteristics.

Sensors: Sensitive & selective sensors are developed using nanoparticles generated from microemulsions. Their special qualities may increase the sensitivity and accuracy of sensors used to detect different chemical or biological analytes.

6.2. Template Method

Materials are vital for human existence and the development of modern society, with quality standards increasing alongside technological advancements. Nanomaterials, ranging from 1 to 100 nm, are extensively used in fields like photonics, spectroscopy, industrial catalysis, and biology due to their unique optical, electrical, magnetic, thermal, and mechanical properties.

The interest in nanomaterials stems from their distinct surface, volume, quantum size, macro quantum tunnelling, and dielectric confinement effects. Common methods for synthesizing nanoparticles include both chemical and physical techniques. Physical methods involve spraying, coacervation, and pulverization, while chemical methods include chemical vapour deposition, precipitation, sol-gel, and hydrothermal processes.

Since the 1990s, template synthesis has become a popular and effective method for creating nanomaterials. This technique uses a template material to control the structure, morphology, and particle size of nanomaterials. The template method is divided into hard and soft templates, with notable research contributions from Fudan University and the University of California in developing various mesoporous materials.

Morphology is crucial for defining the properties and applications of mesoporous materials, which include factors like particle size, surface area, and pore structure. The template method influences product morphology by regulating crystal nucleation and growth during nanomaterial synthesis. The process involves preparing the template, synthesizing the target material, and then removing the template. The choice of template and removal technique is critical to maintaining the chemical and physical integrity of the final product.

1. Hard Template

The size and shape of the sample particle are directly determined by the hard template, which is a stiff substance with a fixed structure. There is a large selection of hard templates, including carbon fibre, polymer microspheres, porous membranes, plastic foam, ion exchange resin, and porous anodic aluminium oxide. They are significant in various disciplines due to their unique architectures and impact on particle size limitation.

a. Porous Anodic Aluminum Oxide (AAO)

Porous anodic alumina features a high pore density with small, uniformly spaced pores. The pore density ranges from 1 × 10^9 to 1 × 10^12 cm−2, and the pore size can be adjusted between 50 and 200 nm. This material is widely used in the development of nanofunctional devices and has been effectively applied in various fields, including magnetic recording materials, optoelectronic components, electronics, and more. It is particularly useful for the deposition of metals, semiconductors, conductive polymers, and other functional materials.

i. Preparation of Porous Anodic Aluminum Oxide (AAO)

The preparation process for anodic alumina oxide (AAO) is not standardized. It typically involves immersing a high-purity aluminium piece in an acidic solution and performing anodic oxidation electrolysis to produce AAO. The pore size and distribution can be modified by adjusting the anodic voltage and the electrolyte's composition and concentration.

As illustrated in the structural diagram of AAO, there is a dense alumina layer, known as the barrier layer, between the porous layer and the unoxidized aluminium matrix. This barrier layer needs to be removed for electrodeposition because it obstructs contact between the electrolyte solution and the electrode. Additionally, to obtain the double-pass AAO template, the aluminium matrix must be eliminated.

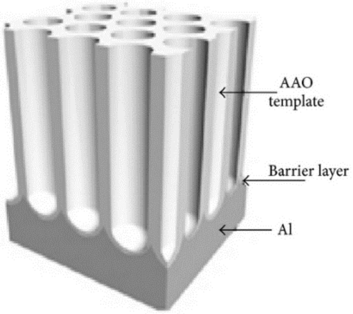

Figure 6.1 Structure diagram of AAO[*]

b. Mesoporous Carbon

One crucial component of mesoporous materials is mesoporous carbon. Its pore diameter typically ranges from 2 to 50 nm, and its pore dispersion is homogeneous. Its specific surface area is large and its pore structure is uniform. In addition, it has chemical and thermal stability. Mesoporous carbon compounds are extensively used in several industries, including batteries, capacitors, adsorption, hydrogen storage, and catalysis.

j. Synthetic Methods of Mesoporous Carbon

Mesoporous carbon synthetic techniques may be further classified into organic sol-gel, template, and catalytic activation approaches. Mesoporous carbon is created via

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[*] https://onlinelibrary.wiley.com/cms/asset/05b6a2d2-91cf-4ed9-9403-ddf9b150c1dd/jona2302595-fig-0001-m.png

catalytic activation, which uses the catalytic properties of metals and related compounds to act on carbon gasification. The activation process mostly takes place in the vicinity of the metal particles, which might promote the growth of mesopores and prevent the creation of micropores. Pekala and Schaefer proposed the organic sol-gel technique. This process employs a gel created when precursors are polymerized as a source of carbon, and high-temperature carbonization is used to produce mesoporous carbon.

To create an organic moisture gel, combine melamine & formaldehyde with $NaCO_3$ as a catalyst. Then, add a phenol and formaldehyde mixed solution and, lastly, phenolic resin. Ultimately, carbonization yields mesoporous carbon. The figure depicts the mesoporous carbon structure.

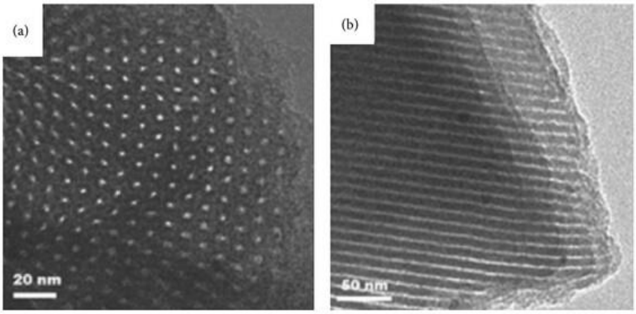

Figure 6.2 TEM image of mesoporous carbon structure[*]

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[*] https://onlinelibrary.wiley.com/cms/asset/04bb9c4e-7675-4842-8bfc-7eac16a83b1e/jona2302595-fig-0004-m.png

2. Soft Template

The soft template lacks a definite, inflexible framework. When creating nanoparticles, the forces of intermolecular or intramolecular interaction—hydrogen bonding, chemical bonding, as well as static electricity—form an aggregate with certain structural characteristics. These aggregates serve as templates for the deposition of inorganic species, which are then formed into particles with certain sizes and shapes by electrochemical processes, precipitation, and other artificial ways on the outside or inside of these templates.

A common soft template may be a polymer, biopolymer, surfactant, and so forth. Due to its many benefits, including strong reproducibility, ease of usage, and no need for silicon removal, the soft template has great potential for advancement in the synthesis of nanomaterials.

a. Surfactant

Ammonium salts, heterocyclic carboxylic acid salts, and sulfonate salts, along with other ionic or nonionic surfactants are examples of amphiphilic compounds that are surfactants. Amphiphilic molecule groups readily form a wide range of ordered polymers in a solution, including microemulsions, liquid crystals, vesicle micelles, and self-assembled films.

According to material chemistry theory, the way surfactants interact with the organic-inorganic interface in their liquid crystal phase determines how mesoporous materials behave morphologically. Weak hydrogen bonds interact with the organic-inorganic interface in highly acidic environments, while significant electrostatic attraction interacts with it in very alkaline environments. Surfactants within the solution generate liquid crystalline phases with a variety of morphologies, including lamellar, cubic, and hexagonal phases. It is also simple to build and modify. As a result, it is the perfect reactor for creating mesoporous materials. The figure displays the cubic, hexagonal, and lamellar structures.

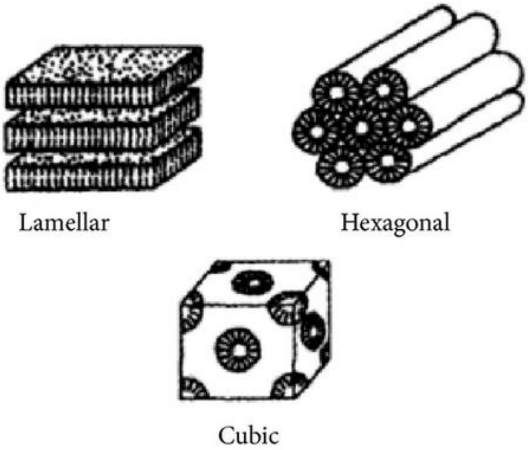

Figure 6.3 Structure of liquid crystals[*]

Controlling the hydrolysis & polymerization of silicon species is quite simple. Furthermore, by combining the combined action of surfactants and the reaction

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[*] https://onlinelibrary.wiley.com/cms/asset/5b29977a-184e-4102-8eca-f9a2e4990f40/jona2302595-fig-0007-m.png

environment, mesoporous silica having fibrous, thin film, tubular, spherical, and various other distinct morphologies may be produced.

6.3. Hydrothermal Synthesis

When using hydrothermal synthesis, chemical reactions are carried out in an autoclave—a sealed container with higher pressure and temperature than the ambient air. The combination is heated to temperatures higher than the boiling point of water throughout the process, which employs water or an aqueous solution as the solvent. This produces a high-pressure environment which may impact the kinetics of the reaction and greatly increase the solubility of reactants, resulting in the production of nanoparticles.

1. Components and Conditions

Reactants: Metal salts or precursors that dissolve in an aqueous solution are the main reactants. These precursors, which provide the components required for nanoparticle creation, might be metal chlorides, nitrates, or other salts.

Solvent: Although other aqueous solutions or just solvents with particular qualities may also be used, water is often used as the solvent. The properties of the nanoparticles and the solubility of reactants may both be impacted by the solvent selection.

Temperature and Pressure: Usually, hydrothermal synthesis is carried out between 100°C and 300°C with correspondingly greater pressures to preserve the liquid phase. Precursor dissolution and reaction rates are accelerated by the high temperature and pressure.

Autoclave: An autoclave is a sealed, pressure-resistant vessel used to carry out the reaction. Due to this equipment's resistance to high pressures and temperatures, synthesis conditions may be regulated.

2. Steps in Hydrothermal Synthesis

Following are the steps in hydrothermal synthesis:

Step-1 Preparation of Solution

To make a homogenous mixture, the metal precursors have to dissolve in an aqueous solution. Additional chemicals, such as stabilizers or pH adjusters, may be added to the solution depending on the desired nanoparticles.

Step-2 Loading the Autoclave

The autoclave is filled with the prepared solution. After that, the autoclave is firmly sealed to maintain the required pressure during the reaction.

Step-3 Heating

The temperature of the autoclave is adjusted to the required level, usually between 100°C & 300°C. The reactants dissolve more easily and the nucleation and development of nanoparticles are encouraged by high temperature and pressure.

Step-4 Reaction

Under hydrothermal conditions, the process proceeds with improved ion diffusion rates and precursor solubility. The aqueous medium is where nanoparticles nucleate and grow. Depending on the precise reaction and required nanoparticle characteristics, the reaction period might vary, lasting anywhere from a few hours to several days.

Step-5 Cooling and Extraction

Once the reaction is finished, the autoclave is gradually left to cool. The nanoparticles are taken out of the autoclave after the system has reached a safe temperature. It is common practice to use centrifugation, filtering, or other separation techniques to extract the nanoparticles from the fluid.

Step-6 Purification

Purification procedures might be used for the recovered nanoparticles to get rid of any remaining reactants, byproducts, or contaminants. To get the required purity, methods like solvent cleaning or dialysis might be used.

Step-7 Characterization

To ascertain the size, shape, & structural characteristics of the finished nanoparticles, they undergo characterisation. For this, analytical methods like Dynamic Light Scattering (DLS), X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM), and scanning electron microscopy (SEM) are often used.

3. Applications

The following are the applications:

Catalysis: Hydrothermally produced nanoparticles may be utilized as catalysts in chemical processes. Their selectivity and catalytic efficacy are enhanced by their large surface area and distinct architectures.

Energy Storage: Due to their large surface area and conductivity, hydrothermally produced nanoparticles are employed in energy storage devices like batteries and supercapacitors.

Sensors: Certain types of nanoparticles may improve a sensor's sensitivity and selectivity for identifying different chemical / biological species.

Environmental Remediation: Nanoparticles' large surface area and reactivity make them useful for eliminating contaminants from air and water.

Chapter Summary

This chapter explored basic synthesis and fabrication methods for nanomaterials, focusing on the microemulsion method, template method, and hydrothermal synthesis. The microemulsion method was discussed, detailing its components, steps, advantages, and diverse applications. Next, the template method was covered, distinguishing between hard and soft templates and their roles in nanomaterial synthesis.

The chapter concluded with hydrothermal synthesis, outlining the essential components, conditions, and steps involved, along with its various applications. This overview provides a solid foundation for understanding these key methods in nanomaterial synthesis and their practical uses.

Assessment Questions

1. What are the main processes in the production of nanomaterials using the microemulsion method?
2. How does the preparation of nanomaterials using the hard template approach operate?
3. How is the hard template technique for producing porous Anodic Aluminium Oxide (AAO) prepared?
4. In the synthesis of nanomaterials, how is the soft template approach different from the hard template method?
5. Which are the primary processes in the synthesis of nanomaterials using hydrothermal methods?
6. Which elements usually make up a microemulsion system?
7. In what ways do microemulsions aid in the creation of nanomaterials?
8. What benefits does the microemulsion approach have over other methods for synthesizing nanomaterials?
9. How does the creation of nanomaterials benefit from hydrothermal synthesis?
10. What functions do template techniques provide in regulating the composition and characteristics of artificial nanomaterials?

CHAPTER 7

Physical Methods

Learning Objective

The physical techniques of ball milling, laser ablation, and physical vapour deposition for nanoparticle creation will be discussed in this chapter.

7.1. Physical Vapour Deposition (PVD)

One popular thin-film coating method that is used in a variety of sectors, including electronics, optical, and aerospace, is physical vapour deposition, or PVD. A solid substance is vaporized in a vacuum atmosphere during PVD. After that, the vaporized atoms or molecules move and settle on a substrate to create a thin layer. PVD includes techniques such as evaporation and sputtering. When a target substance is bombarded with ions, it splatters, releasing particles that cover the substrate.

Thermal energy is needed for evaporation to evaporate the source material and cause condensation on the substrate. PVD provides advantages such as accurate control over thickness, adhesion of coating to intricate forms, and improvement of material properties. It is essential for conductivity changes, optical improvements, hardness improvements, and functional coatings. PVD coatings are essential for permitting specific material properties in semiconductors, solar cells, medical equipment, and other applications.

1. Physical Vapour Deposition working

A complex thin-film coating method utilized in many sectors to improve material qualities and create useful surfaces is called physical vapour deposition, or PVD. PVD requires several basic steps:

Evaporation or Sputtering: The process of PVD begins with the conversion of a solid substance, referred to as the target or source material, to a vaporized state. Sputtering and evaporation are the two main techniques that may be used to accomplish this.

- **Evaporation**: In a vacuum chamber, the source material gets heated to a high temperature. The substance vaporizes in the heat, forming an atom or molecular cloud.
- **Sputtering**: This method involves aiming a powerful ion beam at the desired substance. Atoms on the target are dislodged by the collision of ions, and these atoms evaporate to generate a cloud of particles.

Vapour Transport: Within the vacuum environment, the atoms or molecules that have evaporated or sputter freely move. The substance that will make up the coating is included in this vapour cloud.

Deposition onto Substrate: The substrate on which the coating is to be placed is the target of the vapour cloud. Usually, the substrate is positioned near the source of vapour.

Coating Formation: The vaporized molecules or atoms lose energy upon reaching the substrate and condense onto its surface. They create a thin coating that sticks to the substrate as they compress. The substance that makes up the source and target materials is also present in this thin film.

Film Growth and Control: Until the thin layer reaches the required thickness, the deposition process is continued. The coating is guaranteed to attain the desired thickness and homogeneity via precise control mechanisms, including monitoring the deposition rate and modifying the process parameters.

Coating Properties: The vaporization process, vacuum settings, substrate temperature, and other variables all affect the properties of the deposited coating, such as its thickness, structure, and microstructure.

2. Physical Vapour Deposition

Physical Vapour Deposition is a preferred coating method because of its many benefits and wide range of uses. The following justifies the usage of PVD:

Tailored Surface Properties: PVD enables exact control over coating composition and thickness, allowing material attributes to be tailored to individual needs. Improving qualities like hardness, wear resistance, & corrosion resistance requires this.

Complex Geometries: Many other coating techniques struggle to adhere consistently to complicated geometries and delicate structures, whereas PVD coatings do. PVD may thus be used to cover components of different sizes and forms.

Improved Material Performance: PVD coatings have the potential to greatly enhance material performance. Tools coated with PVDs, for example, have higher cutting efficiency and a longer lifetime because of their improved hardness and resistance to wear.

Aesthetic Enhancement: PVD is a popular material for jewellery, watches, & architectural components because it provides ornamental finishes with distinctive hues and reflecting qualities. The procedure offers both aesthetic appeal and durability.

Consistency and Uniformity: PVD makes sure that the coating is distributed uniformly, which produces constant material qualities throughout the whole coated surface. For situations where evenness is critical, this is vital.

Environmental Friendliness: When compared to certain other coating techniques, PVD is a comparatively ecologically favourable approach. It generates very little trash and doesn't need the use of harsh chemicals.

Compatibility: Polymers, ceramics, and metals are just a few of the materials that PVD coatings may be used on. PVD may be used in a wide range of sectors and settings because of its adaptability.

Microelectronics and Semiconductors: PVD is vital to the production of semiconductors and microelectronic devices, where homogeneous, regulated, and accurate coatings are necessary for optimal device performance.

Optics and Optoelectronics: Optical coatings for lenses, mirrors, and various other optical components are made using PVD. The qualities of light absorption, reflection, and transmission are improved by these coatings.

3. Applications for Physical Vapour Deposition

Cutting Tools and Tool Coatings: Cutting tools with PVD coatings are essential to machining operations. These coatings, which improve tool hardness & wear resistance, include titanium nitride (TiN) and titanium carbonitride (TiCN). PVD-coated tools preserve sharpness & extend tool life by lowering friction and avoiding tool wear. For sectors where accurate and efficient machining is crucial, such as manufacturing, aerospace, and automotive, this application is critical.

Decorative and Architectural Finishes: PVD is often used to create ornamental coatings that are both visually pleasing and long-lasting. PVD coatings, which provide distinctive hues and excellent scratch resistance, are advantageous for watches, jewellery, and fashion accessories.

PVD-coated metal surfaces are employed in architecture for fittings, interior design components, and building facades. The coatings provide durable defence against environmental elements in addition to aesthetic appeal.

Microelectronics and Semiconductors: Using PVD to deposit thin films that are essential to the operation of microelectronic devices is a game-changer. PVD is used to deposit metalization layers, such as copper and aluminium, to provide electrical connections among components. Diffusion barrier films that stop undesired interactions between metals & silicon are also created by PVD. The efficiency and dependability of microelectronic devices depend on these exact and conformal coatings.

Optical Coatings: PVD coatings are essential to optoelectronics and optics. Light transmission is improved and glare is reduced when anti-reflective coatings are applied to optical components such as lenses in cameras and eyewear. Mirrors that have been coated with reflective materials like silver or aluminium have regulated reflectance. PVD coatings affect the characteristics of light absorption and propagation and are also used in photovoltaic cells, optical filters, and lasers.

Advanced Materials Synthesis: PVD is used by researchers to create sophisticated materials with specific characteristics. Diamond-like carbon (DLC) coatings provide remarkable wear resistance, low friction, and hardness because they are made of amorphous carbon that has diamond-like qualities. These coatings are used in a variety of equipment, including industrial and biomedical instruments. Advances in material science and nanotechnology are facilitated by the investigation of PVD-grown nanomaterials, including quantum dots and nanowires, for their special electrical and optical characteristics.

7.2. Ball Milling

During the ball milling process, a mixture of powders is placed inside and subjected to high-energy ball impact. This process was developed at the International Nickel Company by Benjamin and his associates towards the close of 1960. It was found that thin, homogenous dispersions of oxide particles in nickel-base superalloys could be produced by mechanical alloying, an approach that was not possible with more conventional powder metallurgy procedures.

Their innovation has changed the traditional method of synthesising materials at high temperatures. High-energy ball milling may be used not only to synthesise materials but also to modify the usual circumstances that lead to chemical reactions. Mechanochemistry, which includes inducing chemical reactions during the milling process, or mechanical activation, which modifies the reactivity of the solids during the milling process and elevates or decreases the reaction temperature of the ground powders, are two ways to do this. In addition, it is a way to induce phase transitions, including ordered alloy disordering, polymorphic transformations, compound amorphization, etc., in starting powders whose component particles all have the same chemical composition.

The alloying process may be carried out using three different types of equipment: an attritor, planetary mill, or horizontal ball mill. For these processes, all techniques adhere to the same principles. As mechanical alloying requires cold welding & particle breakage, striking a balance between the two processes is essential for efficient alloying. Planetary ball mills are the most often used method because mechanical alloying requires a very small amount of powder.

The technology is thus particularly appropriate for laboratory research. The ball mill system consists of two or four bowls and one turn disc, often referred to as a turn table. The turn disc rotates in one way, while the bowls rotate in the other direction. In addition to turn disc turning, the bowl's own rotation creates centrifugal forces that affect the powder mixture & milling balls within. The mixture of powders is fractured under high-energy impact and then cold welded.

The figure below shows how the balls and powder move. The reason for the different synchronisation of centrifugal forces is that the turn disc and bowl revolve in opposite directions. Friction resulted from hardened milling balls & the powder mixture being ground, rolling on the inside surface of the bowl, and striking the opposite wall. The impact energy of the milling spheres in a normal direction may be up to 40 times more than the acceleration due to gravity. Thus, a planetary ball mill may be used for high-speed milling.

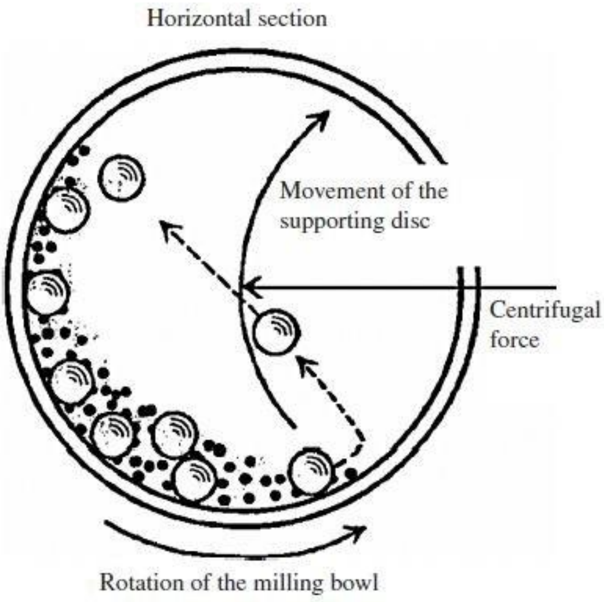

Figure 7.1 Schematic view of motion of the ball and powder mixture.[*]

During the high-energy ball milling process, powder particles are subjected to intense impacts. The mechanical alloying process can be divided into four microstructural phases: (a) initial, (b) intermediate, (c) final, and (d) completion.

a. The powder particles are flattened by compressive forces during the first ball milling stage when the

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[*] https://www.understandingnano.com/ball%20milling.JPG

balls contact. Micro-forging modifies the morphologies of particles by repeatedly striking a cluster or individual particles with high-kinetic-energy milling balls. However, the deformation of the powders shows no overall change within the mass.

b. Notable changes occur when comparing the first stage with the intermediate phase of the mechanical alloying process. Cold welding is vital these days. The intimate blending of the powder's constituents reduces the diffusion distance to the micrometre range. Right now, fracture and cold welding are the two most used milling techniques. Even if there may be some dissolving, the chemical makeup of the alloyed powder is still uneven.
c. By the time the mechanical alloying process is finished, there has been a noticeable decrease in particle size and refinement. On a microscopic scale, the particle's microstructure generally seems more homogenous than those in the initial and intermediate stages. True alloys could have previously been produced.
d. Upon completion of the mechanical alloying process, powder particles exhibit a severely deformed metastable shape. At this phase, optical microscopy is unable to resolve the lamellae. This is the limit of mechanical alloying that can physically increase the dispersoid dispersion. Consequently, an actual alloy is produced with a composition similar to its constituent elements.

For the production of very crushed materials such as cement, refractory materials, chemical fertilizers, glass ceramic, ore treatment of ferrous and non-ferrous metals, etc., ball mills are essential pieces of equipment for many industries. Ores and other materials, both wet and dry, may be ground in a ball mill. Ball mills may be classified into two categories based on how the end products are removed: grate type (a) and overfall type (b). Furthermore, there are many kinds of grinding media available. A grinding medium's size, density, hardness, & composition are essential characteristics.

Size: The size of the grinding medium directly affects the size of the particles produced. Smaller milling balls result in smaller end products. However, there is a limit to how small the grinding medium can be made. The size of the largest material chunks to be crushed sets a minimum size for the grinding medium. Therefore, the milling balls must be significantly larger than the largest particle in the powder mixture to effectively grind it.

Density: The substance being crushed should have less density than the grinding medium.

Hardness: The grinding media's hardness should not be too hard, but rather strong enough to grind material. The cylindrical shell may sustain damage more quickly from very hard material.

Composition: The needs for various grinding applications vary. It is also taken into consideration because the final product may include grinding media, and some applications employ this grinding media. Additional applications include how the material being crushed and the grinding medium interact. Among these applications are:

- Both the colour and the composition of the grinding medium must be taken into account if the colour of the substance that is generated matters.
- The grinding media has to be chosen such that it can be readily removed from the final result if a very pure version of the product is needed (for instance, steel dust generated by stainless steel media may be magnetically separate from non-ferrous items). An alternative is to employ media made of the same material as the substance being ground.
- Steel media may ignite combustible chemicals when they are ground, which might result in an explosion. Wet grinding or non-sparking media, such as ceramics or lead balls, may be employed in certain situations.
- Corrosive materials and certain grinding media, like iron, may react. Grinding media made of flint, ceramic, and stainless steel are often used in these situations.

An inert gas that doesn't react with material being ground may be poured into the reactor to prevent oxidation and explosion.

7.3. Laser Ablation

An established and useful tool in contemporary production is laser ablation. Simultaneously, several ongoing studies are examining the fundamentals and uses of laser ablation. By applying a laser beam to a solid (surface, material may be removed using laser ablation. The substance is heated to the point of evaporation or sublimation at low laser flux levels. On the other hand, the material becomes a plasma with high laser flux. Typically, laser ablation entails removing materials using a pulse wave laser; however, if the laser beam's strength is sufficient to ablate the material, continuous-wave lasers may also be used.

Lasers have been widely used in many different applications since their invention, such as the laser ablation process. Even though laser ablation was first proven experimentally in 1963, it wasn't until the mid-1990s that the process itself could be used for gas sensing.

Laser irradiation is used in laser ablation to remove material from a sample's surface. To emphasize the nonequilibrium vapour/plasma conditions created at the sample surface by the powerful laser pulses, the method is called "laser ablation." Unlike laser evaporation, which involves heating the material and allowing it to evaporate while preserving thermal equilibrium, this method is distinct. The main concept of the laser ablation experiment setup is shown in Figure 7.2.

The pulsed laser and the ablation chamber make up the two main components of a laser ablation device. The laser may be an ArF excimer laser, XeCl excimer laser, CO_2 laser, or Nd-YAG laser. The sample surface absorbs the irradiation laser beam, quickly raising its temperature. The target substance is vaporized as a consequence, entering the laser plume. Particles or clusters may condense out of this evaporated substance.

Notably, the development of these clusters does not entail any chemical interaction. Furthermore, in some cases, the vaporized substance may combine with reactants that have been added, such as reactive gasses, to create new materials. The condensed particles may either be gathered via a filtration device or deposited onto a substrate. These gathered particles may be applied to a substrate using techniques like spin coating and drop casting.

Except for producing vapours from a more constrained plume of material being vaporized rather than the complete sample, it is comparable to the gas phase condensation process. A high-power laser is typically focused on a tiny area of the substance. The laser may be exposed in brief, high-intensity bursts or constantly. A tiny area of material may be quickly heated to the point of vaporization by the high enough laser power. Only modest quantities of nanomaterials can be synthesized using this process because of the small quantity of material needed to produce the vapours. This method has been overused in the synthesis of metal-oxide nanoparticles.

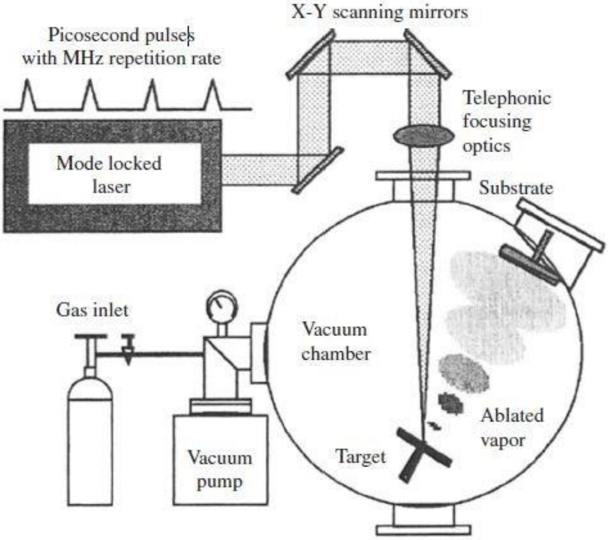

Figure 7.2 Schematics of a typical setup used for the laser ablation technique[*]

The optical characteristics of the material to be ablated determine the depth of laser energy absorption and the subsequent material removal. Other factors influencing this process include the laser's wavelength and the amount of time it is exposed to pulses of light. The ablation rate is the total mass removed from the material by a single laser pulse. The speed of the scanning laser beam & the coverage of scanning lines have an impact on the ablation process as well.

A laser pulse's width may change across a wide range of time intervals, such as milliseconds to femtoseconds.

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[*] https://ebooks.inflibnet.ac.in/msp08/wp-content/uploads/sites/109/2018/12/Untitled-137.png

Furthermore, the laser pulse's flux may be precisely regulated. As a result, there are several industrial and scientific uses for laser ablation.

Another extremely ancient method for creating carbon nanomaterials like carbon nanotubes and fullerenes is laser ablation. In order to create carbon nanomaterials, carbon is vaporized before being deposited in various locations. The carbon is vaporized using an intense laser. A portion of this carbon is transferred into plasma, where it combines with other carbon allotropes to form carbon nanotubes (CNTs) in the plasma plume. The walls of the room are covered with this plasma plume. This approach may be used to create both single-walled and multi-walled CNTs. Multi-walled carbon nanotubes are created when a pure carbon source is employed. Whenever a metal catalyst is added to the carbon source in addition to it, a combination of single- and multi-walled CNTs is produced.

Chapter Summary

This chapter explored physical methods for nanomaterial synthesis, focusing on Physical Vapour Deposition (PVD), ball milling, and laser ablation. The working principles and applications of PVD were examined, highlighting its role in depositing thin films and coatings. Ball milling, a technique for grinding and mixing materials, was discussed, including its impact on particle size and material properties.

Laser ablation was also covered, explaining how high-energy lasers are used to remove material from a target to create nanoparticles. These physical methods are essential for various applications in nanotechnology, offering different advantages for synthesizing and manipulating nanomaterials.

Assessment Questions

1. Define physical vapour deposition
2. What are the main stages in the thin-film coating process using physical vapour deposition (PVD)?
3. In what ways can physical vapour deposition (PVD) improve the performance of materials used in microelectronics and cutting tools?
4. Which areas of advanced materials synthesis, optics, and ornamental finishes are typical uses for PVD coatings?
5. Which major microstructural changes are seen at the start, middle, and end of the mechanical alloying process?
6. What effects do the composition, size, density, and hardness of the grinding medium have on the ball milling process?
7. What factors, such as minimizing contamination or preventing ignition, are crucial to take into account when choosing grinding media for a certain application?
8. In terms of circumstances established at the sample surface and material removal, how is laser ablation different from laser evaporation?
9. What are the main parts of a laser ablation apparatus and how do they contribute to the ablation process?
10. What are the usual uses for this process, and how is vaporized material applied to a substrate after laser ablation?

CHAPTER 8

Microscopy Techniques

Learning Objective

The microscopy methods used to characterize nanomaterials will be covered in this chapter, including atomic force microscopy (AFM), transmission electron microscopy, and scanning electron microscopy (SEM).

8.1. Scanning Electron Microscopy (SEM)

H. Stintzing first proposed the SEM idea in 1927. His proposed method failed to generate a magnified picture since the sample was treated with light, X-rays, and corpuscles in a collimated beam. Then, in 1935, a German electrical engineer by the name of M. Knoll introduced the paradigm of SEM, in which a picture was obtained by scanning a specimen with an electron beam. Von Ardenne introduced DE magnifying lenses, which are used in Scanning Transmission Electron Microscopes (STEMs) to scan thin materials, in 1938, therefore somewhat altering the design of SEM. Zworykin (1942) enhanced SEM with little changes for scanning bulk samples. SEM was eventually brought to market in 1965 after several modifications were made in the Oatley Lab's research and development.

SEMs are a kind of electron microscope which employs an intensely focused electron beam to photograph an item by scanning its surface. The process involves the interaction of electrons with an object's atoms to generate signals that disclose the object's composition and topography. The arrangement of component atoms is studied by means of 2D beam scanning over the sample surface and image collecting from collected secondary electrons. The electron beam forms a scan pattern, and the image is produced by fusing the detected signal with the beam's position.

1. Instrumentation of SEM

The basic components used in an electron optical system are:

- A source of electrons is called an electron gun.
- Lenses.
- Scanning Coils.
- Detectors to collect signals.
- Sample Stage.
- Display/Data output devices.

Infrastructure Requirement

- Power supply.
- Vacuum system.
- Cooling system.
- Vibration-free floor.
- Room free of ambient electric and magnetic fields.

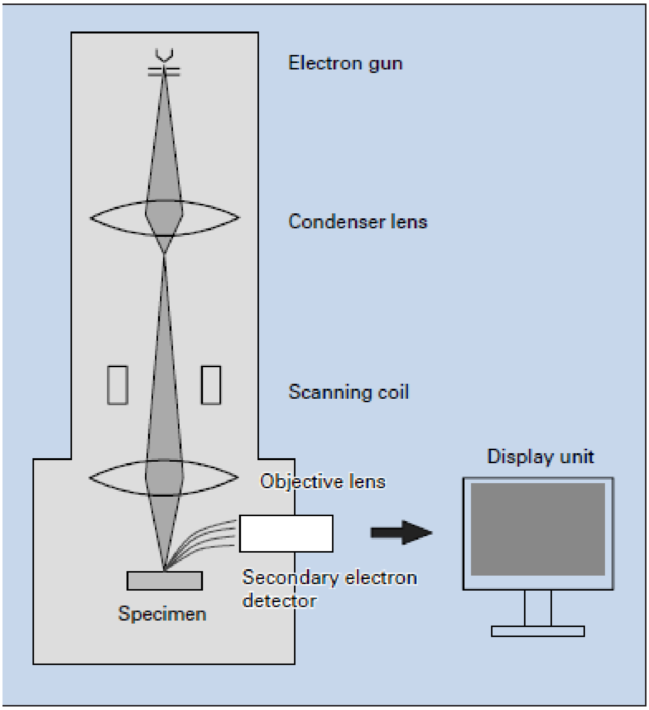

Figure 8.1 Basic Construction of SEM[*]

2. Description of Components

Electron Beam: Energy and current are its two distinct factors. Voltages between 1 and 60 keV & currents among 1e-7 and 1e-12 A are examples of variables. These numbers are specific to the instrument's model.

Electron Gun: It generates fine electron beams, often known as electron probes. The many kinds of electron guns that are used include

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[*] https://ebooks.inflibnet.ac.in/msp08/wp-content/uploads/sites/109/2018/12/Untitled-149.png

- TE (Thermionic- Emission) gun
- FE (Field- Emission) gun
- SE (Schottky- Emission) gun

TE (Thermionic- Emission) gun

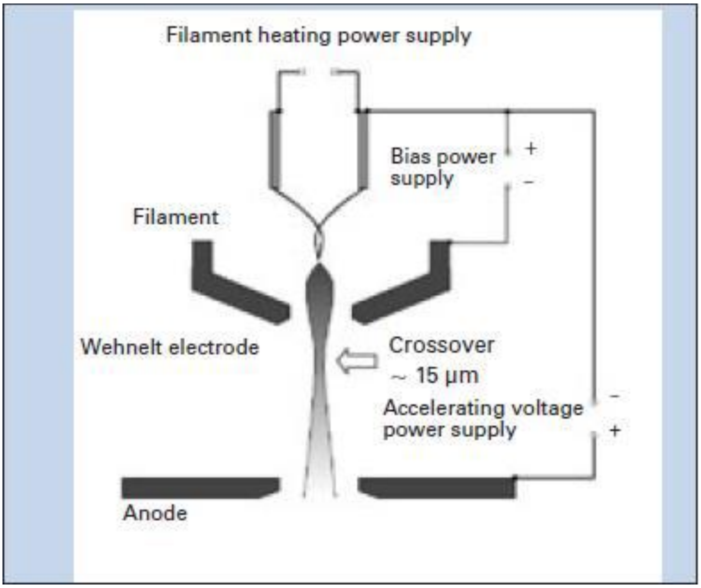

Figure 8.2 Construction of TE gun[*]

- By heating a tiny tungsten wire filament to 2800K, the filament functions as a cathode to produce thermal electrons.
- To gather these thermal electrons, a positive voltage of around 1 to 30 KV is applied to the metal plate serving as the anode.
- The Wehnelt electrode, which is positioned

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[*] https://ebooks.inflibnet.ac.in/msp08/wp-content/uploads/sites/109/2018/12/Untitled-150.png

between the anode and cathode, may be negatively voltaged to change the electron beam's current. Additionally, this electrode aids in concentrating the electron beam.

- The thinnest point in the beam called the cross-over (15–20 μm in diameter), is thought to represent the real electron source.

FE (Field- Emission) gun

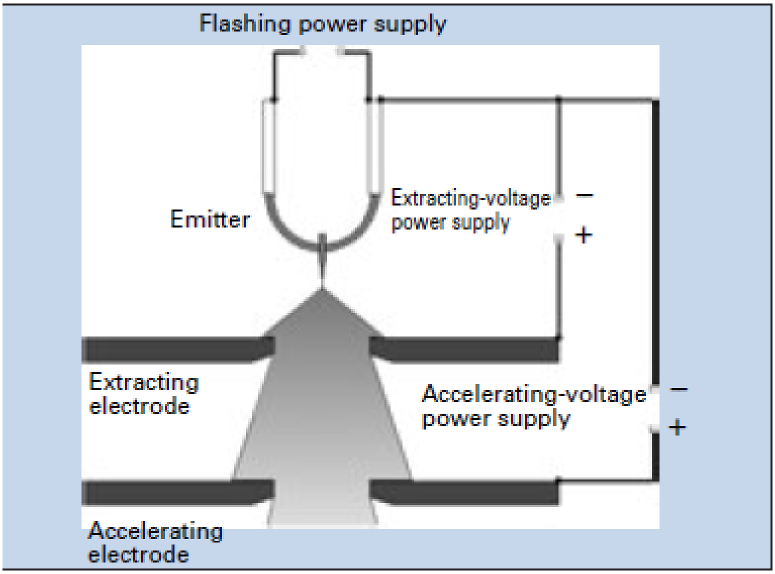

Figure 8.3 Construction of FE gun[*]

- Provides satisfactory resolution for various applications.
- Operates by generating the field-emission effect on

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[*] https://ebooks.inflibnet.ac.in/msp08/wp-content/uploads/sites/109/2018/12/Untitled-151.png

a metal surface through a high electric field.

- Utilises a thin tungsten wire attached to the emitter, which consists of a single tungsten crystal with a radius of approximately 100 nm and a tip bend, as the cathode.
- Electrons are emitted from the emitter through a tunnelling action when a positive voltage is applied to the extraction electrode.
- A hole in the extraction electrode allows electrons to exit, and a high-energy electron beam is formed by applying a voltage to an accelerating electrode below the extraction electrode.
- Minimal energy dispersion occurs due to the narrow electron beam width (5–10 nm) and the absence of heating requirements in an FE gun.

SE (Schottky- Emission) gun

- Works by creating the Schottky emission phenomenon on the heated metal surface by introducing a high electric field to it.
- As the cathode, a single crystal of tungsten coated with ZrO and having a tip radius of a few hundred nm is employed.
- At low cathode temperatures, ZrO coating increases the emission current by reducing the work function.
- By providing the suppressor electrode with a negative voltage, thermo electrons are protected from the emitter.

- Advantage: Since the emitter is positioned in a very high vacuum of around 10-7 Pa, the electron beam current is extremely steady.
- Increases the probe current.

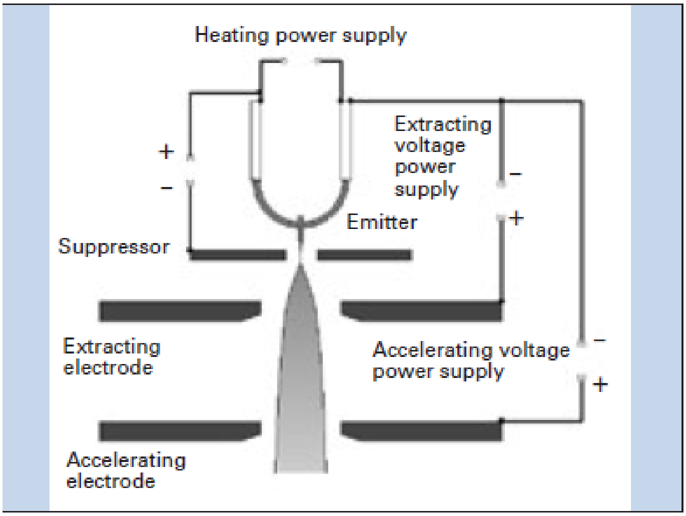

Figure 8.4 Construction of SE gun[*]

3. Lenses

In order to generate the finest electron beam with the appropriate crossing diameter, a two-level lens system consisting of an objective lens and a condenser built of metal cylinders having cylindrical holes that function in a vacuum is used. The electron cannon is situated underneath these lenses. To focus or defocus the beam, a magnetic field is created within the lenses.

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[*] https://ebooks.inflibnet.ac.in/msp08/wp-content/uploads/sites/109/2018/12/Untitled-152.png

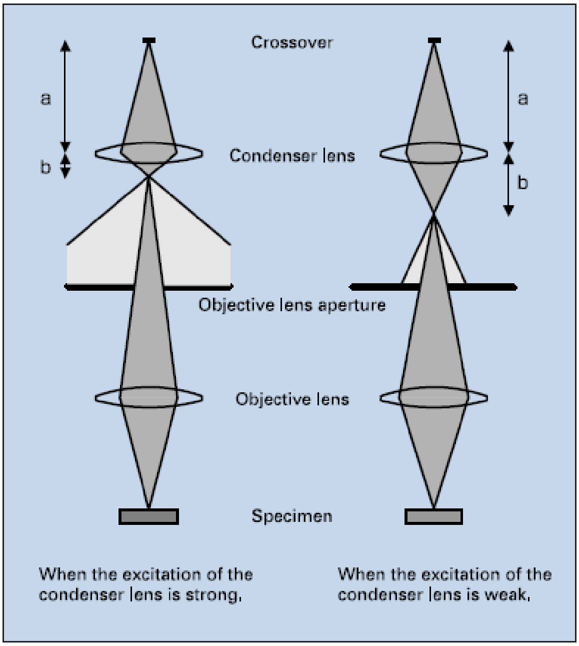

Figure 8.5 Formation of electron probe by lenses[*]

a. Role of condenser lens

The condenser lens activity directly affects the probe size. When the condenser lens is strengthened, the ratio of b/a decreases, resulting in a smaller probe size. Conversely, weakening the condenser lens increases the probe size. The C1 and C2 lenses adjust the beam current by altering the size and intensity of the beam spot. A metal aperture with a small hole, positioned between the condenser and objective lenses, allows light to pass through to the objective lens. This aperture also plays a critical role in

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[*] https://ebooks.inflibnet.ac.in/msp08/wp-content/uploads/sites/109/2018/12/Untitled-153.png

controlling the spot size and, consequently, the resolution of the beam.

Role of objective lens: It establishes the probe's ultimate diameter and is used for focusing.

Scanning Coils- These coils deflect the beam in both the X and Y axes, allowing for a raster pattern scan of the sample surface.

Sample Stage- In reaction to input values supplied into the software, this motorised plate moves in all three directions. The samples are supported by it and move smoothly in the intended direction. While both X and Y are two horizontal motions that are used to change the field of view, Z is a vertical movement that is required for both image resolution and depth of focus. In addition to these movements, it is also possible to tilt and rotate. A single mouse click may also be used to manually modify the stage's movement.

Detector– To create a picture, sample characteristics are assessed at various beam positions. A secondary electron detector is used to measure the secondary electrons that are released by the sample.

8.2. Transmission Electron Microscopy (TEM)

Transmission electron microscopy is an analytical technique used to see the smallest features in materials. Unlike optical microscopes, which rely on light in the visible range, TEMs may display remarkable detail at the atomic scale by magnifying tiny objects up to fifty million times. This is because electrons can possess a wavelength that is about 100,000 times shorter than visible light when they are propelled by a strong electromagnetic field. This may greatly improve the resolution of a microscope.

Applying TEM to the environment we live in has led to many breakthroughs and discoveries. Scientists may get a basic understanding of materials & biological systems by being able to "see" atoms. TEM pictures are works of beauty in and of themselves, in addition to having great scientific significance.

1. TEM for Materials Science and Nanotechnology

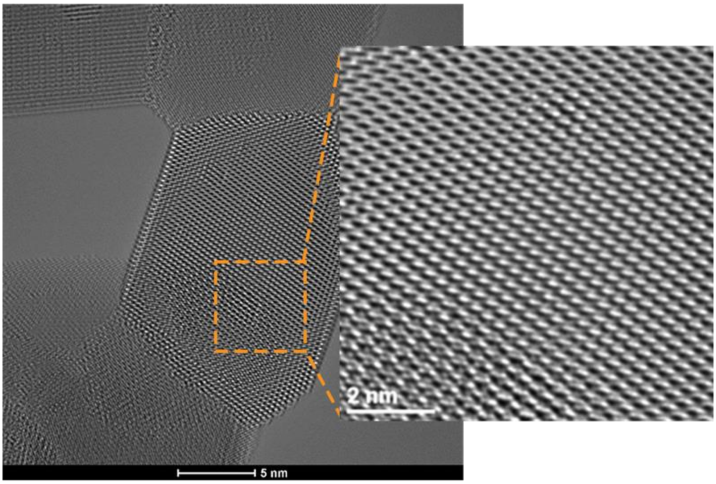

Figure 8.6 TEM image of nanoparticle showing atomic resolution.[*]

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[*] https://www.nanoscience.com/wp-content/uploads/2022/12/TEM-image-of-nanoparticle-from-

Scientists may see the basic components of functional materials such as catalyst nanoparticles, batteries, as well as semiconductor devices by magnifying into the atomic size. In situ material manipulation with focused electron beams enables the study and discovery of "nanofabrication" and other unique phenomena. This scale of detail is really astounding, and it helps engineers grasp the relationships between structure, property, and functionality so they can build nanomaterials from the bottom up.

2. Components of the Transmission Electron Microscope

TEMs are made up of these five essential parts:

- High voltage source
- Vacuum system
- Microscope column
- Detectors
- Control computers and software

At the top of the column is an electron cannon, which regulates the kinetic energy of the electron beam by connecting to a high-voltage source. Typically, accelerating voltages range from 80 kV to 300 kV. Several electromagnetic lenses and apertures (also known as detectors) make up the microscope column, which focuses the electron beam on the sample and enlarges the TEM

DENSsolutions.png

image on the viewing screen. Utilising a vacuum system, the required vacuum levels are maintained throughout the column.

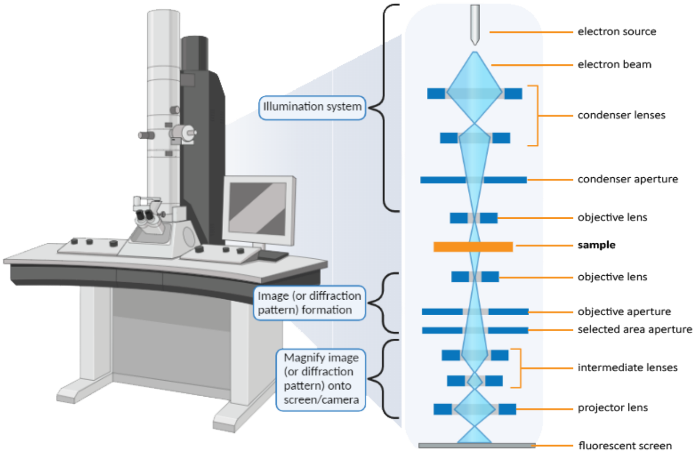

Figure 8.7 Simplified TEM diagram highlighting the major components throughout the column.[*]

Owing to the intricacy of the equipment, the microscopist only has control over a small number of crucial parameters; the majority of the components are continuously computer-controlled. The sample stage location, magnification, objective lens current, beam current, and the selection of apertures and detectors to employ for data acquisition are the primary user-controlled parameters.

In order to digitize TEM pictures, contemporary TEMs come with a retractable fluorescent viewing screen and

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[*] https://www.nanoscience.com/wp-content/uploads/2023/01/TEM-diagram-transparent.png

electronic detectors. To assess composition, the majority of TEMs additionally come with an X-ray detector that may be placed in between objective lens pole-pieces, close to the sample. Electron Energy-Loss Spectroscopy (EELS) is performed using optional electron energy-loss spectrometers at the end of the column.

3. Vacuum system

To ensure that the specimen is the only object in touch with the electron beam, the high vacuum system is fixed to the column. In TEMs, three distinct types of vacuum pumps are frequently used.

a. Roughing pumps reduce air pressure to a vacuum level that is considered "low," around 0.01 mbar. Since these pumps are physically pushing rather huge amounts of air, they are quite noisy. In order to evacuate the specimen load lock chamber before it reaches the column's very high vacuum environment, the roughing pump is sometimes utilized many times in a session. Certain high vacuum pumps may also be "backed" by roughing pumps, adding another pumping layer.
b. A rough pump must "back" one or more kinds of high vacuum pumps to achieve ultra-high vacuum levels (10-5 to 10-10 mbar). Diffusion pumps and turbo pumps are two examples. Pumping down the column is done using these pumps. The backing or just roughing pump is often switched off to

minimize mechanical vibrations after the column achieves the necessary vacuum level. It then automatically activates every few hours for a brief duration to release stored gas.

c. A few high vacuum pumps, like ion pumps, don't need to be backed up. The gun chamber's very high vacuum is maintained by the ion pump. To keep the electron gun from deteriorating, the gun chamber—which is pushed by the ion pump—is isolated from the remainder of the column by a differential pumping aperture.

On TEMs, one may sometimes find additional pump types known as "getters" or "traps"; these are used for the high and low vacuum ranges, respectively. These allow certain gas species to stick to a chemically reactive surface. Cryogenic pumps, often known as 'cold fingers', are frequently positioned within objective lens pole pieces or close to samples to "freeze stray gas molecules" to the sample's surface.

4. Electron Gun

The electron source, sometimes known as the electron "gun," is one of the most crucial components of the TEM. For high-resolution pictures to be produced, the electron source must fulfil specific parameters. Thermionic and field emission are the two primary types of electron cannons used in TEM. The brightness, spatial coherence, & temporal coherence of the emitter dictate the resolution limit of the microscope.

The filament used in thermonucleic weapons is either a ceramic crystal (such as LaB6 or CeB6) with a sharp tip produced at the end, or it may be a tungsten wire that has been bent severely. The filament receives current to heat the tip and release electrons. An electrode shaped like a cup with a tiny hole positioned in the middle under the tip is connected to the thermionic emitter. Often referred to as the Wehnelt cylinder, this apparatus aids in the localization of electron emissions and produces a concentrated beam that the lighting system may further control.

Ceramic crystals have a lower temperature at which they can emit electrons than tungsten, resulting in a brighter beam (i.e., greater current density) plus less energy dispersion. These offer longer lives and improved spatial precision, although they are more costly than tungsten and need higher vacuum levels.

Field emission guns use tunnelling, a separate but more basic process, to emit electrons. To generate tunnelling, an electrical field is provided via the first anode to a tungsten tip that is exceedingly sharp and pointed. The electrons are accelerated to the designated accelerating voltage by the second anode (Anode 2). Since the two anodes work together to concentrate the beam, there is no need for a Wehnelt cylinder. They are thus perfect for high-resolution S/TEM applications since the output beam is far brighter and more coherent than any thermionic emitter.

Schottky FEGs and cold FEGs are the two categories of FEG sources. The Schottky type is aided by thermionic emission, whereas a cold FEG only depends on tunnelling to produce electrons. This is accomplished by applying a small layer of zirconium oxide to the tungsten tip, which reduces the work function and encourages thermal electron emission.

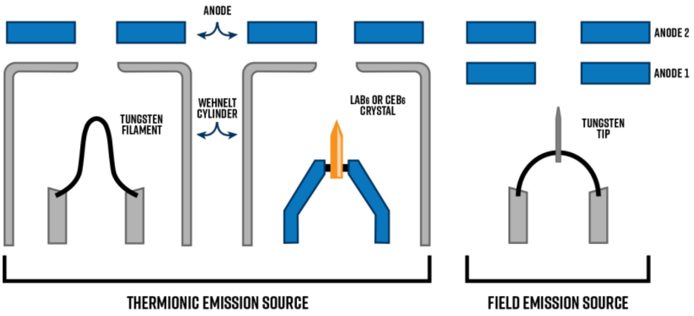

Figure 8.8 Schematic diagram comparing thermionic and field emission electron guns.[*]

4. Electron-Sample Interactions

Understanding every pertinent signal coming from the TEM is essential to choosing the best imaging strategy and accurately interpreting spectral features or picture contrast. Either elastic or inelastic scattering is the source of every signal produced in the TEM.

a. Elastic scattering

There is no energy transfer to incident electrons in elastic scattering events. Elastic scattering is the product of two kinds of interactions between isolated atoms:

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[*] https://www.nanoscience.com/wp-content/uploads/2023/01/Electron-gun-types-diagram-NSI.png

- Low angle scattering is the consequence of interaction with electron cloud.
- Rutherford scattering at high angles is caused by the positively charged nucleus's coulombic attraction.

Atoms are grouped in a consistent three-dimensional configuration (lattice structure) in genuine TEM samples, which are frequently crystalline materials. Elastic scattering will happen at specific angles according to the particular lattice spacings in that material when the electron beam penetrates the crystal.

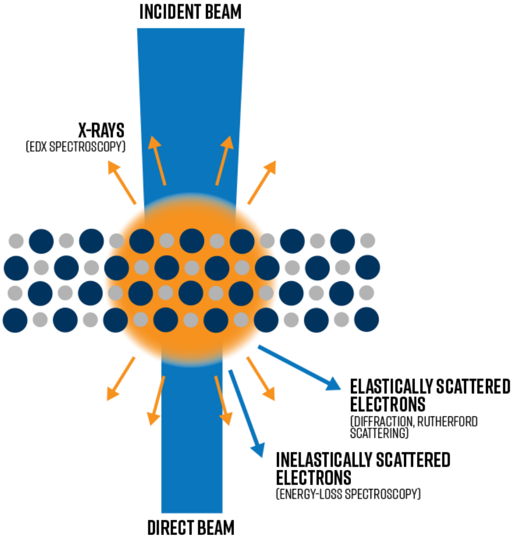

Figure 8.9 Schematic diagram of the different types of signals emerging in the TEM and how they are used for imaging and chemical analysis.[*]

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[*] https://www.nanoscience.com/wp-content/uploads/2023/06/signals-in-the-TEM-diagram.png

Bragg angles are another name for these distinctive scattering angles. Consequently, the diffraction pattern records an imprint of Bragg angles and transmits data on the material's crystalline structure, including flaws, strain, symmetry, and lattice spacings. When a material is polycrystalline or amorphous, the diffraction pattern takes the form of a set of diffuse rings, the radii of which match the lattice spacings. As the average crystallite size decreases, the degree of diffuseness also rises.

b. Inelastic scattering

Whereas inelastic scattering is characterised by a discernible loss of energy to the incoming electrons, elastic scattering is defined by a minute fraction of the incident beam energy, upon the order of meV (1000 meV = 1 eV) that can reach several hundred eV.

Inelastic scattering in TEM gives rise to a variety of signal forms. Strong, correlated data that can only be obtained from an S/TEM is produced by combining this data with high-resolution photos. What makes the current S/TEM so valuable for applications in materials science and nanotechnology is its "holistic" approach to materials characterisation, which includes analytical nano-analysis of composition, chemistry, & bonding.

Energy-loss electrons, X-rays, secondary electrons, and at times visible light (also known as cathodoluminescence, or CL) are all produced via inelastic scattering. The two most often analysed inelastic signals in the TEM are energy-loss electrons as determined by electron energy-loss spectroscopy (EELS) & characteristic X-rays as determined by energy-dispersive X-ray spectroscopy.

8.3. Atomic Force Microscopy (AFM)

The Atomic Force Microscope (AFM) was developed to address a fundamental limitation of the Scanning Tunneling Microscope (STM), which is its ability to image only conductive or semiconductive surfaces. One of the many advantages of AFM is its ability to image almost any type of surface, including biological materials, ceramics, glass, polymers, and composites. The AFM was introduced in 1985 by Binnig, Quate, and Gerber. In the original design, a diamond tip was attached to a piece of gold foil. The interaction between the diamond tip and the surface was facilitated by interatomic van der Waals forces, allowing direct contact with the surface. A second tip, an STM, was positioned above the cantilever to detect its vertical movement.

1. Atomic Force Microscope working

In a way similar to a scanning tunnelling microscope, a sharp tip is raster-scanned over a surface using a feedback loop to alter the parameters necessary to image a surface. Unlike Scanning Tunnelling Microscopes, "Atomic Force Microscope" does not need a conducting sample. Atomic forces are used to map the tip-sample contact instead of the "quantum mechanical effect" of tunnelling.

Scanning probe microscopy (SPM), which can detect almost every kind of force interaction, including van der

Waals, electrical, magnetic, and thermal, is referred to as "atomic force microscopy" (AFM). Some of the more complex processes need software modifications and new guidelines. Deflection with force measurement are the two main components of atomic force microscopy, in addition to feedback loop control and Angstrom-level positioning.

a. AFM Probe Deflection

The majority of Atomic Force Microscopes have historically used a laser beam deflection method, in which a laser is reflected onto a position-sensitive detector from the rear of the reflecting AFM lever. Si or Si3N4 are often used for microfabrication of AFM tips and cantilevers. The tip radius ranges from a few to tens of nanometers.

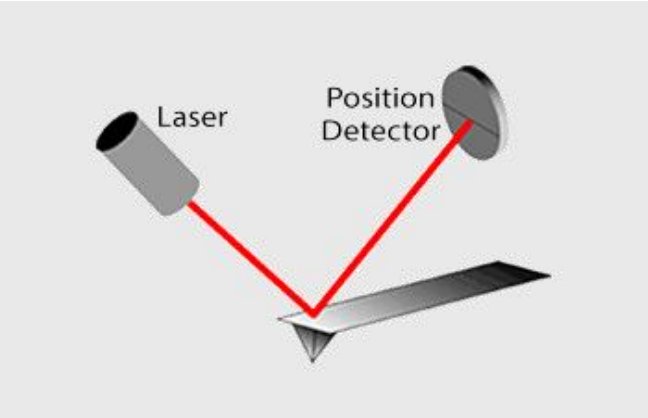

Figure 8.10 Laser beam deflection for atomic force microscopes[*]

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[*] https://www.nanoscience.com/wp-content/uploads/2023/10/Laser-beam-deflection-for-Atomic-Force-Microscopes.png

b. Measuring Forces

These forces affect AFM imaging because the Atomic Force Microscope depends on the forces between the tip and sample. Instead of taking a direct measurement, the force is computed by determining the lever's deflection and the cantilever's stiffness.

According to Hooke's law,

$F = -kz$

Where z is the lever's bent distance, F is force, and k is the lever's stiffness.

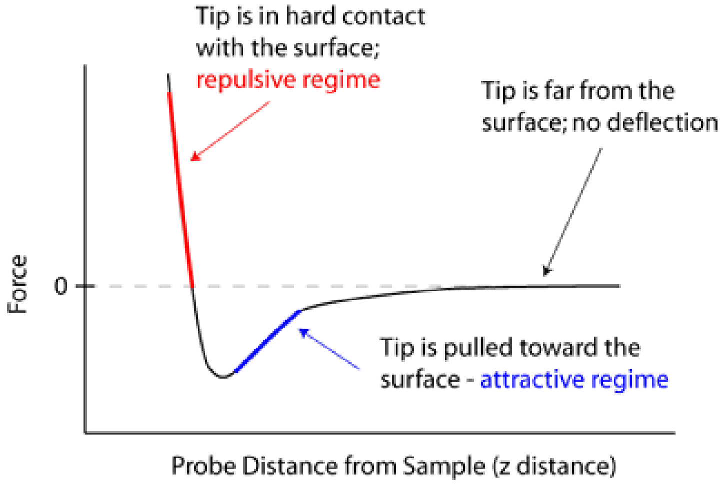

Figure 8.11Probe Distance from the sample (z distance)[*]

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[*] https://www.nanoscience.com/wp-content/uploads/2023/10/Force-distance-curve-for-AFM.png

2. Contact Modes for AFM

Following are the contact modes of AFM

a. Contact Mode

Contact mode is the initial and original way of functioning. The lever deflects as it passes across the topography of the surface and the tip raster scans over it.

Constant force and constant height imaging techniques are available for contact mode. When using constant force mode, the tip is continuously changed to keep the deflection at a predetermined value. This modification is what makes a picture visible. The sample has to be sufficiently flat for the feedback loop to keep control during scanning while the tip is scanning in constant height mode. For quick, small-scale atomic resolution scans, this is helpful.

The stiffness of the lever must be smaller than the effective spring constant that holds atoms together, which is in the range of 1 to 10 nN/nm since the tip makes firm contact with the surface. The spring constant of the majority of contact mode levers is less than 1 N/m.

b. Friction Force Mode

Lateral Force Microscopy is another name for the method used to quantify frictional forces across a surface. Areas of greater and lower friction are imaged by measuring the lateral twist of the cantilever instead of its deflection.

3. Dynamic Modes for AFM

The following are the dynamic modes:

a. Non-Contact Mode

The non-contact mode, which makes use of an oscillating cantilever, is a member of the AC mode family. In an appealing regime, a stiff cantilever oscillates, bringing its tip very near to the sample but keeping it from contacting it (i.e., non-contact). On the order of pN (10–12 N), the forces between the tip & sample are very small. The cantilever's resonant frequency/amplitude is measured as the oscillation is dampened by the contact between the tip and sample, which forms the basis of the detection technique.

b. Dynamic Force Mode

Also referred to as oscillating mode, tapping mode, acoustic AC mode, and intermittent-contact mode. When in contact mode, a stiff cantilever oscillates further away from the sample. The tip taps or contacts the surface every now and then because a portion of the oscillation continues into the repulsive regime. Since tips might get lodged in the layer of water pollution, very rigid cantilevers are usually used.

On soft samples, tapping the surface has the benefit of better lateral resolution. There is almost little lateral force, such as drag, which is typical in contact mode. The benefit is evident for specimens on substrate surfaces that are weakly adsorbed.

4. Electrical Modes for AFM

The following are the electrical modes:

a. Electric Force Microscopy

To detect electric force gradients, an AFM tip that is conducting is oscillated by EFM. Typically, two passes are made: the first is used to measure the topography in a conventional dynamic mode, and the second is used to measure the electric field strength by "lifting" a predetermined amount above the recorded profile. The gradient of the electric field is mapped using the phase signal.

b. Kelvin Probe Force Microscopy

Kelvin Probe Force Microscopy (KFM) is an oscillating method similar to Electrostatic Force Microscopy (EFM) that requires a conducting probe. KFM calculates the surface work function and is also referred to as surface potential microscopy. It can be implemented either as a single-pass approach or using a lift technique. High Definition KFM (HD KFM), a single-pass method, offers higher sensitivity and improved spatial resolution. As shown below, HD KFM requires a second lock-in amplifier. This approach provides much greater electrical signal resolution and additional detail, as there is no need for the tip to "lift" above the surface.

Chapter Summary

This chapter explored microscopy techniques essential for nanomaterial analysis, focusing on Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), and Atomic Force Microscopy (AFM). SEM was detailed with its instrumentation, components, and lens functions, showcasing its utility in surface imaging and analysis. TEM was discussed for its applications in materials science and nanotechnology, including the components like the vacuum system and electron gun, and how electron-sample interactions reveal detailed internal structures.

AFM was examined for its operational principles, including contact, dynamic, and electrical modes, highlighting its capabilities in surface topography and properties measurement. These microscopy techniques are critical for the precise characterization and analysis of nanomaterials, providing detailed insights into their structure and properties.

Assessment Questions

1. Which equipment is essential for doing Scanning Electron Microscopy (SEM)?
2. What are the differences between a Field-Emission (FE) gun and a Thermionic-Emission (TE) gun in SEM?
3. How does scanning electron microscopy (SEM) use the condenser lens?
4. What applications does Transmission Electron Microscopy (TEM) have in nanotechnology and materials science?
5. What constitutes a Transmission Electron Microscope's (TEM) main parts?
6. What is the basic idea behind how an atomic force microscope (AFM) operates?
7. Which contact modes are used in Atomic Force Microscopy (AFM)?
8. What distinguishes contact modes from dynamic modes in Atomic Force Microscopy (AFM)?
9. In Atomic Force Microscopy (AFM), what are the electrical modes and how do they work?
10. What role does probe deflection play in Atomic Force Microscopy (AFM) imaging?

CHAPTER 9

Spectroscopy Techniques

Learning Objective

This chapter will cover spectroscopic techniques for analyzing nanomaterials, including Fourier Transform Infrared (FTIR) spectroscopy, Raman spectroscopy, and UV-visible spectroscopy.

9.1. UV-Visible Spectroscopy

One popular method for analyzing nanoparticles is UV-visible (UV-Vis) spectroscopy, which is especially useful for figuring out the size distribution and optical characteristics of the particles.

1. Principles of UV-Vis Spectroscopy

UV-Vis spectroscopy calculates how much ultraviolet (UV) & visible light a material can absorb or transmit. Certain wavelengths of light are passed through samples, while others are absorbed.

The sample experiences electronic transitions as a result of the absorbed light, which may be identified and examined to provide details about the sample's makeup and characteristics.

2. Application to Nanoparticles

Surface Plasmon Resonance (SPR)

- **Mechanism**: Surface Plasmon Resonance is a phenomenon that is exhibited by nanoparticles, particularly those that are metallic like gold and silver. A distinctive absorption peak appears in the UV-Vis spectrum as a result of the conduction electrons located on the nanoparticle's surface oscillating in resonance with incoming light.
- **Significance**: The size, shape, & aggregation state of nanoparticles may all be inferred from the location and strength of the SPR peak. For instance, the SPR peak in gold nanoparticles usually emerges at about 520 nm for spherical particles, but it might move depending on the size or form of the particles.

Determining Size and Shape

- **Size Effects:** Changes in nanoparticle size cause a shift in the absorption peak position in the UV-Vis spectrum because of the variation in the SPR effect. Larger nanoparticles move to longer wavelengths, whereas smaller ones often peak at shorter wavelengths.
- **Shape Effects:** The absorption spectrum may also be impacted by the nanoparticles' form. For example, anisotropic geometries such as rods or triangles might display several peaks because of

distinct SPR modes, but spherical nanoparticles only have a single SPR peak.

Concentration Measurements

- **Beer's Law:** The concentration of nanoparticles within a fluid may be ascertained by measuring their absorbance. Beer's Law states that the absorbance of a solution is directly correlated with the quantity of nanoparticles present in it. Quantifying the concentration of nanoparticles may be achieved by measuring the absorbance at a certain wavelength.

Aggregation and Stability

- **Aggregation:** One way to tell whether nanoparticles accumulate is to look at the UV-Vis spectrum. The SPR peak often broadens and shifts red or blue as a result of aggregation. Keeping an eye on these alterations helps in determining if the nanoparticle dispersion is stable.
- **Stability**: Shifts in the absorption spectra, which may point to variations in particle size or aggregation, can be tracked using routine UV-Vis studies to track the stability of the nanoparticles over time.

3. Procedure for UV-Vis Spectroscopy of Nanoparticles

The fundamental procedures for UV-Vis spectroscopy of the nanoparticles are as follows:

a. **Sample Preparation**: Prepare a nanoparticle dispersion using the proper medium or solvent. Make sure the concentration is appropriate for UV-Vis measurements; depending on particle size and optical characteristics, it is usually between 0.01 and 1 mg/mL.
b. **Instrument Setup**: Make use of a UV-Vis spectrophotometer with an appropriate wavelength range (200-800 nm) installed. To precisely measure SPR peaks for nanoparticles, the equipment has to have high-resolution capabilities.
c. **Measurement**: Put the dispersion of nanoparticles in a cuvette and put it inside the spectrophotometer. Examine the material using both visible and UV light. Take note of the location and form of the absorption peaks as you record the absorbance spectra.
d. **Analysis**: To ascertain important details such as the SPR peak location, peak breadth, and intensity, analyze the absorption spectra. To determine the size, shape, & concentration of nanoparticles, compare them to theoretical or empirical data.

9.2. Raman Spectroscopy

An approach used to determine the vibrational, rotational, and additional low-frequency modes of a molecule or molecules in a more complicated system is called Raman spectroscopy. The chemical structure of a molecule or molecules, along with other chemical and physical structural characteristics, may then be ascertained via the detection of these modes.

The Raman effect, which happens when a molecule's electric dipole interacts with light photons, is the basis for Raman spectroscopy. Since this interaction makes use of the inelastic scattering of light, the way the molecule(s) get excited (and behave) causes the scattered frequency to vary from the original frequency when an incoming photon of light from a spectrometer strikes them. The characteristics and content of the sample under examination may then be ascertained using these distinct dispersed frequencies.

Raman spectroscopy has emerged as one of the most used techniques for characterizing various nanomaterials. The primary explanation for this is that Raman spectroscopy not only makes it possible to identify individual nanomaterials by determining their composition, but it can also frequently identify the structural configuration that separates two variants of the same type of nanomaterial—separating single-walled carbon nanotubes from multi-walled carbon nanotubes (MWCNTs) is one such example.

1. Principles of Raman Spectroscopy

The "inelastic scattering of monochromatic light" by molecules—typically from a laser—lays the groundwork for Raman spectroscopy. Most light which interacts with molecules scatters elastically, or in an approach known as Rayleigh scattering, at the same wavelength. However, because of interactions with molecule vibrations, rotations, or just other excitations, a tiny portion of the dispersed light is inelastically scattered at various wavelengths. Raman scattering, an inelastic scattering technique, reveals details about the molecular vibrational states.

2. Raman Spectroscopy Working

Laser Excitation: A wavelength-specific laser is pointed at the sample. The molecules within the sample are affected by the laser light.

Scattering: At the same wavelength as the incoming light, the bulk of the dispersed light is elastically scattered. But a tiny percentage of the scattered light experiences inelastic scattering, in which its interactions with molecular vibrations cause the scattered light's wavelength to shift.

Detection: After being gathered and sent into a spectrometer, the dispersed light is broken up into its individual wavelengths. The intensity of scattered light is shown in the ensuing Raman spectrum as a function of the wavelength shift from the input light.

Raman Shift: The wavelength difference between incoming and dispersed light is represented by the Raman shift, which has a unit of measurement of wavenumbers (cm^{-3}). The vibrational energy levels of molecules in the sample are revealed by this change.

3. Key Features of Raman Spectroscopy

Raman Spectrum: Peaks in the Raman spectrum represent the vibrational modes of molecules in the sample. These peaks' location, size, and form provide details about the sample's molecular makeup, interactions, and chemical structure.

Peak Assignment: Every Raman peak may be linked to a particular molecular vibrational mode. Researchers can determine chemical bonds, functional groups, and molecular interactions by examining these peaks.

Raman vs. IR Spectroscopy: Raman spectroscopy detects scattered light as opposed to absorption, which is especially helpful for analyzing non-polar bonds or materials that are poor IR absorbers. Raman spectroscopy works well with watery samples because it is less impacted by water.

9.3. Fourier Transform Infrared Spectroscopy (FTIR)

To determine the infrared spectrum of a sample's absorption or emission, Fourier Transform Infrared Spectroscopy is a potent approach. FTIR spectroscopy measures how different wavelengths of infrared light are absorbed by materials to offer precise information on their molecular makeup and structure. FTIR can provide information on the chemical characteristics, functional groups, & interactions of nanomaterials.

1. Principles of FTIR Spectroscopy

The foundation of FTIR spectroscopy is the idea that molecules absorb infrared light at certain wavelengths that correlate to the frequencies at which their chemical bonds vibrate. An infrared spectrum is produced by measuring these absorptions using an FTIR spectrometer.

Infrared Radiation: Infrared light is used by FTIR to stimulate molecular vibrations in a sample. The bonds among atoms may stretch, bend, or twist as a result of these vibrations.

Interferometer: In order to create an interference pattern of infrared light, FTIR spectrometers use an interferometer. The Michelson interferometer, which divides infrared light into two beams and reflects them off of mirrors before recombining them to generate an interference pattern, is the most widely used kind of interferometer.

Fourier Transform: The interferometer generates a time-domain signal called an interferogram. This signal is transformed into a frequency-domain spectrum by the use of the Fourier Transform, a mathematical method. The spectrum that results shows transmittance or absorbance as a function of wavenumber (cm^{-3}).

2. Application of FTIR to Nanomaterials

Characterizing Functional Groups

- **Identification**: By identifying certain vibrational modes, FTIR is utilized to determine the functional groups present on the surface of nanomaterials. For instance, carbonyl groups (C=O) occur at 1700 cm^{-1}, while hydroxyl groups (–OH) are distinguished by their distinctive absorption bands around 3200–3600 cm^{-1}.

- **Surface Chemistry**: For applications where surface interactions are important, like as drug delivery and catalysis, it is essential to understand the surface chemistry of nanomaterials.

Studying Surface Modifications

- **Functionalization**: Various ligands or compounds are often added to nanomaterials to functionalize them, improve their characteristics, or make them easier to employ in certain applications. The existence of these categories of functions and the effectiveness of surface changes may be verified using FTIR.
- **Binding Interactions**: Additionally, interactions between nanomaterial and different molecules, such as those seen in applications involving sensing or detection, may be studied using FTIR.

Analyzing Chemical Composition

- **Quantitative Analysis**: The number of certain functional groups or just chemical species on the surface of the nanomaterial may be measured using FTIR. Determining the magnitude of chemical reactions/interactions might benefit from this.
- **Material Identification**: By comparing the FTIR spectra of the nanomaterials with reference spectra of known materials, the approach may assist in

determining the kind of nanomaterials and their chemical makeup.

Monitoring Nanomaterial Synthesis

- **Reaction Progress**: FTIR may be used to follow changes in functional groups, keep an eye on the status of chemical processes, and make sure the necessary characteristics are obtained during the synthesis of nanomaterials.
- **Quality Control**: To make sure that the produced nanomaterials fulfil certain requirements and have constant chemical characteristics, FTIR may be used as a quality control instrument.

Chapter Summary

This chapter explored key spectroscopy techniques used for analyzing nanoparticles, including UV-visible spectroscopy, Raman Spectroscopy, and Fourier Transform Infrared Spectroscopy (FTIR). UV-Visible Spectroscopy principles were discussed, highlighting its application in nanoparticle characterization and detailing the procedural steps for accurate measurements.

Raman Spectroscopy was examined with a focus on its operational principles, working mechanism, and distinctive features that make it suitable for molecular and structural analysis. FTIR Spectroscopy was also covered, explaining its principles and how it is applied to study the chemical bonds and composition of nanomaterials. Each technique provides unique insights into nanoparticle properties, enabling comprehensive analysis and understanding of their behaviour and applications.

Assessment Questions

1. What are UV-visible spectroscopy's underlying theories?
2. How can nanoparticle analysis be done using UV-visible spectroscopy?
3. How can UV-Vis Spectroscopy be carried out on nanoparticles?
4. Which tenets guide Raman Spectroscopy?
5. What is the process by which Raman Spectroscopy provides material analysis?
6. What are Fourier Transform Infrared (FTIR) Spectroscopy's fundamental ideas?
7. How is the research of nanomaterials aided by FTIR Spectroscopy?
8. What distinguishing characteristics of Raman spectroscopy?
9. How are nanoparticles found using the UV-Vis Spectroscopy technique?
10. What details about a material's molecular structure may be found using Raman Spectroscopy?

CHAPTER 10

Nanomedicine

Learning Objective

Applications of nanotechnology in medicine, such as cancer treatment, drug delivery systems, and diagnostic imaging, will be covered in this chapter.

10.1. Drug Delivery Systems

In nanomedicine, drug delivery systems make use of nanotechnology to improve the effectiveness, selectivity, and control of medicinal agents. By delivering medications to specific parts of the body via nanoparticles, these technologies increase therapeutic effectiveness and reduce adverse effects.

1. Principles of Nanomedicine for Drug Delivery

The following are some key ideas in nanomedicine for medication delivery:

a. Nanoparticle Design

An important consideration in the creation of efficient medication delivery systems is nanoparticle design. The way that nanoparticles behave inside the body is greatly influenced by their size and form. Since they can efficiently circulate in circulation, pass through biological barriers, and aggregate in target tissues, nanoparticles in the range of one to one hundred nanometers are chosen.

For example, because of their tiny size and the increased permeability & retention (EPR) effect, nanoparticles may enter tumour tissues via leaky blood arteries. Furthermore, it is possible to manipulate the charge and hydrophilicity or just hydrophobicity of a nanoparticle's surface to increase its stability within biological fluids and better its interaction with certain cells or tissues. Selective binding to target cells is made possible by surface modification using ligands, polymers, or targeting moieties. This is essential for minimizing off-target effects and boosting therapeutic efficiency.

b. Drug Encapsulation

One of the main techniques for enhancing drug delivery is the encapsulation of medications into nanoparticles. Depending on the drug's makeup and the kind of nanoparticle being employed, drugs may be incorporated into the core of the particles or bonded to their surface. The medicine is shielded from deterioration, its solubility is increased, and regulated release is made possible via encapsulation.

Numerous variables, including pH shifts, temperature fluctuations, and the presence of certain enzymes, may cause controlled release mechanisms. For instance, temperature-sensitive nanoparticles may release medications at high body temperatures, whereas pH-sensitive nanoparticles may release their therapeutic payload in the acidic environment of a tumour. The medication's therapeutic window is extended by this regulated release, which also reduces adverse effects and boosts patient compliance.

c. Targeted Delivery

The goal of targeted delivery is to minimize exposure to healthy tissues while concentrating the therapeutic ingredient in the desired area. Active targeting and passive targeting are the two main approaches for targeted delivery. The EPR effect, in which nanoparticles gather in tumour tissues or inflammatory regions as a result of their leaky vasculature and inadequate lymphatic drainage, provides the basis for passive targeting.

When wide applications are involved and precise targeting is not necessary, this approach works well. Attaching certain ligands, such as peptides, small molecules, or antibodies, to the surface of nanoparticles is known as active targeting. The exact distribution of the therapeutic substance is made possible by these ligands, which bind to receptors or markers which are overexpressed on target cells or tissues. The specificity of medication distribution is improved by active targeting, which also lowers systemic toxicity and boosts therapeutic effectiveness.

d. Cellular Uptake

The capacity of nanoparticles to infiltrate target cells determines how well drugs are delivered. Two methods of cellular absorption include direct penetration, in which the nanoparticles penetrate the cell membrane, and endocytosis, in which the particles are ingested by the cells via membrane invagination. These uptake methods are influenced by the size, content, and surface charge of nanoparticles. For example, positive-charged nanoparticles tend to be incorporated into cells more easily because of their electrostatic interactions against negatively charged cell membranes. To increase the effectiveness of drug delivery and guarantee that therapeutic molecules reach their designated intracellular targets, it is crucial to comprehend and optimize these characteristics.

2. Types of Nanoparticles for Drug Delivery

Following are the types of nanoparticles for drug delivery system:

a. Liposomes

Lipid-based nanoparticles known as liposomes are capable of encasing both hydrophilic & hydrophobic medications due to their phospholipid bilayer. Their structure is made up of a lipid bilayer that may be altered to accommodate different functional groups around an aqueous core. Among the many benefits liposomes provide are their capacity to prevent medication deterioration, regulate drug release, and improve drug solubility. Additionally, they may be made to specifically target cells or organs by adding ligands or antibodies to the lipid layer. This capacity to target lessens negative effects and enhances treatment efficiency. Applications for liposomes include gene therapy, vaccination administration, and chemotherapy.

b. Polymeric Nanoparticles

Biodegradable polymers, including poly(lactic-co-glycolic acid), which may encapsulate medications and release them under regulated conditions, make up polymeric nanoparticles. These nanoparticles may be designed to deliver medication gradually, resulting in long-lasting therapeutic benefits. It is possible to modify the polymeric matrix to optimize stability, boost biocompatibility, and regulate the drug release profile. Polymeric nanoparticles find use in several medical fields, such as cancer treatment, where they may directly administer chemotherapeutic medicines to tumour cells, and vaccine administration, where they can modulate the release of antigens to boost immune responses.

c. Solid Lipid Nanoparticles (SLNs)

Solid Lipid Nanoparticles (SLNs) are nanoparticles with a solid lipid core that can adsorb or encapsulate drugs on their surface. They offer several benefits, including improved bioavailability, controlled drug release, and protection against drug degradation. SLNs enable sustained drug release, enhancing therapeutic efficacy and reducing the need for frequent dosing. The solid lipid core stabilises the drug, preventing leakage and ensuring long-term efficacy. SLNs are used in various applications, such as delivering poorly soluble drugs and enhancing the effectiveness of active ingredients in cosmetics.

d. Dendrimers

With a surface functional group, branching units, and a central core, dendrimers have extensive branches of macromolecules. Their exact control over size, shape, & surface qualities is made possible by their well-defined structure. Multiple drug delivery techniques are possible by attaching drugs to the surface of the dendrimer or encapsulating them inside its core. Dendrimers may be made to target certain tissues or cells by adding targeting ligands to their surface. They also provide the capacity to administer many medications at once and regulate release qualities. The capacity of dendrimers to transport and release several therapeutic substances may improve treatment effectiveness in a variety of applications, such as gene delivery and cancer therapy.

e. Quantum Dots

Due to quantum confinement phenomena, semiconductor nanoparticles known as quantum dots have special optical characteristics including fluorescence. They are not only useful for medication administration but also for imaging and diagnostics. Since quantum dots glow, it is possible to watch medication distribution and cellular absorption in real time, which yields important insights into how well a drug delivery system works. Therapeutic drugs may be delivered to particular cells or biomolecules by functionalizing quantum dots. This allows for tailored administration of the agents. Their prospective uses in cancer treatment & imaging-guided therapy are currently being investigated, as is their usage in drug delivery.

3. Applications of Nanoparticle-Based Drug Delivery Systems

The following are the applications:

a. Cancer Therapy

Since nanoparticle-based drug delivery methods may specifically target tumour cells and enhance drug accumulation in the tumour microenvironment, they are especially useful in cancer treatment. Nanoparticles may transport chemotherapeutic medicines directly to cancer cells, lowering systemic toxicity and improving treatment success. This is achieved by making use of the EPR effect or by utilizing active targeting tactics. Additionally, combination therapy—a method of delivering many medications at once to combat drug resistance and enhance therapeutic results—can be carried out using nanoparticles. This focused strategy reduces harm to healthy tissues while simultaneously increasing medication concentration at the tumour location.

b. Gene Therapy

Since they make it easier to transfer genetic material—such as genes, RNA, or plasmids—into target cells, nanoparticles are essential to gene therapy. Nanoparticles can guarantee regulated release, improve cellular absorption, and shield genetic material from deterioration. Therapeutic genes for gene editing/gene silencing are delivered using a variety of nanoparticle forms, including liposomes, dendrimers, and polymeric nanoparticles. Gene delivery technologies based on nanoparticles show great promise in treating cancer and genetic problems because of their remarkable accuracy in identifying particular cells or tissues.

c. Vaccines

By serving as adjuvants or antigen transporters, nanoparticles may improve the administration of vaccines. They may boost immunological responses, enable time-controlled antigen release, and increase the stability & bioavailability of antigens. Moreover, DNA or RNA vaccines, which include antigens that elicit an immune response, may be administered using nanoparticles. Nanoparticle-based technologies have the potential to improve vaccination programs' performance and provide novel approaches to treating and preventing infectious illnesses by enhancing the delivery and efficiency of vaccines.

d. Cardiovascular Diseases

Nanoparticles may be utilized to target damaged tissues or atherosclerotic plaques in the cardiovascular system to deliver medications, particularly for the treatment of cardiovascular disorders. For instance, anti-inflammatory medications or thrombolytics may be directly applied to plaques via nanoparticles to prevent plaque development or dissolve blood clots. With targeted medication delivery, cardiovascular diseases may be effectively managed and patient outcomes are improved by increasing the therapeutic benefit and lowering systemic adverse effects.

e. Neurological Disorders

The problem of getting medication across the blood-brain barrier may be solved with the use of nanoparticles. Therapeutic chemicals may be directly administered to the brain to treat neurological illnesses including Parkinson's disease and Alzheimer's disease by developing nanoparticles to pass the blood-brain barrier. Therapeutic drugs may be released under regulated conditions using nanoparticles, which can also be engineered to target certain brain areas and enhance medication stability. With neurological treatments, this focused strategy may improve treatment outcomes and lessen adverse effects.

10.2. Diagnostic Imaging

In nanomedicine, diagnostic imaging makes use of cutting-edge nanotechnology to improve imaging methods, enabling accurate and in-depth molecular visualization of biological tissues & processes. It is possible to create nanomaterials and nanoparticles to increase sensitivity, specificity, and contrast in a variety of imaging modalities.

1. Types of Nanoparticles for Diagnostic Imaging

The following are the types of diagnostic imaging:

a. Magnetic Nanoparticles

MRI contrast is improved by the introduction of magnetic nanoparticles, including superparamagnetic iron oxide nanoparticles. Due to their strong magnetic characteristics, these nanoparticles improve tissue differentiation by changing the local magnetic field. By focusing on certain tissues or cells, they may be used to image tumours, inflammation, or just other pathological situations. Due to their superparamagnetic nature, they are guaranteed to leave no magnetic residue behind when withdrawn from the magnetic field.

b. Quantum Dots

Because of quantum confinement phenomena, semiconductor nanoparticles known as quantum dots have special optical characteristics. When stimulated by light, they release fluorescence at certain wavelengths, which makes them suitable for optical imaging methods such as fluorescence microscopy. Different hues may be produced by engineering quantum dots, which enables multiplexed imaging, which shows numerous targets at once. They can monitor the administration of drugs in real-time and are also used within imaging-guided treatment.

c. Gold Nanoparticles

The significant optical scattering and absorption characteristics of gold nanoparticles make them useful in a variety of imaging modalities. Gold nanoparticles improve contrast in computed tomography imaging by increasing X-ray attenuation. Because of their Localized Surface Plasmon Resonance (LSPR) characteristics, which improve light scattering and absorption, gold nanoparticles may be used as contrast agents in optical imaging. They are useful instruments in diagnostic imaging because of their variety in imaging and capacity to be functionalized for targeting.

d. Silica Nanoparticles

It is possible to construct silica nanoparticles such that they transport imaging agents while offering strong contrast in imaging methods. They are often combined with other substances to form multifunctional imaging agents, such as medicines or quantum dots. They are readily able to have different functional groups or just target ligands attached to their surface, which enables targeted imaging and increased sensitivity. Additionally, multimodal imaging methods that combine many imaging modalities to provide thorough diagnostic information include silica nanoparticles.

e. Upconversion Nanoparticles

Low-energy infrared light is absorbed by upconversion nanoparticles, including those derived from lanthanide-doped materials, and higher-energy visible light is emitted. This characteristic makes it possible to image deep tissue with less interference from the backdrop. When deep tissue penetration and great resolution are needed for optical imaging methods, upconversion nanoparticles are used. Their strong photostability and minimal autofluorescence improve sensitivity and image quality.

4. Challenges and Future Directions

Although there have been many ups and downs in the history of nanomedicine, new technologies are developing to bring this field to the forefront.

a. Safety and Biocompatibility

Achieving the effective use of nanoparticles in diagnostic imaging requires ensuring their safety and biocompatibility. Toxicological effects must be kept to a minimum, immunological responses must be prevented, and the body must be safely cleared of nanoparticles. In-depth preclinical and clinical research is needed to evaluate the safety profiles of imaging agents based on nanoparticles.

b. Regulatory and Ethical Issues

To guarantee the effectiveness and safety of nanoparticle-based imaging agents, regulatory control is applied to both their development and usage. The effective integration of these technologies in clinical practice depends on managing ethical issues and regulatory requirements pertaining to the use of nanotechnology in medicine.

c. Cost and Accessibility

The high development and production costs associated with nanoparticle-based imaging agents may impede their general acceptance and accessibility. In order to lower the cost of these technologies and increase their accessibility for patients and healthcare providers, advancements in production methods and efficient manufacturing processes are required.

d. Integration with Clinical Practice

Overcoming technological and practical obstacles is necessary to incorporate nanoparticle-based imaging technologies into standard clinical practice. This involves making sure that imaging methods are optimized, making sure that they work with the current imaging equipment, and teaching medical personnel how to utilize these cutting-edge technologies.

10.3. Cancer Therapy

The use of nanotechnology in the development of novel cancer therapies and diagnostic instruments is known as nanomedicine in cancer therapy. Researchers want to maximize the benefits and minimize the adverse effects of cancer therapies by using the special qualities of nanoparticles and nanomaterials.

1. Types of Nanoparticles Used in Cancer Therapy

The following are the nanoparticles used in cancer therapy:

a. Liposomes

Liposomes are spherical vesicles that can hold both hydrophilic & hydrophobic medications inside their lipid bilayer. Liposomes may be utilized in cancer treatment to directly administer chemotherapeutic drugs, such as doxorubicin, to tumour cells. Targeting ligands may be used to modify the lipid bilayer to improve accumulation in tumour tissues. Additionally, regulated medication release from liposomal formulations may lower systemic toxicity and enhance therapeutic results.

b. Polymeric Nanoparticles

Biodegradable polymers that can encapsulate and release pharmaceuticals in a regulated way, such as poly(lactic-co-glycolic acid) (PLGA), are used to make polymeric nanoparticles. By adding targeting ligands on their surface, these nanoparticles may be made to specifically target certain cancer cells. In order to improve treatment effectiveness and overcome drug resistance, combination therapies—in which several medications are administered concurrently—can also be given using polymeric nanoparticles.

c. Gold Nanoparticles

Strong optical scattering and absorption characteristics are well-known for gold nanoparticles. They may be used in several medical procedures, such as photothermal treatment, in which gold nanoparticles are utilized to selectively kill cancer cells when exposed to laser light by converting light into heat. In order to improve treatment effects and increase the selectivity of gold nanoparticles for cancer cells, they may also be functionalized with targeting molecules.

d. Quantum Dots

Due to quantum confinement phenomena, semiconductor nanoparticles known as quantum dots have special optical characteristics. Although they may potentially be utilized in therapeutic applications, their primary uses are in imaging and diagnostics. With the ability to provide real-time monitoring of drug distribution and cellular uptake, quantum dots may be designed to deliver medications or therapeutic agents straight to cancer cells.

e. Dendrimers

Highly branching macromolecules called dendrimers may be utilized in cancer treatment to distribute drugs selectively to specific areas. Drugs and targeted ligands may be precisely attached to them thanks to their well-defined structure. Therapeutic chemicals may be attached to the surface of dendrimers or encapsulated in their cores, allowing for regulated release and improved selectivity for cancer cells.

f. Nanorods and Nanospheres

Spherical or rod-shaped nanoparticles, known as nanorods and nanospheres, have a variety of therapeutic uses. Because gold nanorods can absorb near-infrared sunlight and transform it into heat, they can be employed in photothermal treatment. Drugs or genetic material may be delivered to cancer cells using nanosphere engineering, increasing the effectiveness and targeting of therapy.

2. Applications of Nanomedicine in Cancer Therapy

The applications of nanomedicine in the context of cancer treatment are as follows:

a. Chemotherapy

Drug delivery methods based on nanoparticles improve drug solubility, stability, & targeting, which increases the effectiveness of chemotherapy. Chemotherapeutic drugs may be directly delivered to tumour cells via encapsulated nanoparticles, which lowers systemic toxicity and improves therapeutic results. This method reduces negative effects on healthy tissues while enabling larger medication concentrations at tumour locations.

b. Radiotherapy

By facilitating better radiation delivery to malignant cells, nanomedicine may increase the efficacy of radiation treatment. As an example, nanoparticles may be employed as radiosensitizers to make cancer cells more sensitive to radiation. Since gold nanoparticles have a high atomic number, which boosts X-ray absorption and improves radiation treatment effectiveness, they have shown special potential in improving radiotherapy.

c. Immunotherapy

Immunotherapeutic drugs may be administered more effectively and efficiently when combined with nanoparticles. To enhance immune responses against cancer cells, nanoparticles might, for instance, carry immune checkpoint inhibitors, cytokines, or just cancer vaccines to particular tumour locations. Delivery methods based on nanoparticles may also aid in resolving issues with immunotherapeutic drugs' stability and targeting.

d. Gene Therapy

Genetic material, which includes DNA, RNA, or gene-editing instruments (like CRISPR/Cas9), may be delivered to cancer cells via nanoparticles. Targeting certain genetic mutations or just regulatory pathways, gene therapy based on nanoparticles may change the behaviour of cancer cells, cause them to die, or improve the efficacy of other therapies. This method presents a viable plan for tailored cancer treatment.

e. Combination Therapy

Combination treatments that target many facets of cancer biology are made possible by the ability of nanoparticles to transport numerous therapeutic drugs at once. To improve treatment effectiveness and overcome medication resistance, nanoparticles may be used to deliver a mix of immunomodulators, targeted treatments, and chemotherapeutic drugs.

Chapter Summary

This chapter explored the applications of nanomedicine in drug delivery, diagnostic imaging, and cancer therapy. It began with an overview of drug delivery systems, detailing the principles behind nanomedicine and the various types of nanoparticles used to enhance drug delivery, including their specific applications and benefits. The discussion then shifted to diagnostic imaging, where different nanoparticles used for imaging were highlighted, alongside the challenges and future directions for improving imaging techniques.

Finally, the chapter examined the role of nanomedicine in cancer therapy, focusing on the types of nanoparticles employed and their applications in targeting and treating cancer. Collectively, these sections underscore the transformative potential of nanomedicine in advancing medical treatments and diagnostics.

Assessment questions

1. What are the fundamental principles of nanomedicine for drug delivery?
2. How is drug encapsulation achieved in nanoparticle-based drug delivery systems?
3. What methods are used for targeted delivery in nanomedicine?
4. What types of nanoparticles are commonly used for drug delivery?
5. How do polymeric nanoparticles contribute to drug delivery systems?
6. What are solid lipid nanoparticles (SLNs), and how are they used in drug delivery?
7. How are quantum dots utilized in drug delivery applications?
8. What role do magnetic nanoparticles play in diagnostic imaging?
9. How are gold nanoparticles applied in diagnostic imaging?
10. What are the main challenges and future directions for integrating nanoparticle-based drug delivery systems with clinical practice?

CHAPTER 11

Energy and Environment

Learning Objective

The function of nanomaterials in energy & environmental applications will be discussed in this chapter. Examples of these applications include fuel cells, hydrogen storage, solar cells, and nanocatalysts for environmental remediation.

11.1. Nanomaterials in Solar Cells

From first-generation silicon-based cells to more sophisticated thin-film and multi-junction cells, solar cells have seen substantial evolution throughout time. However, solar cell technology has reached unprecedented heights thanks to nanotechnology. Researchers and scientists have improved the efficiency and efficiency of solar cells by modifying materials at the nanoscale.

The control and manipulation of matter at the nanoscale, usually between 1 and 100 nanometers, is the focus of nanotechnology. Nanotechnology makes it possible to create structures like thin-film solar cells, quantum dots, and nanowires in the setting of solar cells. For example, quantum dots are tiny semiconductors that are perfect for improving energy conversion within solar cells because of their high efficiency of both emission and absorption of light.

Increased Efficiency and Energy Conversion: An important factor in raising solar cell efficiency is nanotechnology. More surface area in solar cells means more effective light absorption thanks to the use of nanomaterials like titanium dioxide or nanostructured silicon. Furthermore, numerous layers of semiconducting materials may be integrated thanks to nanotechnology, which improves energy conversion rates.

Flexible and Lightweight Solar Cells: The creation of adaptable and lightweight solar cells is one of the major benefits of using nanotechnology in solar cells. Solar cells may be made thinner, lighter, as well as more flexible by using nanomaterials like graphene or carbon nanotubes. This creates new opportunities for their integration into a variety of sectors. Wearable technology, building-integrated photovoltaics, and portable electronics might all be completely transformed by flexible solar cells.

Improved Durability and Longevity: Solar cell longevity and endurance are also improved by nanotechnology. Solar cells may be shielded from the elements by applying protective layers of the nanoparticles, or nanocoatings, to keep out moisture, dust, and UV rays. Additionally, nanocomposites—materials made up of nanoparticles scattered throughout a matrix—offer higher structural integrity and durability.

1. Types of Nanomaterials Used in Solar Cells

The following are the types of nanomaterials:

a. Quantum Dots

Semiconductor nanoparticles known as quantum dots may be designed to absorb certain light wavelengths. Quantum dots are employed in solar cells to form light-absorbing layers that improve the cell's capacity to absorb and convert a wide spectrum of light. Multi-junction solar cells that can more efficiently absorb various portions of the solar spectrum may be designed thanks to their adjustable optical characteristics.

b. Nanowires and Nanorods:

One-dimensional nanomaterials that have large aspect ratios, such as nanowires and nanorods, may improve light absorption and trapping. Thin-film & organic photovoltaic cells are among the solar cell types that may use them. Their special shape may help with improved charge carrier transit and collecting in addition to improving the interaction with light.

c. Carbon Nanotubes (CNTs)

Cylindrical nanostructures with exceptional mechanical strength and electrical conductivity are called carbon nanotubes. CNTs are employed as conductive materials in solar cells to increase electron collecting efficiency and charge transfer. They may also be used as a framework for other nanoparticles or integrated into transparent conductive films.

d. Graphene

Two-dimensional graphene has exceptional mechanical strength, flexibility, and electrical conductivity. It lowers resistance and enhances charge flow in solar cells. Transparent conductive layers made of graphene may increase a solar cell's overall efficiency. Additionally, because of its flexibility, adaptable and wearable solar cells may be developed.

e. Perovskite Nanomaterials

Due to their unique crystal structure, perovskite materials have become a very effective layer within solar cells for absorbing light. Perovskite nanoparticles are renowned for their excellent power conversion efficiencies and may be designed to absorb a wide range of the solar spectrum. They may be used in a variety of ways, such as perovskite-only and perovskite-silicon tandem cells.

f. Metal Nanoparticles

Through localised surface plasmon resonance, metal nanoparticles like gold and silver may improve the optical characteristics of solar cells. By adding these nanoparticles to the cell's structure, light absorption may be enhanced and photon-to-electron conversion efficiency can be raised. Additionally, metal nanoparticles may enhance light trapping and reduce reflection inside the solar cell.

2. Challenges and Future Directions

Scalability and Manufacturing: Increasing the manufacturing and manufacturing processes' scale is a significant obstacle in the use of nanomaterials for solar cells. Commercializing new solar technologies requires ensuring large-scale, reliable, and affordable production of nanomaterials. The development of scalable manufacturing processes and integration strategies for nanomaterials within solar cells is still under investigation.

Stability and Durability: Practical uses for solar cells depend on the nanomaterials' long-term stability and endurance. For solar cells to last a long time, nanomaterials need to be stable regarding temperature, moisture, and UV radiation. Enhancing the stability and longevity of solar cells based on nanomaterials is the main goal of ongoing research.

Cost and Commercialization: The economic feasibility of improved solar cells may be impacted by the cost of nanomaterials & the related production methods. The goal of research is to lower the cost of nanomaterials and create efficient manufacturing methods so that these technologies may be used more widely and at a lower cost.

Integration with Existing Technologies: The performance and compatibility of integrating nanomaterial-based solar cells with current solar technologies and infrastructure must be carefully considered. The goal of the research is to provide methods for smoothly integrating nanomaterials into the designs and uses of solar cells today, improving their efficiency without sacrificing present technology.

11.2. Nanocatalysts for Environmental Remediation

1. Principles of Nanocatalysts in Environmental Remediation

Below are the basic principles:

High Surface Area-to-Volume Ratio: When compared to bulk materials, nanocatalysts have a very high surface area-to-volume ratio. The efficiency and pace of catalytic processes are improved by the more active sites made possible by the larger surface area. This implies that nanocatalysts may interact with contaminants more efficiently and hasten their destruction or transformation in the context of environmental restoration.

Unique Catalytic Properties: The catalytic characteristics of nanocatalysts are distinct because of size-dependent phenomena such as surface plasmon resonance and quantum effects. In contrast to their bulk counterparts, materials at the nanoscale may possess distinct optical, chemical, and electrical characteristics. These characteristics may be used to create more selective and effective catalysts for certain environmental applications.

Enhanced Reactivity: Since they have many active sites and a high surface energy, nanocatalysts often exhibit increased reactivity. The breakdown of contaminants may occur more quickly and efficiently as a result of this enhanced reactivity. Additionally, by tailoring nanocatalysts to target certain processes, the remediation process may be made more selective and efficient.

2. Applications of Nanocatalysts in Environmental Remediation

The following are the applications:

a. Water Treatment

In order to purify water, heavy metals, pathogens, and organic contaminants are eliminated using nanocatalysts. For example, zero-valent iron nanoparticles may minimize hazardous metals and chlorinated compounds, whereas photocatalytic nanomaterials such as TiO_2 can decompose organic pollutants under UV light. Advanced oxidation procedures (AOPs), which reduce persistent organic contaminants and enhance water quality, may also use nanocatalysts.

b. Air Purification

Nanocatalysts are employed in air purification to break down pollutants such as nitrogen oxides (NOx) and volatile organic compounds (VOCs). In photocatalytic reactors, metal oxide catalysts like TiO_2 may be used to eliminate volatile organic compounds (VOCs) and lower NOx emissions. Air filters that use carbon-based nanocatalysts to absorb and break down contaminants may help enhance the quality of the air within buildings.

c. Soil Remediation

To remove pollutants from soil and groundwater, soil remediation may be done with the use of nanocatalysts. In polluted soil, iron nanoparticles are frequently used to break down organic contaminants such as chlorinated hydrocarbons. By offering reactive surfaces for pollutant degradation, nanocatalysts may also boost the efficiency of bioremediation procedures and make the removal of heavy metals easier.

d. Industrial Waste Treatment

Nanocatalysts are utilized in industrial settings to cleanse and remediate waste streams. They may assist in clearing industrial effluents of dangerous substances, dyes, and byproducts. Nanocatalysts, for instance, may be used in sophisticated oxidation procedures to break down hazardous substances and enhance the sustainability and safety of managing industrial waste.

e. Energy Production

Applications of nanocatalysts for energy generation in environmental remediation are also being investigated. Photocatalytic nanomaterials, for instance, may be used in solar-powered systems to produce hydrogen from water or change CO_2 into useful compounds. These apps provide sustainable energy solutions in addition to addressing environmental issues.

3. Challenges

The field of nanocatalysts for the environment has several obstacles, including:

a. Toxicity and Environmental Impact

It's important to carefully consider the possible toxicological and environmental effects of nanocatalysts. In order to guarantee safe and sustainable usage, it is important to understand how nanoparticles behave in the environment and how they interact with biological systems differently from bulk materials. Research is still being done to evaluate the dangers and create plans to lessen any negative consequences.

b. Scalability and Cost

It may be difficult to integrate nanocatalysts into workable remediation systems and to scale up their production. For these technologies to be economically feasible, the expense of synthesizing and integrating nanomaterials into large-scale processes must be addressed. The development of affordable synthesis techniques and enhancing the scalability of applications using nanocatalysts are the main goals of the research.

c. Stability and Durability

For nanocatalysts to be used effectively, real-world environmental conditions must guarantee their stability and longevity. Under a variety of environmental circumstances, including high temperatures, acidic or alkaline environments, & exposure to pollutants, nanocatalysts must continue to function and be resistant to deterioration.

d. Regulatory and Standardization Issues

The laws governing nanomaterials and nanocatalysts are constantly being developed. To guarantee the secure and efficient use of nanocatalysts within environmental cleanup, precise protocols and norms are required. Regulatory agencies, businesses, and researchers must work together to develop guidelines and standards for responsible use of nanotechnology.

11.3. Hydrogen Storage and Fuel Cells

Fuel cells and hydrogen storage are essential elements in the creation of sustainable energy systems. As a clean and effective energy source, hydrogen has a lot of promise to reduce greenhouse gas emissions and dependency on fossil fuels. Fuel cell performance and hydrogen storage are being improved in large part by nanomaterials and cutting-edge technology.

11.3.1. Hydrogen Storage

One of the main obstacles to using hydrogen as an energy carrier is hydrogen storage. Hydrogen needs effective storage options to be a realistic and sustainable substitute for conventional fuels. Hydrogen may be stored using a variety of techniques and materials, each having pros and cons.

1. Compressed Hydrogen Storage

Principle: Gases such as hydrogen may be kept at high pressures (usually 350–700 bar). By compressing hydrogen, this technique lowers its volume and facilitates storage and transportation.

Materials: The pressure vessels are built using high-strength composite materials, which guarantee their longevity and safety. These substances need to be able to tolerate the high pressures & stop hydrogen from leaking.

Challenges: Two major obstacles are the energy needed for compression and the possibility of high-pressure tanks. Furthermore, making and maintaining pressure vessels may be expensive.

2. Liquid Hydrogen Storage

Principle: It is possible to preserve hydrogen as a liquid at very low temperatures (around -253°C). Higher energy density is possible with this approach as opposed to gaseous hydrogen storage.

Materials: Cryogenic tanks with insulation are used to keep the temperature down to the lows required for liquid hydrogen. Reduced heat transmission and boil-off need the use of advanced materials and insulating methods.

Challenges: Two significant obstacles are the energy needed for liquefaction & the intricate infrastructure necessary to handle cryogenic hydrogen. It also takes a lot of energy to sustain such low temperatures.

3. Metal Hydrides

Principle: Compounds known as metal hydrides are created when metals and hydrogen combine. Hydrogen may be stored in solid form thanks to these materials' reversible absorption and release of hydrogen gas.

Materials: Many metal hydrides are used, including titanium hydride (TiH_2), sodium alanate ($NaAlH_4$), and magnesium hydride (MgH_2). The kinetics, release temperatures, and storage capacities of these materials vary.

Challenges: The weight of the hydride components and the high energy needed to liberate hydrogen through metal hydrides are the key obstacles. The main goals of the research are reducing operating temperatures and increasing hydrogen release rates.

4. Chemical Hydrogen Storage

Principle: The process of storing hydrogen chemically entails placing it in substances that react to release hydrogen. This technique can provide substantial concentrations of hydrogen storage.

Materials: Hydrogen-rich substances like ammonia (NH_3), hydrazine (N_2H_4), & formic acid (HCOOH) are a few examples. These substances can react chemically or catalytically to release hydrogen.

Challenges: The intricacy of chemical processes, the need for catalysts, and the safe handling of chemical substances are the primary obstacles. Chemical recovery and recycling also need to be controlled.

5. Nanomaterial-Based Storage

Principle: Nanomaterials' large surface area and adjustable architectures provide them special advantages for storing hydrogen. They can improve the kinetics of hydrogen release and absorption.

Materials: The potential of nanomaterials like graphene, carbon nanotubes, and Metal-Organic Frameworks (MOFs) for hydrogen storage is being investigated. High storage capacities and ideal release conditions are possible with these materials.

Challenges: Increasing the manufacturing of nanomaterials and guaranteeing their stability and functionality under real-world circumstances present formidable obstacles. To solve these problems and improve nanomaterial-based storage systems, research is still being done.

11.3.2. Fuel Cells

Fuel cells are devices that use an electrochemical process to directly transform chemical energy into electrical energy. Specifically, hydrogen fuel cells employ airborne oxygen as the oxidant and hydrogen as the fuel. Fuel cells provide an energy conversion technology that is both clean and efficient, with the sole waste being water.

1. Proton Exchange Membrane Fuel Cells (PEMFCs)

Principle: The electrolyte in PEMFCs is a Proton Exchange Membrane (PEM), which allows protons (H+ ions) to flow through while obstructing electrons. Protons and electrons are created at the anode when hydrogen gas is supplied there. While the protons go through PEM to react with oxygen in the cathode to make water, the electrons travel via an external circuit to the cathode to create electrical power.

Materials: A PEM often composed of Nafion or similar fluorinated polymers is used in PEMFCs. The reactions at electrodes are aided by platinum or platinum alloy catalysts.

Challenges: Two major obstacles are the high cost of platinum catalysts & the need for efficient water management. Furthermore, research is still being done to enhance PEMFC performance and durability under varied working environments.

2. Solid Oxide Fuel Cells (SOFCs)

Principle: The electrolyte used in SOFCs is either solid oxide or ceramic, and it transmits oxygen ions ($O2^-$) from the cathode to the anode. The anode receives hydrogen, which combines with oxygen ions to form water and releases electrons that power the anode. Typically functioning between 600 and 1000°C, SOFCs have a high temperature that facilitates effective energy conversion.

Materials: Ceramic materials for the electrolyte, such as yttria-stabilized zirconia (YSZ), and perovskite materials for electrodes are used in SOFCs. Both high temperatures & chemical reactions must be tolerated by these materials.

Challenges: Thermal stress and material deterioration may result from SOFCs' high operating temperatures. A major area of research interest is also developing durable and affordable materials for SOFCs.

3. Alkaline Fuel Cells (AFCs)

Principle: Typically, potassium hydroxide (KOH) is used as an alkaline electrolyte in AFCs to promote the interaction between hydrogen & oxygen. Hydroxide ions (OH^-) are transferred from the cathode to the anode by the electrolyte. Water is produced at the anode by the reaction of hydrogen gas with hydroxide ions, and electricity is produced by the passage of electrons via an external circuit.

Materials: Silver or nickel are used as catalysts in anode and cathode processes in AFCs. KOH solutions are often used as the alkaline electrolyte.

Challenges: Since AFCs are dependent on carbon dioxide (CO_2), carbonate may develop and lower the electrolyte's effectiveness. Important research topics include controlling CO_2 pollution and enhancing the robustness of AFC components.

4. Direct Methanol Fuel Cells (DMFCs)

Principle: Methanol (CH_3OH) is the fuel directly used in DMFCs. Protons, electrons, and carbon dioxide are produced at the anode during the oxidation of the methanol. Protons go to the cathode via a PEM, where they combine with oxygen to create water. Electrical power is produced by the electrons as they go through an external circuit.

Materials: Similar to PEMFCs, DMFCs use a PEM and catalysts—typically platinum-based—to speed up the processes. The anode receives and stores methanol directly.

Challenges: One major difficulty is methanol crossover, when methanol migrates across the PEM and decreases efficiency. The goal of the research is to decrease crossover by optimizing the PEM and increasing the selectivity of the catalysts.

Chapter Summary

This chapter explored the integration of nanomaterials in advancing energy technologies and environmental solutions. It began with an examination of nanomaterials used in solar cells, including the types employed and the challenges faced in this field, highlighting future directions for improvement. The discussion then moved to nanocatalysts, focusing on their principles and applications in environmental remediation, and addressing the challenges associated with their use. The chapter concluded with a comprehensive overview of hydrogen storage and fuel cells.

It covered various hydrogen storage methods, such as compressed, liquid, and metal hydride storage, as well as nanomaterial-based storage solutions. The section on fuel cells detailed different types, including Proton Exchange Membrane Fuel Cells, Solid Oxide Fuel Cells, Alkaline Fuel Cells, and Direct Methanol Fuel Cells. Overall, this chapter underscores the significant role of nanotechnology in enhancing energy efficiency and addressing environmental challenges.

Assessment Questions

1. Which major categories of nanomaterials are used in solar cells?
2. How can perovskite nanoparticles increase the efficiency of solar cells?
3. What function do metal nanoparticles play in improving the efficiency of solar cells?
4. What is the use of nanocatalysts in environmental remediation?
5. What are the main ways that environmental contaminants can be cleaned up using nanocatalysts?
6. Which techniques are used in fuel cells to store compressed hydrogen?
7. In comparison to other hydrogen storage techniques, how does liquid hydrogen storage fare?
8. What function do metal hydrides serve in the storage of hydrogen?
9. What distinguishes solid oxide fuel cells (SOFCs) from proton exchange membrane fuel cells (PEMFCs)?
10. What advantages can direct methanol fuel cells (DMFCs) provide in terms of nanomaterial application?

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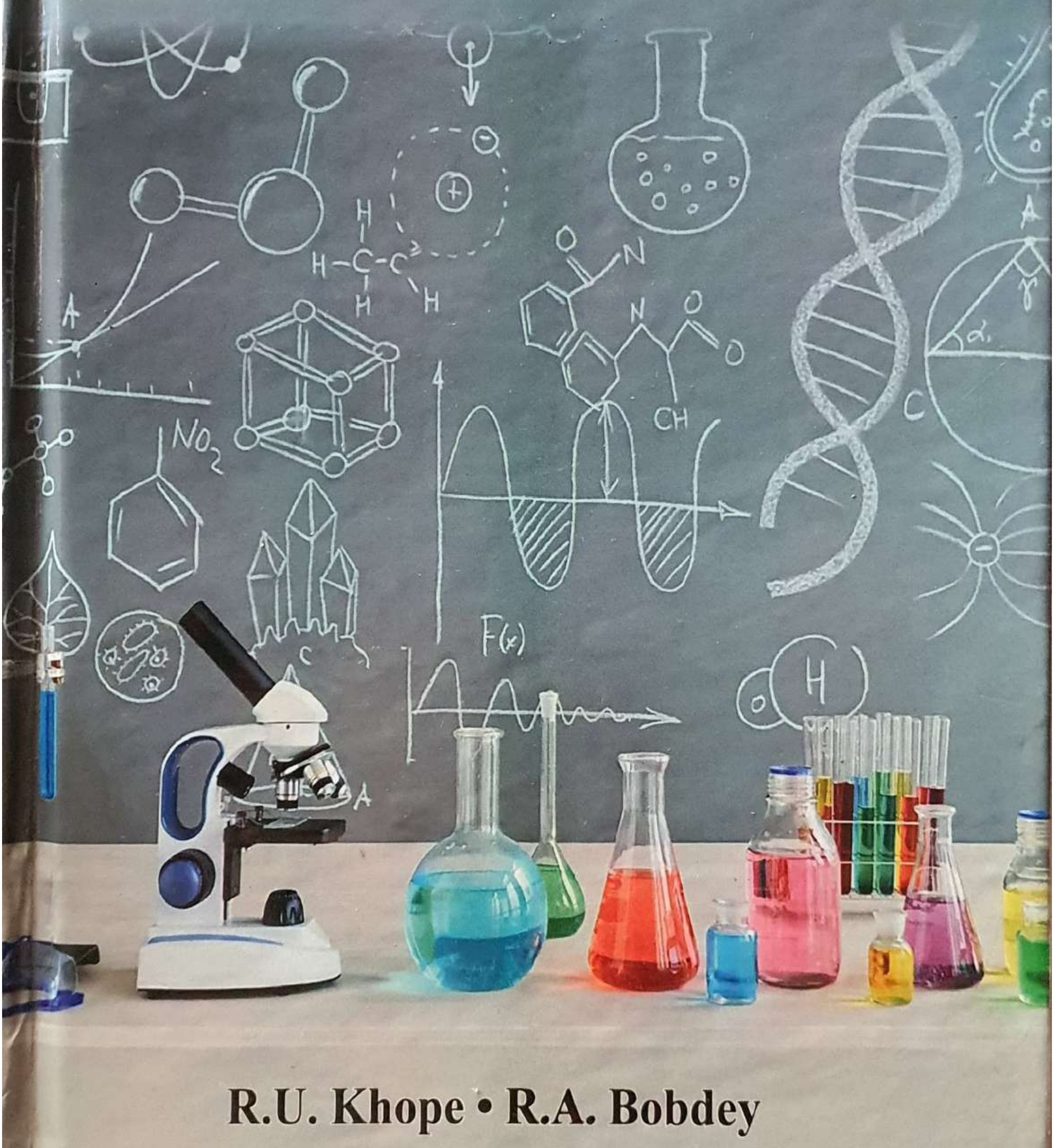

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