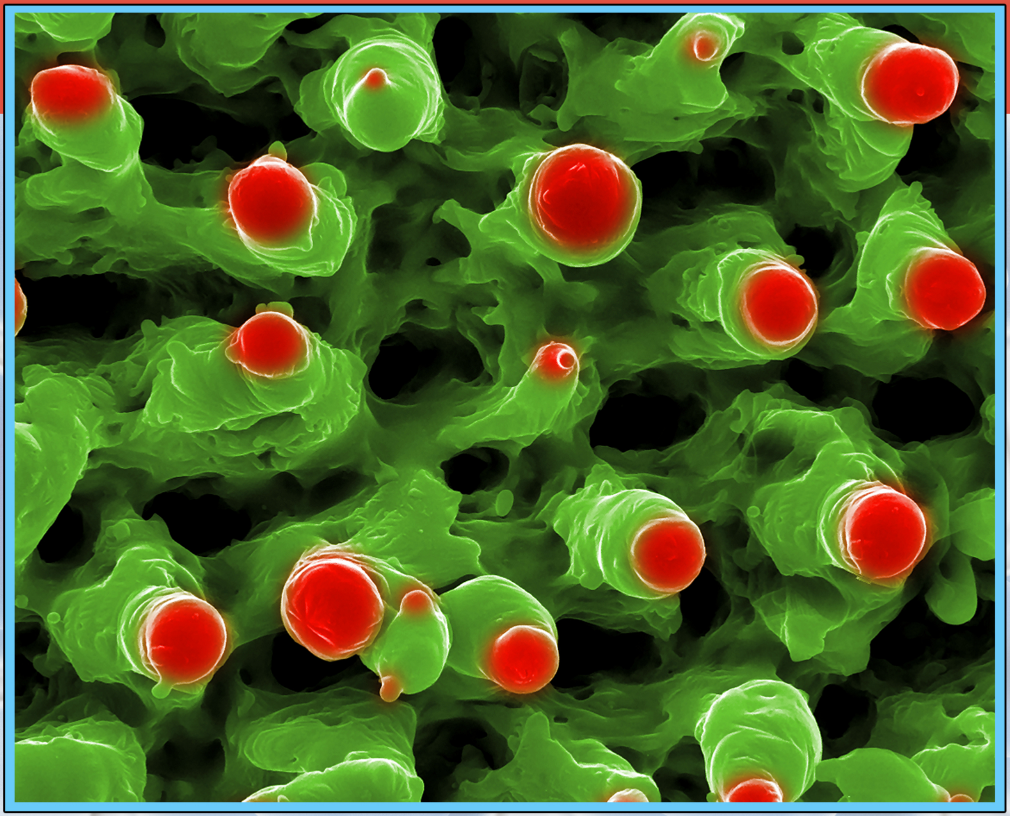
SYNTHESIS AND APPLICATIONS OF SEMICONDUCTOR NANOSTRUCTURES



Editor:

Karamjit Singh Dhaliwal

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Current and Future Developments in Nanomaterials and Carbon Nanotubes

(Volume 4)

Synthesis and Applications of Semiconductor Nanostructures

Edited by

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FOREWORD

It gives me immense pleasure to write this foreword for the book titled *"Synthesis and Applications of Semiconductor Nanostructures"*, which is the fourth volume of the book series titled *"Current and Future Developments in Nanomaterials and Carbon Nanotubes"*. For the last four decades, semiconductor nanostructures have been the subject of scientific interest because of their size-tunable optical and electrical properties caused by unique quantum confinement effect and augmented surface-to-volume ratio at nanoscale size dimensions. A thorough study of these materials constitutes a new perspective for basic and applied research in nanophotonics, opto-electronics, nanobiotics, nanocosmetics, nanomedicine, and photo-chemistry. This book provides adequate knowledge about the fundamentals of semiconductor nanostructures, synthesis and characterization of nanostructures of various morphologies, as well as metal-organic frameworks and nanostructure-impregnated metal-organic frameworks. Multidisciplinary smart applications of these materials are described in a lucid way in this volume. All the chapters have been appositely chosen to justify the theme of the book. I think this book would be of immense use to academicians, researchers and technocrats, who may like to get a better understanding of synthesis and applications of semiconductor nanostructures.

Prof. Arvind
Vice Chancellor
Punjabi University
Patiala, Punjab, India

PREFACE

Nanotechnology is a multidisciplinary field benefitting from efforts and developments in the various spheres of science and technology, such as applied physics, materials science, interface and colloid science, supramolecular chemistry, chemical engineering, biological engineering, mechanical engineering, electrical engineering and computer engineering. Its theme is the design, fabrication, characterization and application of structures, devices and systems by controlling shape and size at the nanometer scale. This book focuses on the synthesis, characterization and multifaceted potential applications of semiconductor nanostructures, metal-organic frameworks (MOFs) and nanostructure-impregnated MOFs, along with some glimpses of doped glasses, functionalized carbon nanotubes, doped graphene and graphene nanoribbons. Numerous bottom-up and top-down synthesis techniques opted for the synthesis of various morphologies of semiconductor nanostructures have been discussed at length, along with details of synthetic metal-organic frameworks and nanostructure-impregnated MOFs constructed from a variety of inorganic and organic components. The photocatalytic activity potential of synthetic materials for hydrogen production, wastewater treatment, carbon dioxide reduction, environmental pollution monitoring and management, as well as oxidation of alcohols has been described comprehensively. The sensing ability of nanostructures and MOFs has been thoroughly illustrated to utilize these materials as chemical sensors, gas sensors and biosensors. Many other smart applications in gas separation, gas storage, drug delivery, nanomedicine, nano-cosmetics as well as antibacterial uses have been reported lucidly in this book. This book also deals with the geometric and electronic properties of doped graphene and graphene nanoribbons. Spin-polarized density functional study results have been included to describe the structural, electronic and magnetic properties of strained graphene nanoribbons.

Although this book is not edited with any special course in mind, it may serve as a unique source of knowledge for postgraduate students, academicians, researchers and technocrats, who want to carry out R&D activities with nanomaterials and metal-organic frameworks.

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DEDICATION

Dedicated to My Father Late S. Major Singh Dhaliwal.

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List of Abbreviations

AC	Acetylacetone
AD	Alzheimer's Disease
AF	Antiferromagnetic
AFM	Atomic Force Microscope
AGNRs	Armchair Graphene Nanoribbons
ALP	Alkaline Phosphatase
AOPs	Advanced Oxidation Processes
API	Active Pharmaceutical Ingredients
AR	Analytical Reagent
ATP	Adenosine Triphosphate
AZT-Tp	Azidothymidine Triphosphate
Aβ	Amyloid-β
BAU	Bangladesh Agricultural University
BDC	Benzene-1 4 Dicarboxylic Acid
BE	Binding Energy
BET	Brunauer Emmett and Teller
BPA	Bisphenol A
BSG	Box-shaped Graphene
Bu	Busulfan
CB	Conduction Band
CDV	Cidofovir
CGNRs	Chiral Graphene Nanoribbons
CL	Chemiluminescence
CNF	Cellulose Nanofiber
CNS	Central Nervous System
CNTs	Carbon Nanotubes
COF	Covalent Organic Framework
CoPc	Cobalt-phthalocyanine
CQDs	Carbon Quantum Dots

CRET	Chemiluminescence Resonance Energy Transfer
CSF	Cerebrospinal Fluid
CTAB	Hexadecyltrimethyl Ammonium Bromide
CVD	Chemical Vapour Deposition
CuPc	Copper-phthalocyanine
D	Dimensional
DBI	Dihydroxybenzene isomers
DDF	Doctor’s Dermatologic Formula
DEF	N,N-diethylformamide
DFT	Density Functional Theory
DMF	Dimethylformamide
DNA	Deoxyribonucleic Acid
DOE	Department of Energy
DOS	Density of States
Doxo	Doxorubicin
DRIFTS	Diffuse Reflectance Infrared Fourier Transform Spectroscopy
DSM	Double Solvent Method
2DEG	Two-dimensional Electron Gas
EDS	Energy-dispersive X-ray Spectroscopy
ERGO	Electrochemically Reduced Graphene Oxide
Erα	Estrogen Receptor Alpha
FC	Field Cooled
FCC	Face Centred Cubic
FDA	Food and Drug Administration
FFT	Fast Fourier Transform
fGO	Functionalized Graphene Oxide
f-MWCNTs	Functionalized Multi-walled Carbon Nanotubes
FRET	Fluorescence Resonance Energy Transfer
FTIR	Fourier Transform Infrared
FWHM	Full Width at Half Maximum
5-FU	5- ourouacil
GAs	Graphene Aerogels
GC-MS	Gas Chromatography Mass Spectrometry
GMS	Glycerol a-monostearate
GN	Graphene Nanosheet

GNPs	Gold Nanoparticles
GNRs	Graphene Nanoribbons
GO	Graphene Oxide
HA	Hyaluronic Acid
HER	Hydrogen Evolution Reaction
HKUST	Hong Kong University of Science and Technology
HOMO	Highest Occupied Molecular Orbital
HPLC	High-performance Liquid Chromatography
HPLC-DAD	High-performance Liquid Chromatography with Diode Array Detector
HPLC-PDA	High-performance Liquid Chromatography with Photodiode Array Detector
IBU	Ibuprofen
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
IMI	Imidacloprid
IONPs	Iron Oxide Nanoparticles
LBNP	Lipid-based Nanoparticle
LC	Liquid Chromatography
LMM	Localized Magnetic Moment
Ln-MOF	Lanthanide Organic Framework
LSPR	Localized Surface Plasmon Resonance
LUMO	Lowest Un-occupied Molecular Orbital
M	Metal
MB	Methylene Blue
MBB	Molecular Building Blocks
MBE	Molecualr Beam Epitaxy
MDR	Multiple Drug Resistant
MEMS	Micro-electromechanical Systems
MIPs	Molecularly Imprinted Polymers
miRNA	Micro Ribonucleic Acid
MM	Magnetic Moment
MNase	Micrococcal Nuclease
MNP	Magnetic Nanoparticles
MNPs	Metal Nanoparticles
MO	Methyl Orange
MOCVD	Metal Organic Chemical Vapor Deposition

MOFDC	Metal Organic Framework Derived Carbon
MOFs	Metal Organic Frameworks
MOVE	Methane Opportunities for Vehicular Energy
MOXs	Mixed Oxides
MP	Methyl Parathion
MPA	Mercaptopropionic Acid
MPcs	Metallophthalocyanines
MW	Microwave
MWCNTs	Multi-walled Carbon Nanotubes
NBOs	Non-bridging Oxygens
NCs	Nanocrystals
NEMSs	Nano-electromechanical Systems
NESD	Nano Enabled Scaffold Device
NHE	Normal Hydrogen Electrode
NMR	Nuclear Magnetic Resonance
NPs	Nanoparticles
PAHs	Polycyclic Aromatic Hydrocarbons
PBUs	Primary Building Blocks
PCA	Photo-catalytic Activity
PCFs	Porous Carbon Fibers
PCL	Poly (ε-caprolactone)
PD	Parkinson’s Disease
PEC	Photoelectrochemical
PET	Photo-induced Electron Transfer
PL	Photoluminescence
PVD	Physical Vapour Deposition
PVP	Polyvinyl Pyrrolidone
PXRD	Powder X-ray Diffraction
QDs	Quantum Dots
QE	Quantum Efficiency
QW	Quantum Well
RE	Rare Earth
RET	Radiative Energy Transfer
rGO	Reduced Graphene Oxide
RhB	Rhodamine B

RNA	Ribonucleic Acid
RON	Research Octane Number
ROS	Reactive Oxygen Species
rpm	Revolutions per minute
RT	Room Temperature
SAW	Surface-acoustic Waves
SBUs	Secondary Building Units
SCs	Semiconductors
SCF	Solid Carbon Fiber
SCNSs	Semiconductor Nanostructures
SEM	Scanning Electron Microscope
SHE	Standard Hydrogen Electrode
SLNs	Solid Lipid Nanoparticles
SNPs	Silver Nanoparticles
SPE	Solid Phase Extraction
SPIONs	Superparamagnetic Iron-oxide Nanoparticles
SPR	Surface Plasmon Resonance
SQDs	Semiconductor Quantum Dots
SQUID	Superconducting Quantum Interference Device
ss-DNA	Single-stranded Deoxyribonucleic Acid
SS-NMR	Solid-state Nuclear Magnetic Resonance
STM	Scanning Tunneling Microscope
SWCNTs	Single-walled Carbon Nanotubes
TB	Tuberculosis
TEM	Transmission Electron Microscope
TFA	Trifluoroacetic Acid
TGA	Thermogravimetric Analysis
TMM	Total Magnetic Moment
TNase	Thermonuclease
TNP	Trinitrophenol
TNR	Titanium Nanorod
TNT	Trinitrotoluene
TNW	Titanium Nanowire
tRNA	Transfer Ribonucleic Acid
TYL	Tylosin

UV	Ultraviolet
VB	Valence Band
VOCs	Volatile Organic Compounds
VPc	Vanadium-phthalocyanine
WF	Week Ferromagnetic
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
ZFC	Zero Field Cooled
ZIF	Zeolite Imidazolate Framework
ZGNRs	Zigzag Graphene Nanoribbons

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CHAPTER 1

Semiconductor Nanostructures and Synthesis Techniques

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Abstract: Semiconductor nanostructures show different properties compared to their bulk counterparts due to quantum confinement effects and enhanced surface-to-volume ratio with the reduction in particle size on nanoscale dimensions. This chapter introduces the nanomaterials, especially semiconductor nanostructures of various morphologies, quantum nanostructures (quantum dots, quantum wires and quantum wells) along with conventional 3D nanostructures. The present time is the introductory era of nanoscience and nanotechnology; synthesis of highly monodisperse nanostructures for device applications is a challenge for researchers and technocrats. This chapter discusses at length fascinatingly the bottom-up and top-down synthesis approaches along with the commonly used nanomaterial synthesis techniques, such as mechanical milling, lithography, electrospinning, template synthesis, chemical precipitation, sol-gel method, hydrothermal/solvothermal method, laser ablation, and other vapour processing methods.

Keywords: Electrospinning, Lithography, Laser ablation, Milling, Sol-gel, Semiconductor nanostructures, Template synthesis, Vapour deposition techniques.

INTRODUCTION

In 1959, Nobel laureate Richard P. Feynman, in his famous talk “There is plenty of room at the bottom [1, 2]”, contemplated a remarkable technology on the scale of a few nanometers. This was the beginning of a new branch of science and technology, which nowadays is known as nanotechnology. The length of a nanometer can be understood through the example of ten hydrogen atoms lined up in a row, which is one nanometer (nm). Materials are defined as nanomaterials if their size or at least one dimension of the structure is in the range of 1 to 100 nm. Nanotechnology is an interdisciplinary paradigm, which conjoins diverse fields of science and engineering at the nanoscale. Numerous research disciplines like physics, chemistry, biotechnology, *etc*., and technology and industry sectors like

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information technology, energy, environmental science, medicine/medical instrumentation, homeland security, food safety, and transportation, among many others, are to be revolutionized by this interesting science. Many techniques which Feynman envisioned are now well-developed [3, 4]. Multifunctional nanomaterials and devices can behave in extremely different ways, and their physical and chemical properties change drastically if subjected to different external parameters, resulting in variations due to their large surface area to volume ratio and quantum size effect. Technological development in recent years has led to the development of crystalline materials with assured desired qualities, facilitating their applications in areas like electronics (optoelectronics), spintronics, medicine, superconductivity, nuclear and electron resonance, molecular structure investigation, photonics, photocatalysis and photovoltaics. Amongst these crystalline materials, semiconducting nanomaterials are of immense interest because their properties can be easily modified or improved through doping, thus enabling them to cover a wide range of promising applications. Semiconductor nanostructures form a class of materials with a large degree of freedom to design optoelectronic properties through variations in composition, size and dimensionality. Currently, semiconductor nanomaterials are still in the research phase; they are promising contributors to the development of technology in a disciplined manner, for instance, in lighting and displays, laser technology, telecommunication, quantum information processing and sensing. Scaling down feature sizes into the nanometer range is a common trend in advanced compound semiconductor devices, and the progress of nano-fabrication technology has opened up exciting possibilities for constructing novel quantum devices for which the operations are directly based on quantum mechanics. Size tunable physical and chemical properties of semiconductor nanocrystals make these materials very attractive both from a scientific view and optical device application aspect [5 - 11]. This was made possible by the availability of semiconducting materials of unusual purity and crystalline excellence. Such materials can be structured to contain a thin layer of highly mobile electrons. Motion perpendicular to the layer is quantized so that the electrons are confined to move in a single plane. This two-dimensional electron gas (2DEG) combines several required properties not shared by thin films. It has a low electron density, which may be readily varied by employing an electric field. The low density implies a large Fermi wavelength (typically 40 nm), comparable to the dimensions of the smallest structures (nanostructures) that can be fabricated today. Quantum transport is conveniently studied in a 2DEG because of the combination of a large Fermi wavelength and a large mean-free path. Quantum interference becomes more important as the dimensionality of the conductor is decreased [12]. The quantum confinement effects in low dimensional semiconductor systems were studied two decades ago with the stress on the optical properties, including absorption and luminescence [13, 14]. The confinement of an electron and a hole in nanocrystals significantly depends on the material properties, namely the exciton Bohr radius (a_B). For most of the commonly studied semiconductor nanostructures, such as ZnO, ZnS, CdS, CdSe, ZnSe, Cu_2O, SnO_2, TiO_2, Cu_2S, exciton Bohr radius values are less than 10 nm.

This chapter focuses on the basic understanding of semiconductor nanostructures and nanomaterial synthesis techniques. The target is to present upcoming and potentially leading nanomaterials and structures, highlighting various stages of their applications and synthetic methods. Most semiconducting materials, such as the II-VI or III-V compound semiconductors, show quantum confinement behaviour in the 1-20 nm size range. Size reduction affects most of the physical properties (structural, magnetic, optical, dielectric, thermal, *etc*.) due to surface effects, enhanced surface-to-volume ratio, and quantum size effects. Owing to the extremely small dimensions, these materials exhibit properties, which are fundamentally different from, and often superior to those of their conventional bulk counterparts. Optical spectroscopy, being the non-contact method, has proven to be the most suitable technique to monitor the size evolution of the electronic structure [15 - 18]. Due to morphology dependent properties of semiconductor nanostructures, it becomes much more important to understand different nanostructure morphologies and their synthesis.

SEMICONDUCTOR NANOSTRUCTURES

Electronic nanostructures include 2D materials, nanowires, and quantum-confined heterostructures, which reveal fascinating properties from traditional quantum transport to correlated effects, including spintronics.

The fabrication of nanostructures for quantum information is a flourishing field that looks to control electrons' degrees of freedom by local and wide-range interactions. In many cases of both optical and electronic nanostructures, surfaces and interfaces and their control play a significant role in deciding the nature of the properties.

Recently, there has been significant interest in the construction, characterization, and implementation of semiconductor nanoparticles that play a substantial role in numerous novel technologies. The conductivity of the semiconductor and its optical properties (absorption coefficient and refractive index) can be manipulated. Semiconductor nanomaterials and devices are still in the research stage, but they are promising for applications in many fields, such as solar cells, nanoscale electronic devices, light-emitting diodes, laser technology, waveguide, chemical and biosensors, packaging films, parts of automobiles, and catalysts.

CHAPTER 2

Photocatalytic and Sensing Applications of Semiconductor Nanostructures

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Abstract: Semiconductor Nanostructures (SCNSs) are of great interest due to their excellent optical and electronic properties. As a result of their unique properties, semiconductor nanostructures have found applications in several fields, including optoelectronics, solar energy conversion, photocatalysis, and sensing. SCNSs show promising prospects in photocatalytic and sensing applications. Photocatalytic application of SCNSs provides potential solutions for environmental remediation and energy generation. Several strategies have been developed to achieve high efficiency for photocatalytic processes using semiconductor nanostructures. Efforts have also been made to achieve high sensitivities in sensing applications using SCNSs. In the present chapter, the photocatalysis activity of semiconductor nanostructures has been discussed along with the photocatalytic mechanism and strategies for enhancing photocatalytic efficiency. Several applications of semiconductor photocatalysis in wastewater treatment, hydrogen production, and air purification are cited in recent literature. The sensing applications of semiconductor nanostructures have also been discussed, including their use as chemical sensors, gas sensors, and biosensors.

Keywords: Biosensors, Fluorescence sensors, Gas sensors, Photocatalysts, Photocatalytic efficiency, Semiconductor nanostructures.

INTRODUCTION

The semiconducting nanostructures (SCNSs) with sizes between 1 and 100 nm are particularly attractive in material science due to the quantum confinement effects, which attribute unique optical and electronic properties to these materials [1]. The unique properties attract researchers to investigate these materials for their broader applications in several fields, including optoelectronics, solar energy

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conversion, photocatalysis, and sensing [2, 3]. Semiconductors possess band structures that can be conveniently adjusted to improve their properties [4]. Photocatalytic application of SCNSs provides potential solutions for various energy and environment-related issues [5]. The increasing discharge of contaminants into freshwater systems from a wide variety of industrial, municipal, and agricultural sources has seriously affected water quality. These contaminants, including pharmaceuticals, pesticides, dyes, personal care products, and synthetic hormones, present adverse health effects [6]. Several conventional physical and chemical processes have been adopted for the removal of organic pollutants. However, these conventional techniques are not very effective and have some limitations. Many contaminants are recalcitrant and cannot be degraded by conventional methods resulting in their presence in treated wastewater. Moreover, many conventional processes can convert organic pollutants from one phase to another, which requires further treatment to avoid secondary pollution. Advanced oxidation processes (AOP) have been proposed for the efficient removal of toxic pollutants. The AOP processes involve the generation of hydroxyl or sulphate radicals in sufficient quantity to remove organic and inorganic pollutants [7]. Photocatalysis using semiconductor materials is one of the most promising advanced oxidation processes (AOPs) for the treatment of contaminated wastewater. It has been demonstrated recently that the photocatalytic degradation of organic pollutants from the water by semiconductors is a viable alternative to conventional methods [8]. SCNSs possess high degradation and mineralization efficiency, low toxicity, and low cost over other AOPs, such as electrochemical oxidation, ozonation, H_2O_2/UV oxidation, and biodegradation [9]. Their use as catalysts under photolytic conditions can potentially solve the serious environmental and energy-related crisis the world is facing today [10]. Hydrogen is renewable energy of high calorific value and clean, pollution-free fuel. Hydrogen production with the use of semiconductor nanostructures as photocatalyst is the most promising technology [11]. Visible light-driven photocatalysis for the production of hydrogen from H_2O, H_2S, and organic waste has attracted attention due to the depletion of fossil fuel reserves [2]. Semiconductor nanostructures can also contribute to reducing the carbon dioxide concentration in the air. Semiconductor nanostructures of n- and p-type can potentially convert carbon dioxide into hydrocarbons, such as methane and ethane [12]. Human health, environmental protection and safety require regular sensing and monitoring of pollutants, toxic substances, and gases in real samples. Semiconductor nanomaterials have aroused great interest as sensors. This is due to the many desirable features offered by them, including unique optical and electrical properties, excellent light stability, narrow emission spectrum, and wide excitation spectrum [13]. SCNSs are capable of forming sensitive, selective, and stable sensing platforms, achieving great performance in sensing applications.

PHOTOCATALYTIC ACTIVITY

General Photocatalytic Mechanism

The characteristics of a bulk semiconductor depend largely on the bandgap energy (Eg). The Eg is the minimum energy required to excite an electron from the ground state valence band (VB) into the vacant conduction band (CB). The type of light energy absorbed by the semiconductor material depends on the bandgap. The wide bandgap semiconductor materials ($TiO_{2,}$ ZnO) that absorb in the UV region pose a serious limitation [14]. They can absorb photons with light wavelengths shorter than 400 nm. This accounts for the loss of solar energy as UV radiations comprise only 5% of the total solar spectrum, whereas visible radiations comprise 45% of the total solar spectrum. To make maximum utilization of solar energy, various strategies have been adopted to synthesize visible-light-driven nanostructures [15]. Bandgap engineering is an efficient approach to developing visible-light-responsive photocatalysts [16]. Tuning the bandgap makes it possible to harvest maximum light energy and produce sufficient charge carriers, which are responsible for photoreduction and photooxidation in photocatalysis. The process of photocatalysis can be divided into three steps; (a) light absorption, (b) charge separation and transfer, and (c) surface reactions, which occur in sequence [17].

a. Upon sunlight irradiation, the photons with energy equal to or more than the optical band gap (*E*g) of the photocatalyst are absorbed and utilized for the generation of charge carriers. An electron in the valence band (VB) gets excited to the conduction band (CB) on the absorption of a photon. The negative electron and positive hole are mobilized with an electric field to generate the current. The electrostatically bonded electron-hole pair is named an exciton.
b. The generated charge carrier electrons (e^-) and holes (h^+) react with the surrounding oxygen and water molecules to form OH free radical ($OH^•$) with powerful oxidation strength. The photogenerated holes (h^+) in the valence band react with either H_2O or OH^- to produce the $OH^•$. The extremely reactive oxygen species thus formed transfer across the interface.
c. The transferred oxygen species are capable of destructive removal of adsorbed organic species on the semiconductor photocatalyst surface. The generated charge carriers can diffuse toward the surface of the photocatalyst particles. However, during this process, the electrons and holes tend to recombine either in bulk or on the surface of photocatalysts. The surviving photogenerated electrons and holes can reach the surface of particles and participate in the

CHAPTER 3

Titania Nanoparticles: Electronic, Surface and Morphological Modifications for Photocatalytic Removal of Pesticides and Polycyclic Aromatic Hydrocarbons

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Abstract: Tailoring the electronic, surface and morphological properties alter the catalytic properties of the material(s), specifically at the nanoscale. In the past years, a plethora of research has been reported to find sustainable and eco-friendly catalysts for environmental pollution remediation. In this direction, titania nanoparticles have been intensively explored to check their potential for photocatalytic removal of various pollutants. In the current scenario, where the growing population needs to feed on an everyday basis, abundant pesticides indiscriminately are being used to increase crop yield, thus causing environmental pollution and ecological imbalance. In order to remove these environmental pollutants along with the polycyclic aromatic hydrocarbons (PAHs) that are formed by incomplete combustion of crop residue or any other organic matter have been studied, and the results reported for these two categories of pollutants are summarized in this chapter.

Keywords: Pesticides, Photocatalysis, Polycyclic aromatic hydrocarbons (PAHs), Titania nanoparticles.

PRINCIPLE OF TIO$_2$ PHOTOCATALYSIS

Nanocrystalline TiO$_2$, an n-type semiconductor of bandgap energy (Eg) ~3.0-3.2 eV [*vs.* NHE (Normal Hydrogen Electrode)], has been widely studied [1 - 10] as a photocatalyst for the decomposition of environmental pollutants. It mainly exists in three crystal phases, namely, anatase, rutile, and brookite. Generally, TiO$_2$ having anatase (~70%) and rutile (~30%) phases exhibit higher photocatalytic activity (for degradation of pollutants) than any of these phases alone and is found

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in commercially available P25-TiO_2 (P25). Upon photo-irradiation of TiO_2 (Fig. **1**) under ultraviolet (UV) and/or visible (Vis.) light from sunlight or an illuminated light source having energy ≥ its Eg, electrons (e^-) in its valence band (VB) get excited to the conduction band (CB) resulting into the formation of the positively charged holes (h^+) in the VB and diffuse [1 - 3] to the surface from the bulk of the catalyst.

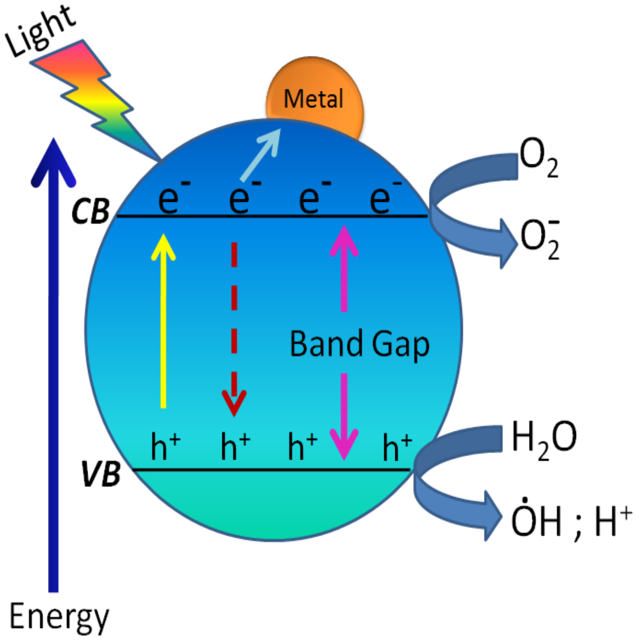

Fig. (1). Mechanism of photocatalysis.

The photogenerated h^+ having strong oxidizing power (+3.1 V *vs.* NHE) reacts with either adsorbed water molecules or other chemical species to form hydroxyl radicals or directly oxidizes [1 - 5] the molecules at the interface of TiO_2 and e^- in the CB (-0.5 to -1.5 V *vs.* NHE) participates for reduction processes that convert the adsorbed molecular oxygen to oxidative superoxide radical anions ($O_2^{\bullet-}$) or reduces [1 - 10] the substrate molecule. In the presence of metal deposited onto its surface, there is an enhancement in the recombination time between the excited charge carriers that further improve their respective oxidation/reduction abilities. There are indeed other good reasons for favoring TiO_2, which include strong oxidizing power, photogenerated e^- that reduces enough to produce superoxide from molecular oxygen, antibacterial activity, self-cleaning activity, cost-effective, chemically inert, and most importantly, its non-toxicity to living beings, favouring its use as a photocatalyst.

Influence of Metal Loading on Photocatalytic Performance of TiO_2

The photocatalytic activity of TiO_2 can be further improved by metal (M) loading and is frequently used for a variety of applications, *viz.*, in solar energy conversion, photocatalysis and electronic devices [1, 4, 5, 11]. These M-TiO_2 hybrid nanoparticles often exhibit noticeably different properties than the individual components due to separate electron and dielectric confinement in the TiO_2 and M parts, respectively [4, 5]. The photo-produced charge carriers in the TiO_2 can be transferred efficiently to the M part, resulting in the shifting of plasmon frequency and/or promotion of redox reactions by suppressing the recombination of excited charge species, as seen in Fig. (**1**). Another advantageous function of metal loading is comprehensible and incoherent interactions between M and TiO_2, leading to the broadening and extension of its absorbance spectra to the visible region [1, 2, 4, 5, 8]. Generally, noble metals (*e.g.*, Au, Ag, Ni, Cu, Pt, Rh, and Pd) with Fermi levels lower than TiO_2 should have been deposited on its surface for enhanced charge separation [1, 4, 5, 8], which is advantageous compared to other photosensitized systems because of its relatively more stability in an aerated atmosphere [1]. Therefore, these M-TiO_2 composites have been utilized for the photodegradation/decomposition of toxic organic pollutants, such as for the wastewater treatment and removals of other pollutants, such as dyes [1 - 6, 8 - 10], dehydrogenation of alcohols [12, 13], reduction of pharmaceutically important nitro compounds [14 - 16], degradation of polycyclic aromatic hydrocarbons (PAHs) [17 - 29] and other heteroatom-containing organic molecules, such as pesticides [30 - 55].

Role of Non-Metal Loading on Photocatalytic Activity of TiO_2

One of the major reasons for loading the TiO_2 nanoparticles with a non-metal dopant is to narrow down its E_g [56]. Initially, a non-metal dopant, such as nitrogen, that has an energy level slightly higher than that of oxygen, is introduced into the lattice of TiO_2, and the generation of a mid-gap energy level takes place [57, 58]. Upon irradiation with suitable light energy, the excitation of charge carriers takes from this newly created energy state rather than the VB of TiO_2. It means the E_g is now lower than before the loading with non-metal. This excited electron then shifts to the CB, creating a hole in the mid-way energy state. Afterward, the charge carriers thus generated migrate to the surface of nanoparticles, where they participate in the redox reactions. Apart from nitrogen, other non-metal dopants, such as boron, carbon, and sulphur, have also been studied and found [59] to impart a similar role except for the position of energy level created, which is different from that created by nitrogen.

CHAPTER 4

Antimicrobial Properties of Semiconductor Nanoparticles

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Abstract: Several metals have been reported to possess antimicrobial properties. Out of these metal nanoparticles, some semiconductor nanoparticles are expectant solutions to the pathogenic activities of microorganisms. Many studies have proved that these nano-sized particles are effective against several Gram-positive as well as Gram-negative pathogenic bacteria. Different types of nanoparticles are synthesized from different metals, and according to their size, they show effective responses against the target microorganisms. The exact mechanism of the antimicrobial effect has not been confirmed, but some supposed methods have been described. These particles also help to decrease antibiotic pollution as the hefty use of antibiotics can bring drastic changes in the environment and livings beings in the form of side effects.

Keywords: Antibiotic pollution, Gram-positive bacteria, Gram-negative pathogens, Nanoparticles, Semiconductor nanoparticles.

INTRODUCTION

Antibiotic pollution reforms the pathogenic microorganisms through which they alter their resistivity against antibiotics to cause incurable diseases. Therefore, it is a need of the hour to explore alternative treatment ways to deal with these bacteria to lessen the side effects. Nanoparticles have become a promising solution to this problem. Nano-technology is an advanced technology that has become the first choice of researchers. Many studies proved that semiconductor nanoparticles might be used as the best alternative to treat pathogens. Semiconductor nanoparticles are generally crystalline solids that lie between conductor and insulator due to their structure. Metals are well-known solids for their antimicrobial activities. In Indian culture, silver, zinc and copper have been used for centuries [1]. A drastic improvement in the optical and electrical properties of these nanostructured materials has been reported that depends on the size and

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shape of the nanoparticles. This is due to the confinement of the charge carriers in the narrow space of the nano-crystals [2]. Although the exact mechanisms for the antimicrobial properties of these metal nanoparticles are still under investigation, two popularly proposed mechanisms for the antimicrobial properties are: (a) free metal ion toxicity arising from the dissolution of the metals from the surface of the nanoparticles and (b) oxidative stress *via* the generation of reactive oxygen species (ROS) on surfaces of the nanoparticles. Besides the nano nature of these metal particles, the morphological and physicochemical properties of these nanoparticles play a significant role in enhancing their antimicrobial activities. Bactericidal properties of nanoparticles are associated with size in such a way that the smaller the nanoparticles are, the higher the bactericidal potential. Since metals have a strong tendency to donate the electron, hence are positively charged, which facilitates their binding to the negatively charged cell surface leading to an enhanced bactericidal effect.

A significant number of metals, such as silver, copper, gold, titanium, and zinc, have been accounted as bactericidal agents for centuries with wide properties and spectra of activity [3]. Different foods and daily use commodities, such as toothpaste, are now composed of powdered zinc citrate or acetate to combat dental plaque [4]. Titanium oxide has been used as a whiting agent in toothpaste for a long time [5]. Since zinc is an essential micronutrient required by the human body, zinc oxide (ZnO) has been treated as an important inorganic semiconductor material due to its GRAS (generally regarded as safe) status, high thermal and photostability, oxidation resistivity along with high electron mobility [6]. Zinc oxide nanoparticles are easy to synthesize, biologically safe, compatible with biological tissues as well as environment-friendly [7]. Hence, ZnO nanoparticles have been exploited for their wide application in different fields (Fig. **1**), such as biological sensing, gene delivery, drug delivery, wound dressing material, and antifungal and antibacterial activities [8, 9]. Along with all the above-mentioned properties of ZnO nanoparticles, these are quite cheap and readily available. ZnO nanoparticles exhibit morphological versatility, such as nanorods, nanoflowers, nanospheres, nanotubes, *etc.* and are more influential on rheological parameters [10]. The morphology and texture of these nanomaterials are significantly controlled by the organic components used during the synthesis process [11]. Besides the biological uses, ZnO semi-conductor nano-material also possesses photocatalytic properties that lead to use their great potential for decontamination of organic compounds in water along with associated environmentally friendly ease and complete mineralization of pollutants. Similarly, other semi-conductor photocatalysts have recently reported high photocatalytic activity for decontamination. Silver nanoparticles may also combine with semi-conductor material, leading to the separation of charges and producing more photo-generated charges. Heterogeneous hybrid systems have also been developed as compelling methodologies for the decontamination of aqueous solutions containing non-biodegradable compounds.

ANTIBIOTIC POLLUTION

Antibiotic pollution is a deadly threat to humans and the environment due to its hazardous consequences (Fig. **2**). The massive use of antibiotics and their improper disposal is a major cause of antibiotic pollution. This leads to an upsurge in antibiotic-resistant microorganisms. Incurable diseases are on the rise due to antibiotic waste, which leads to the development of antibiotic resistance among pathogenic microorganisms. Therefore, it is necessary to combat this pollution. Researchers find many different ways to tackle this pollution by targeting the pathogens which become resistant to the medicine. Many studies have been conducted to find an effective way to fight and degrade these microorganisms.

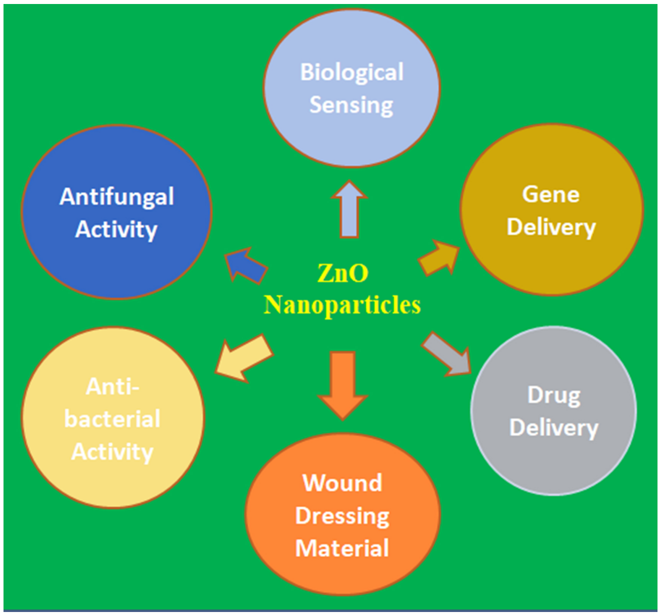

Fig. (1). Biological uses of ZnO nanoparticles.

NANOPARTICLES

Nanoparticles (NPs) are small materials with sizes ranging from 1 to 100 nm. Due to their high surface area to volume ratio and nano-scale size, they have unique chemical and physical properties compared to their bulk counterparts. Generally, the size, structure and shape of these particles have a great influence on their

CHAPTER 5

Metal-Organic Frameworks: Synthesis, Characterization, and Applications

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Abstract: Metal-organic frameworks (MOFs) are structurally complex structures constructed from inorganic and organic components. MOFs are highly ordered porous structures with special characteristics, such as high thermal stability, tunable surface properties, and large surface area. The MOFs demonstrate a wider range of potential applications in adsorption, gas storage, catalysis, drug delivery and sensing. As a result, the research in the area of MOFs is experiencing rapid growth. Considering the promising prospects of MOFs, this chapter presents an overview of the general synthesis and characterization methods for MOFs. Besides, the applications of MOFs in adsorption, sensing, and catalysis are also highlighted.

Keywords: Adsorbent, Catalyst, Characterization, Electrochemical, Mechanochemical, Microwave, Solvothermal, Sonochemical, Sensors.

INTRODUCTION

Metal-organic frameworks (MOFs) are an evolving group of crystalline porous substances comprising 3D structures containing metal ions that are coordinated by organic linkers [1, 2]. Multidentate organic ligands containing O or N donors (such as carboxylates, azoles, and nitriles) are employed as linkers to provide linkage sites with metal clusters (Fig. **1**) [3]. The characteristic properties of the MOFs network are reflected by metal ions as well as linkers. Moreover, solvent, pH, ligand metal ratio and temperature can influence the structural characteristics of the synthesized framework [4]. They can offer tunable pores with a precise dimensional distribution, arbitrary characteristics, reduced density, and regulable chemical affinities for unique applications like magnetism and luminescence [2]. MOFs have earned much consideration owing to their excellent characteristics,

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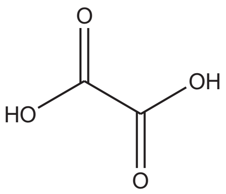
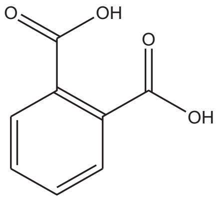
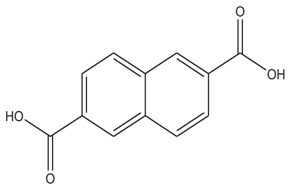
such as high thermal stability, tunable surface properties, and larger surface area than other classical porous materials (like silica and zeolites) [5, 6]. All these characteristics make them desirable materials for gas storage, separation, catalysis, adsorption, and drug delivery [7 - 10]. The elegance of chemical structures and the strength of both organic and inorganic chemistry are epitomized by MOFs; two disciplines sometimes considered contrasting.



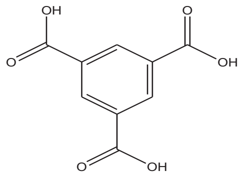
Ethane 1,2-dioic acid



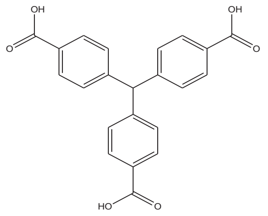
Benzene 1,2-dicarboxylic acid



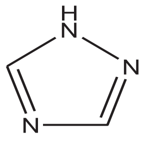
Napthalene-2,6-dicarboxylic acid



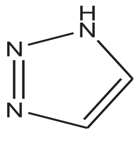
Benzene 1,3,5-tricarboxylic acid



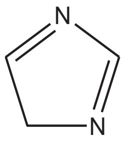
4,4',4"-Methanetriyltribenzoic acid



1H-1,2,3-triazole

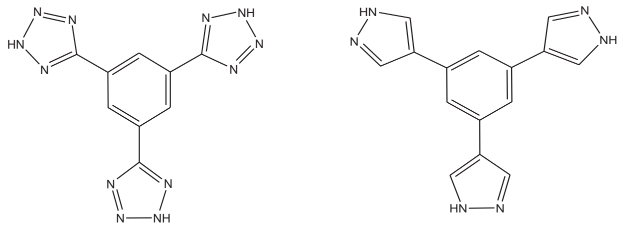


4H-imidazole



1,2,4-Triazole

(Fig. 1) contd.....



1,3,5-tris(2H-tetrazol-5-yl)benzene

4,4',4''-Benzene-1,3,5-triyltris(1H-pyrazole)

Fig. (1). Some common organic linkers used in MOF synthesis.

This field of chemistry has expanded almost incomparably since the 1990s, not only because of the large number of published research articles but also due to the growing scope of these investigations. Since the field of MOF is very broad, this chapter emphasizes the typical methods for synthesizing and characterizing these materials. The present chapter also covers the applications of MOFs in adsorption, sensing, separation, and catalysis.

SYNTHETIC METHODS FOR MOFS

A lot of attention has been paid to the synthetic methods used for MOFs because they have a wide range of interesting and variable structures that may also be of huge interest in a number of applications in several fields relevant to porous materials. The main objective of MOF synthesis is to create favourable synthetic conditions, leading to established inorganic building blocks without the deterioration of the linkers. At the same time, the kinetics of crystallization should be sufficient to permit nucleation and proper growth of the desired phase. Several synthesis methods have been reported to date, including but not limited to solvothermal, microwave, electrochemical, mechanochemical, and sonochemical (Fig. **2**) methods. Table **1** summarizes the representative MOFs synthesized by different synthetic methods.

Table 1. Different synthetic methods for MOFs.

Order	**Name of MOF**	**Metal/Metal salt**	**Organic linker**	**Synthetic method**	**Refs**
1	Amino-MIL-53(Al)	Aluminium chloride hydrate	Terephthalic acid	Solvothermal	[16]
2	Zr-MOF, UiO-66	$ZrCl_4$	Terephthalic acid	Solvothermal	[17]

CHAPTER 6

Nanostructure Impregnated MOFs for Photocatalytic and Sensing Applications

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Abstract: Metal-organic frameworks (MOFs), due to their high porosity, enhanced surface area, rich topology, diverse structures and controllable chemical structures, have recently emerged as an exciting class of porous crystalline materials. The integration of nanostructures with MOFs generates MOF composites with synergistic properties and functions, attracting the broad application prospect. In this chapter, the primary strategies guiding the design of these materials, including MOFs, are described as host materials that contain and stabilize guest nanoparticles. A detailed discussion about the recent progress of nanostructure-impregnated MOFs based on diverse photocatalytic (*e.g*., environmental remediation, oxidation of alcohols, CO_2 reduction, and H_2 generation) and sensing (organic pollutants, gaseous pollutants, and heavy metal ions) applications has been provided. With a deeper knowledge of nanostructure-impregnated MOFs, this book chapter will provide better guidance for the rational design of high-performance MOF-based materials and is likely to shed new light on future research in this promising field.

Keywords: Composites, Environmental remediation, Metal-organic frameworks (MOFs), Porous material, Photocatalysis, Sensing.

INTRODUCTION

Nanotechnology refers to a multi-disciplinary area in which the structure of materials is modified at the nanometer scale through chemical, physical, and biological paths. Nano-structured materials are materials that have at least one dimension in the nanoscale range (1-100 nm), or their basic units are in a three-dimensional space. Compared with conventional materials, nanomaterials are

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garnering a lot of attention in the scientific community because of their amazing properties (*e.g*., small size, large surface area to volume ratio, high surface reactivity, adaptive surface functionalities, short diffusion, high sensitivity, quantum confinement, and compactness) [1]. With the advancements in nanotechnology, nanomaterials have been recognized as an excellent potential candidate in various fields owing to their size-dependent properties and high chemical, thermal, mechanical, optical, electrical, and biological properties. They have been extensively studied in diverse fields, such as photocatalytic, adsorption, sensing, medicine and health, aerospace, energy resources, environment, biotechnology, *etc*. The exploitation of nanostructured materials has led to fundamental changes in analytical sciences during the past few decades [2].

Recently, metal-organic frameworks (MOFs), a novel type of porous crystalline compounds, have sparked a lot of curiosity due to their plethora of advantages (*e.g*., ultrahigh porosity and surface area, fully exposed active sites, uniform but tunable pores, plentiful compositions, and tunable morphologies), which makes them extremely useful in a variety of applications [3]. The structure of MOF can be tuned according to targeted properties by converting the geometry of the metal ions or clusters and multifunctional organic linkers, which are put together with the help of well-defined coordination linkages. For many advanced applications in nanotechnology, it is mandatory that the MOF must be impregnated with nanostructured materials. Through the integration of diverse building blocks, the impregnation of nanostructured materials within MOF has been pursued to develop new multifunctional composites/hybrids that demonstrate advantages of all of them that are superior to those of the individual components.

In this chapter, efforts were made to emphasize the promising applications of nanostructured impregnated MOF materials for photocatalytic (removal of environmental pollutants, CO_2 reduction, the hydrogen evolution reaction (HER), and organic photo-redox reactions) and target-specific sensing (organic pollutants sensing, gaseous pollutants sensing, and heavy metal ions sensing). A few reports concerning the investigation of such composites for photocatalytic and sensing applications have appeared, but there is still plenty of scope for improvement and optimization. Finally, the bottlenecks and perspectives for future work on nanostructured impregnated MOF materials in this highly significant area are critically proposed. Our purpose is to encourage the attention of researchers toward the application of nanostructure-impregnated MOF materials and thus further promote their development.

SYNTHESIS OF NANOSTRUCTURED IMPREGNATED MOFS

Due to their unique functional and structural features, MOFs are now recognized as a key category of porous compounds. These frameworks are fabricated by bridging organic linkers and metal ions or their clusters. The chosen primary building blocks are another important element playing a vital role in the final structure and properties of MOFs. Nonetheless, various additional synthetic processes and parameters, such as pressure, pH, temperature, reaction time, and solvent, must be taken into account. The "ship in bottle" strategy, "bottle around ship" approach, and one-step synthesis approach are three important proven approaches for immobilizing functional nanoscale objects inside the pores of MOFs. The "ship in bottle" method combines the encapsulation of MOF cavities with active small molecules or nanoparticle (NPs) precursors, followed by further processing to provide the desired functional structure (Fig. **1a**) [4]. Various methods have been used to incorporate NP precursors into MOFs, such as vapor deposition, solution infiltration, and solid grinding [5, 6]. However, it is quite difficult to precisely manage the structure, composition, location, and morphology of integrated guests using this synthetic technique.

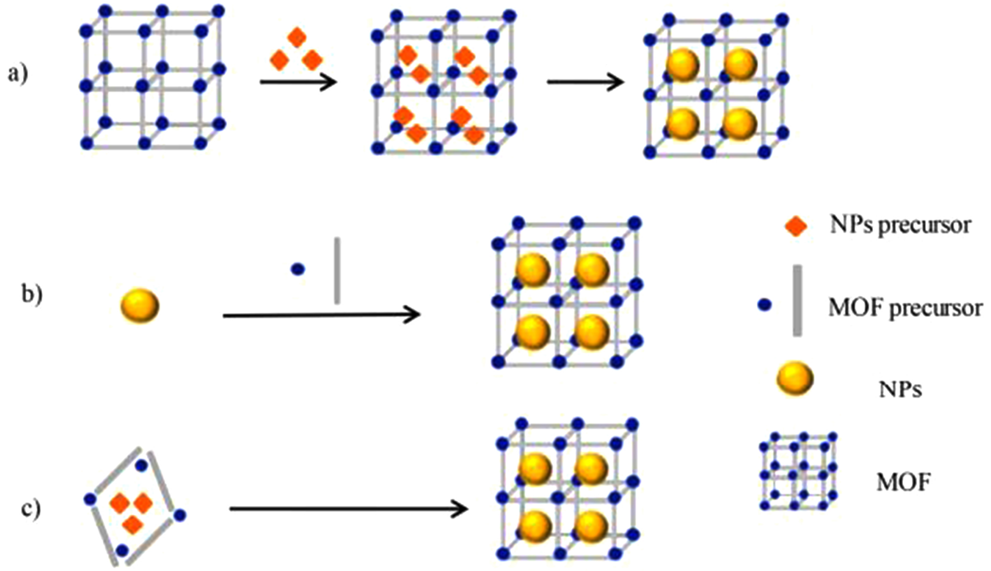

Fig. (1). Main approaches for the fabrication of nanostructure-impregnated MOF composites **(a)** Ship in the bottle; **(b)** bottle around the ship; and **(c)** in situ one-step synthesis [4].

In addition, the development of precursors and products on the exterior surface of MOFs must be taken into account. To prevent NPs accumulation on the exterior surface of MOFs, a double-solvent method (DSM) was successfully devised to

CHAPTER 7

Metal-Organic Frame Works (MOFs) for Smart Applications

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Abstract: Metal-organic framework (MOF) is a class of materials, which is formed by combining metal/inorganic and organic linkers, resulting in the formation of a framework with high surface area and permanent porosity. The freedom to vary inorganic and organic linkers stimulated the synthesis of thousands of MOF structures, for their utility in various applications. The presence of high porosity, high surface area and high free volume made these materials a perfect choice among the class of solid adsorbents. The metal nodes, tunable pore, versatile structure and functionalized surface allow various types of chemical interactions, *viz*. electrostatic interactions, π complexation, H-bonding, coordination bonding, van der Waals interactions, hydrophobic/hydrophilic interactions. All these features made MOF a customizable material to be utilized for targeted applications. This chapter involves a discussion about the usage of versatile MOFs in smart applications, such as gas storage, gas separation and drug delivery, along with a brief discussion about the synthesis of MOFs.

Keywords: Alkane separation, Carbon dioxide storage, Drug delivery, Gas storage, Gas separation, Hydrogen storage, Methane storage, Molecular building approach, Membrane, Nano synthesis, Porous coordination framework, Reticular chemistry, Toxic gas storage.

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INTRODUCTION

Coordination compounds engulf the class of materials formed by the uni-dimensional or cross-linked array of repeating units, to give macrostructures of various fashions [1]. As a subclass of coordination polymers, metalorganic framework (MOF) represents a class of compounds having inorganic clusters integrated with organic units, leading in the formation of a crystalline network with high porosity and surface area [2]. MOF possesses very high porosity with ~90% free volume, a high surface area of ~7000 m^2/g, and low densities of ~0.13 g cm^{-3} [3]. MOFs might resemble to sponge but they differ from sponge form in the aspect that MOFs have uniform, programmable, controllable pores, which can be used and altered as per desired functionality.

The reticular synthesis is responsible for the creation of strong bonds between organic-inorganic counterparts. By choosing a desirable metal-organic linker combination, the properties of MOF can be tailored as per desire, which is the driving force backing the hot market of MOF in present times. This field experienced unprecedented growth compared to any other field, as a result, vast literature is available on this class of material [4].

The presence of permanent and tunable porosity, functionally alterable surface and high surface area worked as key features for the exploitation of MOFs in gas storage [5], as good quality adsorbents [6], catalysis [7], biomedical imaging [8], drug delivery [9], optoelectronics [10], *etc.*, as shown in Fig. (**1**). Apart from the experimental work, a plentiful interest is also shown by computational researchers in predicting the new MOFs for modifying the properties/performance of currently existing systems. Having a customized MOF is not the ultimate goal, the designed MOF should be chemically, mechanically and thermally stable to withstand the conditions encountered during practical exploitation. Different applications demand a different type of stability of MOF, such as the need of tolerable mechanical stability for electrocatalysis. Metal nodes in MOF are chemically weak points,which poses serious concerns about the chemical stability of MOF. Moreover, weak node-linker bonds are prone to thermal degradation and hydrothermal instability of framework. The boon of porosity in MOF is actually the bane in the context of its mechanical stability, which is detrimental to the palletization process at the application stage. The stability of MOF is judged by variation in properties (structure, surface area or adsorption isotherm) upon exposure to such an environment. So, it can be stated that key features of MOFs may somehow invite some sort of instability in the structure. However, these factors did not create any serious dents on the popularity and employability of MOFs and great attention is also devoted to addressing the stability issues in MOFs. Several measures, like the presence of anionic or nitrogen-containing linkers, absence of polar groups or small apertures, catenation, strong metal-oxyanion bonds, less or no defects, metal centres with high valency *etc.*, are found to be helpful in gaining reasonable chemical, thermal and hydrothermal stability in MOF structures [3]. The pore size, functionality, metal centre and its environment are all customizable, which makes it an interesting playground for researchers. The interesting features of pores are observed in the form of the breathing effect and gate phenomenon, which are the result of the ability of pores to change their dimensions without rupturing the chemical bonds [11].

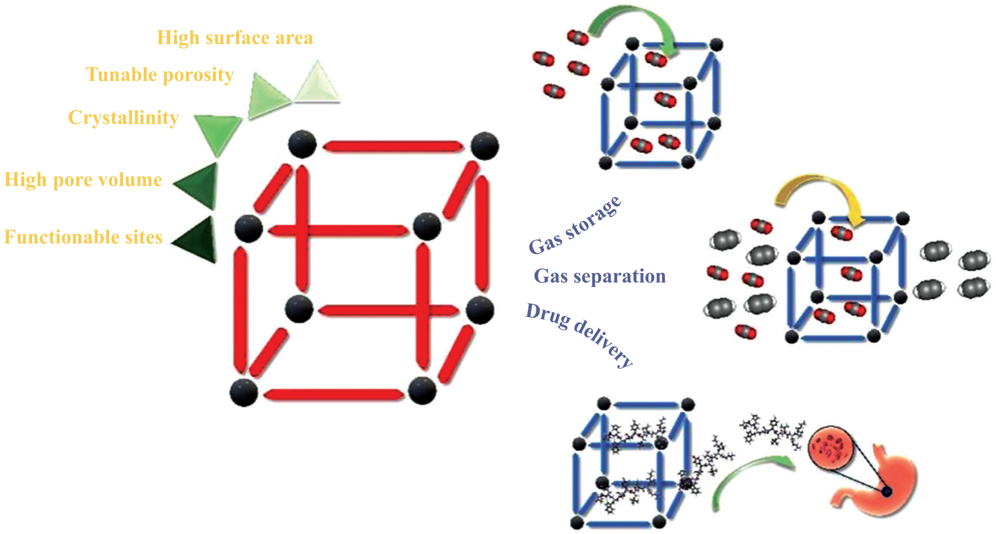

Fig. (1). A diagram representing general properties of MOFs for their application in gas storage, gas separation and drug delivery, discussed in the chapter.

Among porous solid adsorbents, zeolites have also been extensively explored owing to their high surface area and enough active sites available for chemical interactions. These were found to be reducing the power consumption compared to the conventional distillation process. The ability to synthesize zeolites as powder as well as membrane posed them as a good choice for gas storage and separation applications. Zeolites also provide uniform pore distribution, but less room for chemical tailoring to modify or customize it, as in the case of MOFs. On the other hand, MOFs were found to be exhibiting higher surface area than zeolites, holding the position of most porous materials known to date. The presence of metal nodes directly in the framework enhances the chemical interactions to a bigger extent. MOFs outperformed zeolites in selectivity, regeneration, reusability and cost. Moreover, structural versatility and pore tuning are more feasible in MOFs as compared to zeolites, which resulted in a sudden shift of research interest from later to the former [12 - 14].

CHAPTER 8

Understanding Synthesis and Characterization of Oxide Semiconductor Nanostructures through the Example of Nanostructured Nickel Doped Hematite

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Abstract: Hematite is an n-type semiconductor, and its semiconducting properties can further be improved by nano-structuring and doping. In several optoelectronic devices, such as thermoelectric and solar cells, both n- and p-type semiconductors are required. The p-type hematite can be synthesized by doping cations, such as Ni^{2+}, Mg^{2+}, Cu^{2+}, and Mn^{2+}. Furthermore, hematite is a weak ferromagnetic material, and its magnetic properties vary with the size of nanoparticles, doping of cations as well as doping concentration. This chapter discusses various properties of nanostructured nickel-doped hematite. As nickel is a ferromagnetic divalent dopant with a high magnetic moment, its doping in hematite together with nano-structuring shows a large variation in both electrical and magnetic properties in nickel.

Keywords: Hematite, Magnetic behaviour, Nano-structuring, Nickel doped.

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INTRODUCTION

Hematite (Fe_2O_3) is one of the most abundant materials on the earth's surface. In it, the iron atom has four unpaired electrons in its 3d orbital; therefore, it exhibits a strong magnetic moment. Furthermore, the crystals of hematite show different magnetic states with variations in temperature. At room temperature, the spins are canted at a small angle with the c-axis of hematite, due to which a net magnetic moment arises. Therefore, it behaves as a weak ferromagnetic (WF) material. However, as the temperature increases, the randomness in the orientation of spins increases. As a consequence, above Neel temperature ~ 950 K, the net magnetic moment becomes zero, and, in turn, it behaves as a paramagnetic material. When the temperature goes down to ~265 K (Morin temperature of bulk hematite), the basal spin plane (111) gets reoriented and aligns in an exactly antiparallel configuration along the axis of the electric field gradient, giving a zero net magnetic moment again, and, in turn, it attains antiferromagnetic (AF) state [1, 2].

The net magnetization of the bulk material, in the absence of an applied external magnetic field, is less than the vector sum of the magnetic moment of the individual atoms. This is because the bulk material contains domains whose magnetic moments may not be aligned in the same direction, consequently leading to reduced magnetization. Furthermore, the magnetic behaviour of hematite depends on crystallinity, particle size, morphology, nature and concentration of the dopant [1, 3, 4].

Hematite is widely used in technical applications like pigmentation, ceramics, wastewater treatment, photocatalyst, solar cells, gas sensors, lithium-ion batteries, thermoelectric devices [5 - 14], etc. Moreover, solar cells and photocatalytic applications need a material with a high absorption coefficient in a wide spectral range of absorption. The hematite is an n-type semiconductor exhibiting both direct (2.7eV) and indirect (2eV) bandgaps [15, 16].

Furthermore, nanostructures provide considerably different magnetic properties in comparison to their bulk counterpart due to their high surface-to-volume ratio and different crystal structure. Among magnetic nanoparticles, mainly iron oxides, *e.g.*, tetragonal maghemite and hexagonal hematite, are used in biomedical applications, such as *in-vivo* analysis. These are non-toxic and naturally found in many biological systems. Nanoparticles of 10-50 nm size with nearly uniform size distribution are preferred for these applications. Metallic magnetic nanoparticles like Co, Fe and Ni are toxic to human bodies [17].

This chapter discusses the effect of nickel doping on the properties of nanostructured hematite. Due to its ferromagnetic nature, it significantly affects magnetic behaviour and also alters other properties of hematite, like electrical and optical properties.

SYNTHESIS PROCESS

The nickel-doped hematite nanoparticles have been synthesized using the facile wet chemical method. For this, the ferric nitrate nonahydrate and nickel nitrate hexahydrate precursors were dissolved separately in the ethanol. The oxalic acid (taken equal to nickel and iron gram equivalent weights) was taken as a chelating agent. Nickel nitrate hexahydrate was used according to [Ni/(Ni+Fe)], *i.e.*, 0, 1, 2 and 4 wt% of nickel content. Finally, all solutions were mixed via continuous stirring to get a homogeneous solution and dried subsequently at 70°C to make flakes, and after grinding, a fine powder was formed. The final product formed was in the form of oxalate, which was then calcined at 600°C to obtain nanoparticles of pure and nickel-doped hematite. The crystallite sizes calculated using the Scherer formula, $d= k\lambda/\beta\cos\theta$, were 44, 47, 43 and 40 nm for 0, 1, 2, and 4 wt% nickel contents, where 'd' is crystallite size, 'k' shape factor, 'λ'X- ray wavelength, 'β' full width half maximum of diffraction peak and 'θ' is the Bragg's angle [1, 18].

PROPERTIES

Structural Properties

The formation of nickel-doped hematite (JCPDS # 86-0550) and nickel ferrite (JCPDS # 74-1913) phase by the wet chemical method was verified by the XRD pattern, as shown in Fig. (**1a**). Hematite has the same structure as corundum, Al_2O_3, with hexagonal or rhombohedral unit cells. The cell parameters of pure hematite were for a and b= 5.021 Å, c=13.620 Å and the volume of the cell was 297.3 Å^3 [18]. The average crystallite size values measured with the help of the Scherer formula from Fig. (**1a**) were 44, 47, 43 and 40 nm for 0, 1, 2 and 4 wt % nickel, respectively. In the case of bulk hematite synthesized by thermal decomposition of Fe and Ni oxinates at 700 °C in the presence of air, it was found that nickel doping decreased the cell parameters, though the ionic radius of Ni^{2+}cation (0.69 Å) was larger than Fe^{3+}cation (0.64 Å) [2]. However, in the case of nanostructured hematite synthesized by the facile wet chemical method, the cell parameters and cell volume increased continuously with the increase in nickel content. The morphology of nanostructured hematite synthesized by the wet chemical method, as shown in Fig. (**1**), looks like the clusters of closely packed nanorods oriented in different directions.

CHAPTER 9

Nanostructures for Cosmetics and Medicine

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Abstract: The application of various nanoparticles and nanotechnology in cosmetics and pharmaceuticals is an interesting area of research and development. The use of nanotechnology has also emerged as an important tool for gene manipulations, diagnosis of several diseases along with improvement in treatment efficacy. This chapter has emphasized the use of nano-materials in cosmetics and pharmaceuticals globally with associated legislation in different countries. More than 100 different products have been listed and discussed with their uses in different fields along with associated concerns.

Keywords: Nanotechnology, Nano-carriers, Nano-cosmetics, Nano-pharmaceuticals.

INTRODUCTION

Nanotechnology is recognized as the most promising technology of the twenty-first century, and it is expected to be a major boon to science, where atoms are manipulated at the nanometer scale (1nm=10^{-9}m). Nanotechnology creates new legislative structures; they demonstrate the various behaviours and features of previously recognized materials [1]. Nanotechnology is made up of two words: technology and the Greek number "nano," which signifies dwarf in Greek. As a result, nanotechnology is defined as the science and technology used to improve or utilize particles with a diameter of 1 to 100 nanometers [2]. The Egyptians, Greeks, and Romans all recorded the practice of nanotechnology throughout the 4000 BC era, with the concept of hair dye processing using nanotechnology. Nanotechnology has risen to prominence in a number of scientific domains over the previous decade. Meanwhile, from 1959, nanotechnology developed in several sectors, such as engineering, physics, chemistry, biology, and science, and approximately 40 years later, it has infiltrated the domains of cosmetics, health products, and dermal necessities, as shown in Fig. (**1**) [3].

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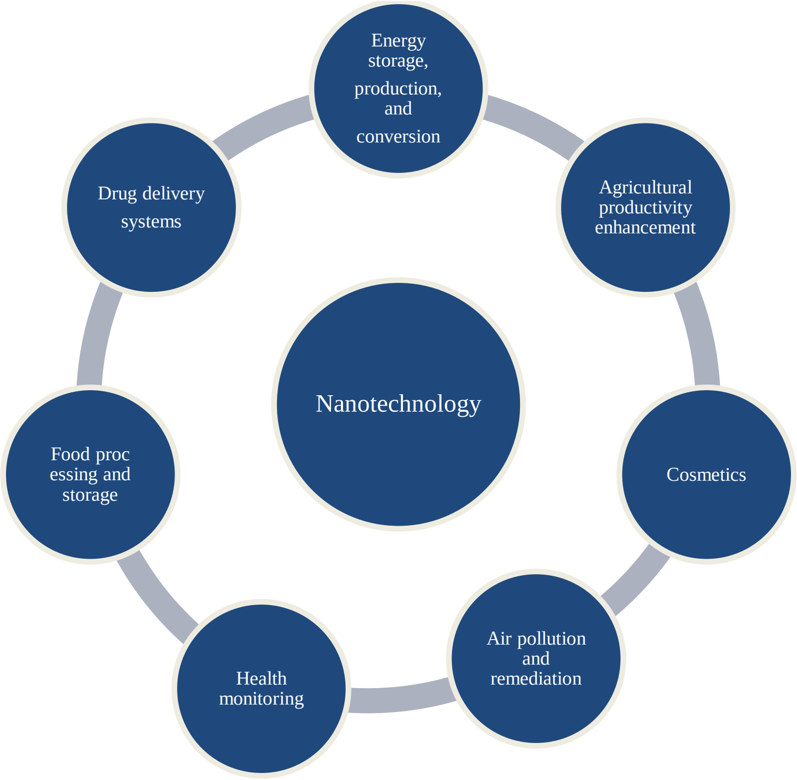

Fig. (1). Applications of nanotechnology in different fields.

Nanotechnology is progressively introduced into our everyday existence and is employed as a raw material in cosmetics and pharmaceutical goods, as well as in the packaging industry [4]. Nanotechnology also emerges as a vector in gene manipulation, diagnosis and anticancer treatments. The technology acts as an adjuvant in the formulations of antimicrobials and vaccines. This plays a significant part in the progress and designing of new tools and analytical instruments [5]. The *National Science Foundation* evaluates that nanotechnology reached the global economy by about $ 1 trillion in 2015, demanding around two million employees. In the United States of America, the European Union and Japan, developments in the field of nanotechnology are on the highest level, investing about a billion dollars per year and symbolizing more than half of the world's reserves. Countries like Russia, China, India, and Brazil, on the other hand, have made significant investments in nanotechnology in recent years. Between 2001 and 2006, the Brazilian government invested $ 140 million in nanotechnology research networks and projects [6].

THE ROLE OF NANOMATERIALS IN COSMETICS

Nanotechnology is one of the most rapidly advancing scientific topics nowadays. Nanotechnology products have become common in our daily lives. Supervisory agencies, on the other hand, have yet to agree on a unified definition for nanomaterials and nanotechnology. As a result, each country has its own definitions and legislation for regulating nanomaterials-containing items. As these materials are relatively new, there is no long-term research on their impact on human health and the environment [7]. Subsequently, countries regulate the amount of nanomaterials in cosmetics, allowing consumers to choose between products that include or do not contain nano-materials. As a result, the primary goal of this research was to identify the most commonly used nanomaterials in cosmetics and determine whether these formulations are in violation of laws in force in the United States, the European Union, and Brazil, thereby determining whether cosmetics on the market are compliant with these three economic powers' laws. This research is unique, and it will contribute to a broader discussion of existing rules governing the use of nanotechnology in cosmetics [6]. In 1995, *Lancôme,* the luxury division of *L'Oréal,* was the first company to introduce a nanotechnology-based cosmetic, with the launch of a face cream composed of nano-capsules of pure Vitamin E to combat skin aging [8]. In the meantime, companies, such as Christian Dior, Anna Pegova, Procter & Gamble, Estee Lauder, Dermazone Solution, Johnsons & Johnsons, Skinceuticals, Shiseido, Garnier, Chanel, and Revlon, developed products in this track [6]. Other international companies started to finance research to develop nano-cosmetics. The first company to develop and market a nano-cosmetic in Brazil was *O Boticário.* Nano-serum, an anti-aging lotion for the eyes, forehead, and around the mouth, was developed by the company. The nanostructure work includes active ingredients, such as vitamins A, C, and K, as well as a whitening substance. The technology developed in collaboration with the French laboratory Comucel and cost $ 14 million is part of the active range, which was introduced in 2005 [6]. VitActive Nano-peeling Renovator Microdermabrasion, a functional nanotechnology-based anti-aging cosmetic, was introduced in 2007. During these days, lift serum anti-aging and anti-aging 65+ advanced systems were introduced. At the same time, Natura released “Brumas de Leite,” a body hydration product containing particles that are approximately 150 nanometers in size. It also introduced the “Refreshing Body Spray” to the male public in the same year [8].

Nano-cosmetic purposes products, which are anticipated for use on the face and body skin, with anti-aging and light protection properties, are capable of penetrating the deep layers of the skin and potentiating the active ingredients [6]. Fronza and their collaborators defined nano-cosmetic as “comparing with the traditional products, a cosmetic preparation that contains actives or other

CHAPTER 10

Nano-cosmetics and Nano-medicines

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Abstract: In today's fast-moving scenario, nanotechnology has already spread its wings to nanocosmetics and nanomedicines due to the wide range of physical and chemical properties associated with nanoparticles. Different types of nanoparticles, like nanoliposomes, fullerenes, solid lipid nanoparticles *etc.*, have made their entrance into the nanocosmetic industry. However, the safety concern of nanoparticles has forced the cosmetic industry to limit their applications. The pharmaceutical industry has explored the benefits of nanotechnology; it has developed dendrimers, micelles, drug conjugates, metallic nanoparticles *etc.* The brief explanation of these nanoparticles provides a salient glimpse of why they are used in nano pharmaceutical and medicinal chemistry.

- Metallic nanoparticles: Used for drug delivery, cancer treatment, and also in biosensors.

- Nano-liposomes: Bio-compatible and possess entrapment efficiency.

- Nano-emulsions: Used for controlled delivery of bioactive materials.

Keywords: Fullerenes, Metallic nanoparticles, Nanocosmetics, Nanomedicines, Nanoliposomes, Solid lipid nanoparticles.

INTRODUCTION: NANO-COSMETICS

Introduction to Cosmetics

Cosmetics are a class of skincare and personal care products that are used to modify and improve a person's appearance. A large number of cosmetics are available in the market; each is designed for different purposes and possesses di-

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verse characteristics. Cosmetics are constituted of a mixture of chemical compounds. Cosmetics designed for skincare can be used to perform the following functions:

a. Cleanse
b. Exfoliate
c. Protect the skin
d. Replenishing
e. Toners, moisturizers, and balms

Cosmetics designed for personal care are as follows:

a. Shampoo
b. Body wash, which can be used to cleanse the body

Cosmetics designed to enhance one's appearance (makeup) are as follows:

a. To conceal blemishes
b. Enhance one's natural features (such as the eyebrows and eyelashes)
c. Add color to a person's face

Extreme forms of makeup are used for performances, fashion shows and by people in costume to change the appearance of the face entirely to resemble a different person, creature or object. Cosmetics can also be designed to add fragrance to the body. Fig. (**1**) shows the pictorial presentation of the classification of cosmetics based on the area of usage and side effects on human health based on the information provided by the Food and Drug Administration (FDA).

Opportunities in Cosmetics and Problems

Around the globe, the cosmetic industry is the fastest-growing industry in 2023, garnering $ 429.9 billion [1]. Out of the list of more than 12000 chemicals, which are used in cosmetics, only 205 chemicals are considered to be safer to use [2]. Cosmetic products are toxic in terms of neuro and reproductive functionalities, carcinogenic and considered endocrine disruptors [3]. Rapid innovation and inclination in the cosmetic industry have arisen due to various toxic chemicals used as additives to enhance functionalities. Table **1** shows some toxic chemicals, which are widely used in almost every cosmetic product, whether skincare or personal care, with the transmission route and hazardous effects on human health.

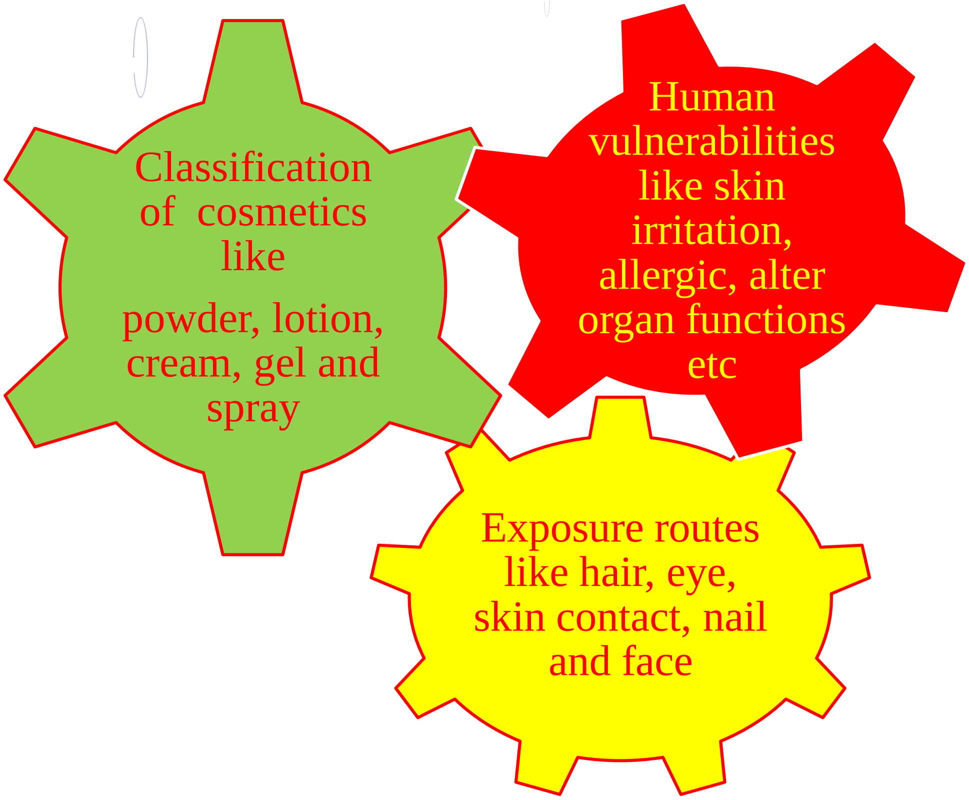

Fig. (1). Classification of cosmetics and side-effects on human health.

Table 1. Commonly used toxic chemicals in the cosmetic industry.

Sr. No.	Chemical	Formula (Chemical or Molecular)	Transmission route	Exposure	Human Vulnerabilities	References
1.	1,4- dioxane	$C_4H_8O_2$	1. Inhalation 2. Skin contact 3. Ingestion	Personal care products like mouthwash, shampoos, toothpaste	Carcinogenic, breathing issues, irritation to eyes and throat.	[4, 5]

CHAPTER 11

Nano Ferrites for Biomedical Applications

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Abstract: Superparamagnetic iron oxide nanoparticles have attracted attention due to their compatibility with various biomedical applications. The quantum confinement and increased surface area to volume ratio of the nanostructures alter their magnetic properties. There are several bottom-up techniques to synthesize superparamagnetic iron oxide nanoparticles; however, they offer certain limitations, like the existence of a secondary phase. The reaction parameters can be controlled to form pure-phase nanoparticles to increase their scope of applications in the field of medicine. Moreover, different applications demand different surface coatings of iron oxide nanoparticles.

Keywords: Drug delivery, Hyperthermia, Iron oxide, *In vitro*, Nanostructures, Superparamagnetism.

INTRODUCTION

Nanotechnology has emerged in recent years to the extent that it is now possible to synthesize, characterize, and modify its functional properties for biomedical applications [1 - 3]. Nanostructures and systems with tunable chemical and physical characteristics are preferably synthesized by inorganic nanoparticles [1, 4]. For some years, small iron oxide particles have been used for *in vitro* diagnostics [5]. There have been several research projects on various forms of magnetic iron oxide nanostructures from which magnetite, because of its biocompatibility, is the most promising candidate [6]. Magnetite (Fe_3O_4) is a magnetic type of iron oxide with a cubic inverse spinel structure and oxygen tightly packed into the FCC structure. The interstitial tetrahedral and octahedral positions are filled by the Fe cations [7]. Electrons appear to jump between Fe^{2+} and Fe^{3+} ions in octahedral positions at room temperature, making magnetite an important class of semi-metallic materials [8].

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Nanostructures are not physically or chemically distinguished by either an atom or a mass twin [9]. Quantum confinement effects and magnetic nanostructures' broad surface-to-volume ratio change some magnetical properties unexpectedly and reveal superparamagnetic behavior as every component acts as a single magnetic field [10]. Biomedical applications, such as drug delivery, hyperthermia, and MRI, based on the unique physical, chemical, thermal and mechanical features, are promising for superparamagnetic nanoparticles [11 - 14]. The particles should have combined characteristics of high magnetic saturation, biocompatibility, and surface interaction. However, it is possible, by adding different bioactive molecules, to change the surface of these particles by forming a few atomic layers that are suitable for more functions [15]. In the identification of such anti-cancer therapies, the aggregation of magnetic ions, *e.g.*, in tumour tissue, is crucial to the development and assessment of binding and drug carriers. The ideal surface properties of magnetic nanoparticles have high potential in many *in vitro* and *in vivo* applications [16]. The performance of the particles is based on different factors like:

a. Strong sensitivity to magnet enrichment for efficient purposes [17],
b. Particles of a single magnetic domain, that is, particles with uniform magnetization, with super-paramagnetic and high saturation values, will be of a size in the range of 6–15 nm (Particles below critical particle size (~15nm) [18], are easily separated by extravasations and clearance [19]),
c. Superparamagnetic conduct [16],
d. Produced unique bio-medical uses for surface chemistry [1], *etc.*

SYNTHESIS OF MAGNETIC IRON OXIDE NANOPARTICLES

For researchers, it is often a struggle to synthesize iron oxide nanoparticles of a particular shape and structure. Three key pathways, chemical, physical, and biological, can be used to synthesize iron oxide nanoparticles. These techniques have been studied with a view to synthesizing nanoparticles that are more stable, soluble and size-controlled [20]. Co-precipitation of Fe^{3+} and Fe^{2+} aqueous salt solutions by adding a base can be used to prepare iron oxide nanoparticles (Fe_3O_4 or γ-Fe_2O_3). Synthesized nanoparticles can be regulated by their size, structure, and shape based on the nature of the salt used, pH, and the medium's ionic strength [21].

Magnetite is typically formed in 2:1 molar ratios by adding a base to an aqueous mixture of Fe^{3+} and Fe^{2+} chlorides. The synthesized nanoparticles have black colour; the chemical reaction for the magnetite nanoparticles' co-precipitation route is presented below:

$$Fe^{2+} + Fe^{3+} + 8OH^{-} \rightarrow Fe_3O_4 + 4H_2O \qquad \textbf{(1)}$$

According to the thermodynamics of the above reaction, the total precipitation of magnetite is expected between a pH of 9 and 14. To prevent the oxidation of synthesized nanoparticles, the molar ratio of Fe^{3+}:Fe^{2+} as 2:1 should be preserved. Fig. (**1a**) shows magnetite formation at room temperature nearly immediately, while Fig. (**1b**) shows maghemite formation by chemisorption of magnetite oxygen. Fig. (**1c**) shows the final colloidal magnetite formed by peptizing an alkaline source.

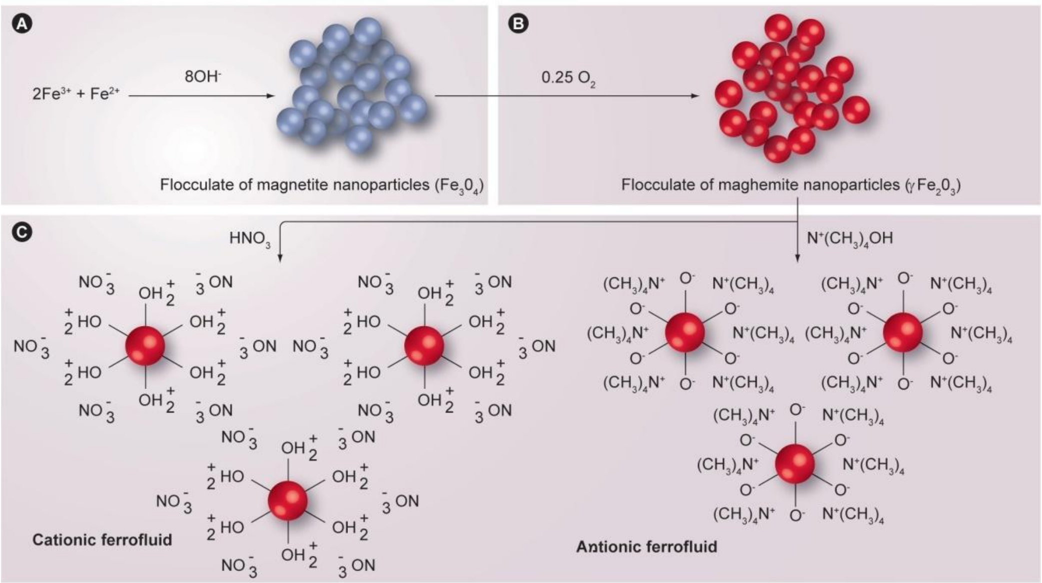

Fig. (1). (a) Flocculation of magnetite nanoparticles, **(b)** Flocculation of maghemite nanoparticles, **(c)** Colloidal magnetite dispersions obtained after peptization [22].

The physical and chemical properties of synthesized magnetic nanoparticles are seriously compromised by oxidation. They are also coated with organic/inorganic molecules during the precipitation process to avoid the oxidation of synthesized Fe_3O_4 nanoparticles in the air.

IRON OXIDE NANOPARTICLES COATING AND FUNCTIONALIZATION

Core-shell nanoparticles appear to bind different medicines with nanoparticles of iron oxide. In contrast to the surface layer working, stability enhancement, biocompatibility, and biodiversity [23], the center is the nanoparticles. Thus, the

CHAPTER 12

Rare-earth Induced Nano-crystallization Study of Borate Glass System

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Abstract: The study of the physical and structural properties of rare-earth doped borate glasses is discussed in this chapter. The glasses have been synthesized using the conventional melt quenching technique. X-ray diffractometer has been used to determine the amorphous nature of the prepared glass samples. Upon closer inspection of the XRD patterns, it is observed that the peak width changes, which indicates that the increase in the concentration of rare earth induces a localized devitrification of the prepared glasses around the rare earth. To investigate the structural dependence on the chemical composition of the manufactured glass, various parameters were determined. The molecular vibrations and rotations related to covalent bonds found in the glasses were studied using the infrared spectrum.

Keywords: Borate glass, Fourier transform infrared spectroscopy, Nano-crystallization, Rare-earth, X-ray diffraction.

INTRODUCTION

In solids, the absence of long-range order is one of the main characteristics of the amorphous materials, while short-range order is exhibited by crystalline materials. The word glass tells about the state of the material. It can be defined as an inorganic product of fusion, which has been cooled to a rigid condition without crystallizing. Thus, glass is an amorphous solid that possesses glass transition temperature and is obtained by supercooling of melt without any crystallization [1]. Generally, when a liquid is cooled slowly from the high temperature to its melting temperature, T_m, the liquid attains a crystalline phase. To form the glass, the cooling must be very fast, so that it bypasses the crystalline phase. It is safe to say that we live in a world, where glass is an important part of the daily life schedule. Therefore, it is very important to study the properties of glass to explore

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its applications in different areas. The widely used glasses are the oxide glasses and based on the former used, the glasses are of different types: borate, silicate, germanate, phosphate, *etc.* [2].

Borate glasses have become increasingly prevalent in the industrial, medical, and environmental monitoring aspects of modern society. The research interest in borate glasses is due to their promising properties, like high transparency, low melting point, effective atomic number, high thermal stability, and good solubility of rare earth (RE) ions [3 - 5]. However, the hygroscopic characteristic of these glasses has a detrimental effect on their properties, making them unstable. Modifiers, such as alkali and alkaline earth metals, have been used to mitigate thisproblem. These dopants have been found to not only improve moisture resistance but also function as activators in enhancing the glasses' emission qualities [6 - 8]. Of late, sodium oxide (Na_2O) and strontium oxide (SrO) are considered to be especially good modifiers for improving the features of borate glasses, such as moisture resistance and structural stability, to a substantial measure [9].

The rare-earth ions (RE^{3+}) possess a wide number of applications in the field of laser technology, solid-state lighting system, computer technology and optical communication systems. The applications of the rare-earth can be further enhanced, if they are doped in borate glass, which acts as a suitable host material. The change in the chemical composition of the glass matrix can modify the properties of RE^{3+} doped glasses, which are dependent on the environment around rare-earth ions [10]. It is interesting to analyze the effect of different modifiers on the physical and structural properties of the borate glasses.

In view of this, a study has been undertaken to analyze the physical and structural properties of the sodium strontium borate glass system doped with the different concentrations of dysprosium oxide (Dy_2O_3), erbium oxide (Er_2O_3), and neodymium oxide (Nd_2O_3). The synthesis method used for the glass preparation is the melt quenching, which is fast, easy and can be used to prepare glasses in bulk quantities. Important physical parameters have been calculated using suitable techniques, and structural properties have been analyzed using X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR).

EXPERIMENTAL PROCEDURE

The choice of method for the preparation of the samples for any study is very important. There are various methods, which can be employed for the synthesis of glasses. In the present work, the glasses have been synthesized using the conventional melt quenching technique. Stoichiometric amounts of analytical reagent (AR) grade B_2O_3, Na_2O and SrO in the form of H_3BO_3, Na_2CO_3 and $SrCO_3$ were taken as initial glass constituents. The sodium strontium borate glasses were doped with the different concentrations of Dy_2O_3, Er_2O_3, and Nd_2O_3, respectively. The constituents were weighed on an electronic balance with the sensitivity of 1mg, mixed, and grinded in an agate mortar for 1 hour. The mixture was then transferred to a silica crucible and placed in an electronic muffle furnace. The temperature was initially maintained at 120ºC for 2-3 hours to remove the moisture. After that, the temperature was increased slowly to 1000ºC and maintained there for 1 hour to attain a bubble-free melt by stirring frequently. The melt was cast into a prepared graphite mould after it reached the desired viscosity. The mould was then put in an annealing furnace,set at 350°C for two hours to reduce internal stress, after which the glass sample was left in the furnace to cool. The prepared samples were transparent, uniform, and free of bubbles. The nomenclature and the chemical composition of the glass samples are detailed out in Tables **1**, **2**, and **3**.

Table 1. Chemical composition (in mol %) and glass codes nomenclature of dysprosium oxide doped sodium strontium borate glass samples (DyNaSrB).

Glass codes	**B_2O_3**	**Na_2O**	**SrO**	**Dy_2O_3**
Dy0	70.0	20.0	10.0	0.0
Dy1	69.8	20.0	10.0	0.2
Dy2	69.6	20.0	10.0	0.4
Dy3	69.4	20.0	10.0	0.6
Dy4	69.2	20.0	10.0	0.8
Dy5	69.0	20.0	10.0	1.0

Table 2. Chemical composition (in mol %) and glass codes nomenclature of erbium oxide doped sodium strontium borate glass samples (ErNaSrB).

Glass codes	**B_2O_3**	**Na_2O**	**SrO**	**Er_2O_3**
Er0	70.0	20.0	10.0	0.0
Er1	69.8	20.0	10.0	0.2
Er2	69.6	20.0	10.0	0.4
Er3	69.4	20.0	10.0	0.6
Er4	69.2	20.0	10.0	0.8
Er5	69.0	20.0	10.0	1.0

CHAPTER 13

Functionalization of Carbon Nanotubes for Sensing Applications

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Abstract: Carbon nanotubes (CNTs) composed of sp^2 carbon units oriented as one rolled-up graphene have provided exceptional advances in the design of chemical sensors for environmental and health monitoring. The remarkable properties of CNTs, such as high active surface area, chemical inertness, high strength, high electrical conductivity, excellent thermal stability, and low charge-transfer resistance, have made them a potential candidate for the detection of various explosive, combustible, and toxic gases, such as hydrogen sulfide (H_2S), nitrogen oxides (NO_x), ozone (O_3), and halogens (Br_2, Cl_2, and I_2). However, CNT-based sensor shows issues like low sensitivity and slow response/recovery time due to minimum charge transfer between the pristine CNTs and target analytes. The functionalization of CNTs with metal oxides, noble metal nanoparticles, and organic semiconductors not only improves the gas sensing parameters but also enhances their selectivity toward a particular type of target analyte due to the better charge transfer between the composite and gas analytes. This book chapter focuses on the ways to create CNT-based sensors exhibiting selective responses to different target analytes, future developments in the field of chemical sensors, and the viewpoint of their commercialization.

Keywords: Carbon nanotubes, Chemiresistive sensor, Metal phthalocyanine, Sensing mechanism, X-ray photoelectron spectroscopy.

INTRODUCTION

Since their discovery, carbon nanotubes (CNTs) have achieved tremendous consideration due to their extraordinary physical, chemical, structural, mechanical, and electronic properties [1]. CNTs are cylinder-shaped macromolecules, and the walls of these tubes are made up of a hexagonal lattice of carbon atoms analogous to the atomic planes of graphite [2]. These CNTs can

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be either single-walled or multi-walled, where single-walled carbon nanotubes (SWCNTs) possess a single carbon layer with diameters ranging from 0.4 to 3 nm, while multi-walled carbon nanotubes (MWCNTs) consists of various layers of carbon (Fig. **1**) that can reach diameters of up to 100 nm [3, 4]. The CNTs can be synthesized using chemical vapor deposition, arc discharge, or laser ablation methods [3].

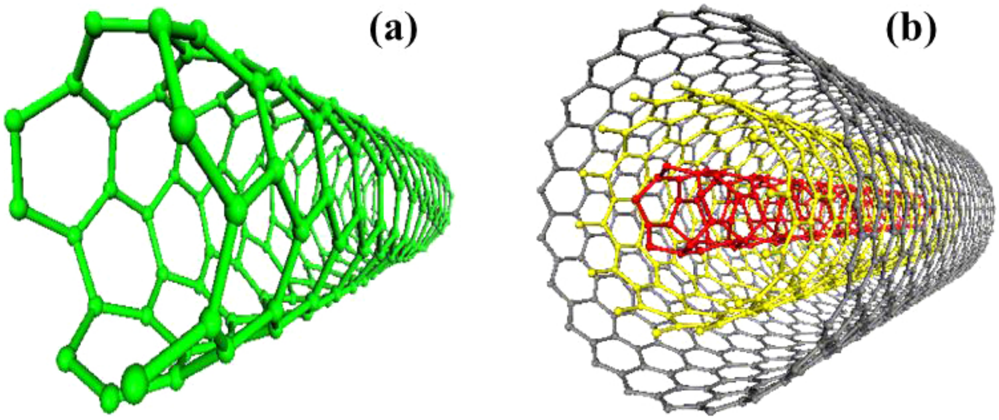

Fig. (1). Basic structures of **(a)** single-walled carbon nanotubes and **(b)** multi-walled carbon nanotubes.

Moreover, depending on the diameter, direction, and functionalization of graphene sheets, CNTs can exhibit metallic, semi-metallic, or semiconducting properties [5, 6]. However, in MWCNTs, a weaker coupling bond between the individual cylinders occurs in comparison to SWCNTs. In addition, due to the 1D structure of CNTs, ballistic transportation of electrons takes place in them. The thermal conductivity of the CNTs at room temperature is found to be <3000 W/(m.K), which is higher than that of diamond and the basal plane of graphite. Owing to these unique properties, a variety of potential applications of CNTs, such as energy storage [7], chemical sensors [8], field emitters in display technology [9], electrodes for rechargeable batteries [10], resistors, and interconnects [11], have been explored in recent years. Among these potential applications, chemical sensors based on CNTs have recently attracted a great deal of attention due to their small size, good response, and low operating temperature. In general, for good and competent gas sensing systems, there are many basic criteria, such as (i) high selectivity, (ii) small power consumption, (iii) low analyst consumption, (iv) fast action in terms of response and recovery time, and (v) stability in performances. It is worth mentioning that commonly used materials in gas sensing applications, including semiconductor metal oxides, vapor-sensitive polymers, and some other structured materials, such as porous silicon [12], often work at high temperatures and suffer from cross-sensitivity issues. Recently, progress and improvement in nanotechnology have demonstrated a high potential to develop cheap, sensitive, and portable sensors with very small power utilization. In view of this, sensors based on nanomaterials, such as CNTs, nanowires, nanofibers, and nanoparticles, have been broadly investigated due to their large surface to volume ratio and hollow-type structure, which facilitates gas adsorption [13].

Based on the operating principle or output signal, the gas sensors are classified into various categories. Table **1** lists the different types of gas sensors along with their operating principles. This book chapter is limited to chemiresistive gas sensors, the detection mode of which relies on changes in the device's electrical current, resistance, or conductance. The fact that all the carbon atoms in a CNT are surface atoms, and this unique property makes them optimally suited for components of chemical sensors. Hence, it is not surprising that gas sensors made from individual nanotubes show good sensitivities even at room temperature in comparison to commercially available traditional semiconductor sensors, which generally operate above 200°C [2].

Table 1. A list of gas sensors with their operational principles.

Sensor Type	Sensor Configuration	Detection Principle
Solid-State Sensors	Chemiresistive	Resistance of sensor changes on exposure to analyte gas.
	Chemical field-effect transistors	Current-Voltage (I–V) curves of a field-effect transistor are sensitive to a gas when it interacts with a gate.
	Colorimetric	Change in temperature due to the oxidation process on a catalytic element.
	Potentiometric	Change in potential difference (voltage) between the working electrode and the reference electrode.
	Amperometric	Diffusion limited current of an ionic conductor is proportional to the gas concentration.
Mass Sensitive Sensors	Acoustic	Variation in frequency of surface-acoustic waves excited on quartz or piezoelectric substrate upon absorption of gas in a suitable sorption layer (*e.g.,* metals, polymers).
	Micro-electromechanical systems-based sensors	On adsorption of gas, mechanical bending of micro or nano cantilevers occurs.
	Surface Plasmon Resonance (SPR)	The amount of bound gas molecules is observed by a change in SPR signals, which is proportional to the refractive index.
Optical Sensors	Optodes	Based on the measurement of change in optical properties, such as absorbance, reflectance, luminescence, Raman, and others.

CHAPTER 14

Graphene Nanoribbons and Doped Graphene

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Abstract: Graphene has been an interesting material for scientists and engineers by virtue of its remarkable properties. It has unique electronic properties with zero bandgap at the Dirac point. The absence of bandgap in graphene limits its application in electronics. The formation of graphene nanoribbons and substitutional doping of graphene are the methods to manipulate the geometric and hence electronic structure of graphene. Starting from the geometric and electronic properties of graphene, this chapter involves a discussion on the geometric and electronic structure of graphene nanoribbons and substitutionally doped graphene systems based on first principles studies.

Keywords: Doping, Electronic properties, Graphene nanoribbons, Graphene.

INTRODUCTION

Graphene [1, 2] is a one-atom-thick monolayer of carbon atoms arranged in a two-dimensional honeycomb lattice, as shown in Fig. (**1**). Carbon ($2s^2 2p^2$) has four valence electrons in s and p orbitals. The sp^2 hybridization between one s and two p orbitals leads to a trigonal planar structure with the formation of σ bonds between carbon atoms. The resulting C-C bond length and C-C-C bond angle are 1.42 Å and 120°, respectively. The unaffected p orbital remains perpendicular to the planar structure. It can bind covalently with neighbouring carbon atoms, leading to π-bonding.

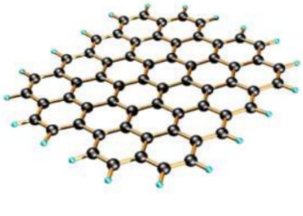

Fig. (1). Pristine graphene.

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The unit cell of graphene contains two carbon atoms denoted by A and B, as shown in Fig. (**2**).

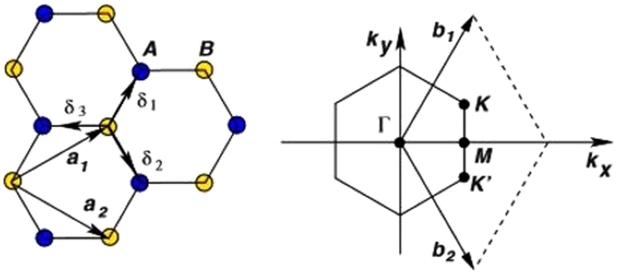

Fig. (2). (a) Lattice structure and **(b)** first Brillouin zone of graphene (Adopted from reference 3).

The primitive translation vectors are:

$$\mathbf{a}_1 = \frac{a}{2}\left(\sqrt{3},1\right)\mathbf{a}_2 = \frac{a}{2}\left(\sqrt{3},-1\right) \quad \textbf{(1)}$$

where a= 2.46 Å is the lattice constant.

The vectors drawn from one carbon atom to its three nearest neighbours in real space are:

$$\boldsymbol{\delta}_1 = \frac{a}{2\sqrt{3}}\left(1,\frac{1}{\sqrt{3}}\right)\boldsymbol{\delta}_2 = \frac{a}{2\sqrt{3}}\left(1,-\sqrt{3}\right)\boldsymbol{\delta}_3 = -\frac{a}{\sqrt{3}}(1,0) \quad \textbf{(2)}$$

The reciprocal lattice vectors are:

$$\mathbf{b}_1 = \frac{2\pi}{\sqrt{3}a}\left(1,\sqrt{3}\right)\mathbf{b}_2 = \frac{2\pi}{\sqrt{3}a}\left(1,-\sqrt{3}\right) \ (3) \quad \textbf{(3)}$$

The first Brillouin zone of graphene is a hexagon. Due to symmetry, six points at the edges of the hexagon reduce to three special points denoted by Γ, K and M. These points are also known as high symmetry points. The band structure of graphene is plotted along the lines joining these points. Two points K and K' are non-equivalent points known as Dirac points [3].

The position of these points in momentum space is:

$$\boldsymbol{\Gamma} = (0, 0) \quad \textbf{(4)}$$

$$\mathbf{K} = \frac{2\pi}{\sqrt{3}a}\left(1,\frac{1}{\sqrt{3}}\right)\mathbf{K}' = \frac{2\pi}{\sqrt{3}a}\left(1,-\frac{1}{\sqrt{3}}\right) \quad \textbf{(5)}$$

$$\mathbf{M} = (\frac{2\pi}{\sqrt{3}a}, 0) \tag{6}$$

Since its experimental isolation in 2004 [4], graphene has attracted the great attention of various researchers because of its extraordinary properties [5, 6]. It has a high electron mobility of about 15,000 cm^2/Vs at a charge density of 10^{12} cm^{-2} [7] and high electrical conductivity [8] at room temperature, owing to its perfect crystal quality. It exhibits anomalous quantum Hall effect [9] and ambipolar charge transport at room temperature [10]. Electrons in graphene behave as massless relativistic fermions, which satisfy the Dirac equation [11]. The electron wave function has non-zero Berry's phase of π as a consequence of unique electronic properties of graphene.

The low energy band structure of graphene is depicted by conical forms of conduction and valence bands located near K and K' points of the Brillouin zone, as shown in Fig. (**3**). The π band is completely filled and π* is completely empty and meets at these k-points, forming the singular point at the Fermi level [3, 6]. The two-dimensional energy dispersion relation is linear in crystal momentum near the Fermi level and given as:

$$E = \pm \hbar \upsilon_f k = \pm \upsilon_f p \tag{7}$$

Where ħ is reduced Planck's constant, V_f is Fermi velocity and given by $V_f \approx c / 300 \approx 10^6$ m/s (c is the speed of light), k is the wave vector measured from one of the Dirac points, and p is crystal momentum.

Due to the linear dispersion relation, one can expect the quasiparticles in graphene to behave differently as compared to those in semiconductors and metals, where energy dispersion is approximated by a parabolic curve.

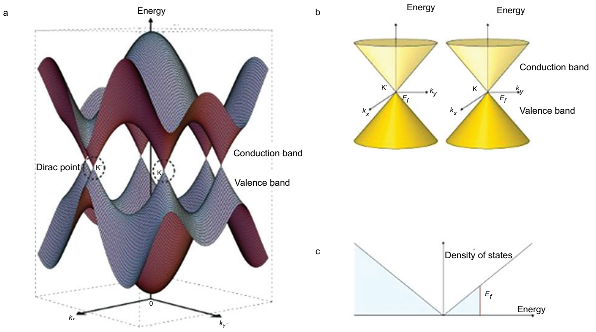

Fig. (3). (a) Energy bands near the Fermi level in the graphene **(b)** conic energy bands near the vicinity of the K and K' points **(c)** density of states near the Fermi level E_f (Adopted from reference 6).

CHAPTER 15

Strain-Induced 2D Materials

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Abstract: In this chapter, different structural, electronic and magnetic properties of strained graphene nanoribbons are examined. All the calculations are performed by using density functional theory. Compressive stress along a nanoribbon's longer axis and tensile stress at the midpoint and perpendicular to the nanoribbon's plane are studied. There are remarkable changes in the structures, including the formation of nanoripples in the ribbons. The shape and size of the ribbons lead to variation in their electronic and magnetic properties. Strained nanoribbons show tunable magnetic properties that can be used for developing magnetic nano-switches.

Keywords: Density functional theory, Graphene nanoribbons, Magnetism, Nanoripples, Strain.

INTRODUCTION

Semiconductors form the basic components of many important devices used in the fields like electronics, sensors, computers, spintronics, *etc.* The parameter which decides the semiconducting, electronic and optical properties of different materials is bandgap. Bandgap engineering or modulation of materials has shown completely different properties from their respective constituents.

At the nanoscale, the bandgap plays a very significant role as it modifies the optoelectronic properties, leading to other exciting applications. One more factor that can modulate the bandgap is the effect of the strain. Different 2D materials show different behaviour under the influence of strain. For example, uniaxial strain is applied by either stretching or bending the substrate beneath the 2D material or by the introduction of ripples in the material. Strain engineering has recently been utilised to construct 2D semiconductor-based straintronic devices. This chapter focuses on the effect of axial strain on different properties of graphene nanoribbons.

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Graphene nanoribbons (GNRs) are quasi-one-dimensional nanostructures with distinct electronic, optical, and transport properties [1 - 3]. As a result, several investigations have been conducted on their prospective uses as FETs, spintronics and optoelectronic devices [4 - 6]. This area of GNRs has attracted a lot of interest as their characteristics can be controlled by applying external electric and magnetic fields, doping, defects and edge-modification [7 - 9]. GNRs have also been used in hybrid materials, such as vanadium dioxide-graphene structures [10], and have demonstrated exceptional electrochemical performance, indicating that they might be used in high-power lithium batteries as an electrode material. The finding of graphene [11] has paved the way for the discovery of other two-dimensional materials [12], which show promise in sectors like photonics [13] and nanomedicine [14]. The counterparts of graphene nanoribbons, i.e., silicene [15, 16], stanene [17], phosphorene [18], germanene [19, 20] and new monolayer materials [21], have been explored for their electronic and magnetic properties by applying density functional theory and other first principle methods.

GNRs have been successfully synthesized using a variety of top-down techniques, such as graphene etching [22], chemical vapour deposition [23], scanning probe lithography [24] and unzipping of single- [25] and multi-walled carbon nanotubes [26]. Still, their specific electrical structure cannot be completely predicted by the above-mentioned approaches; therefore, a bottom-up approach can be applied. A significant work [27] is based on some suitably designed precursor molecules which react in a selective way to produce GNRs [28, 29] and has paved the way for a number of techniques to form GNRs. Furthermore, the method has been used in solution [30] and supported on solid surfaces [31].

It has been observed that graphene has the greatest stiffness and strength among known materials and hence shows exceptional stress-strain behaviour [32, 34]. It can be bent readily to produce intricate folded shapes [35], and it can endure elastic deformations of up to 25% [32], which is far bigger than any other known material. Graphene is an excellent contender for nanomechanical systems [36] and flexible electronic devices [37] due to its superior mechanical characteristics. Measurements of the elastic response of graphene indicated that it is extremely nonlinear for stresses exceeding 10% [32]. Interpretation of the experiments in terms of a generalised nonlinear stress-strain relationship includes cubic components in strain, and nonlinear elastic coefficients are calculated using atomistic simulations [33].

Owing to the lattice mismatch [38] or the substrate's surface corrugation [39], stresses appear impulsively when graphene is put on a substrate. Moreover, intrinsic edge stress exists along the edges of graphene, which causes warping instability [40]. Strain can be purposely caused and regulated in addition to naturally occurring strain. Bending the flexible substrate can cause uniaxial strain [41]. Biaxial strain can be induced by exploiting the temperature mismatch between graphene and the substrate [43], shrinking or elongating the piezoelectric substrate with a bias voltage [42], or pushing graphene clamped on top of a hole in the substrate with an atomic force microscope tip [32].

The quantized pseudomagnetic field [44], zero-field quantum Hall effect [45], increased electron-phonon coupling [46], and shifting of Dirac cones [47] are only a few of the remarkable physical phenomena of graphene generated by the strain. While graphene's bandgap remains near zero even under enormous strain, GNRs' bandgap is extremely sensitive to both uniaxial and shear strain. Uniaxial weak strain alters the band linearly for an armchair GNR, while significant strain causes periodic oscillation of the bandgap. Shear strain, on the other hand, tends to narrow the bandgap. Strain changes the spin polarisation at the edges of ribbons, modifying their bandgap in a zigzag GNR [48].

Due to an applied uniaxial strain, the planar structure of GNRs is distorted by the production of ripples [49 - 51]. Furthermore, molecular dynamics investigations have demonstrated that applied strain may readily regulate the amplitude and orientation of ripples [52, 53]. Additionally, spin-polarized first principle calculations have revealed that zigzag GNRs are magnetic, but armchair GNRs are not [54]. The magnetic moment is generated along zigzag edges with sinusoidal deformations when strain is applied to magnetic GNRs [55].

Under the influence of strain, the structural, electrical, and magnetic characteristics of the armchair and zigzag graphene nanoribbons change. Nanoribbons with square, triangular, rectangular, or circular geometries with their core atom exposed to focused load have varied characteristics.

The geometric and electrical features of graphene and small fullerenes were investigated, and it was found that they were consistent with prior research [60 - 64]. The same parameters to get the stable structures of GNRs were used.

GNR ground-state structures were optimized for axial loads applied at the two parallel edges of rectangular GNRs and a load applied at the centre and perpendicular to a plane of square, triangular, rectangular, and circular nanoribbons. In the case of axial load, the three types of boundary conditions were considered: three, one, or two atoms of the hexagons at the edges were relocated and stayed fixed (Fig. **1**). The atoms were pushed inwards in steps of 0.2 Å along the longer edge of a 3 nm by 1 nm nanoribbon, resulting in compressive strains ranging from 1.3% to 6.7%. The free boundary conditions were applied at the two unloaded edges in all three cases of axial loads. In the case of the point load, the

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Dr. Karamjit Singh Dhaliwal is working as an Assistant Professor in the Department of Physics, Punjabi University, Patiala, Punjab (India). He has 14 years of teaching and 19 years of research experience. His areas of interest are nanotechnology, materials science, laser spectroscopy and atmospheric sciences. He is trying to explore the potential of nanomaterials of various morphologies for phosphor, photo-catalytic, photo-voltaic and sensing applications. He has authored/co-authored more than 75 research papers and presented research findings on various national/international platforms. He has completed three research projects funded by the University Grants Commission (UGC), New Delhi (India) and the Department of Science and Technology (DST), New Delhi (India). Presently, he is handling a major research project funded by Indian Space Research Organisation (ISRO). He has authored 2 books and many book chapters. He has delivered more than two dozen invited expert talks, radio talks and TV interviews. He is a known columnist who writes frequently in Punjabi newspapers to popularize science among the masses. He is a recipient of the Young Scientist Award of the Punjab Academy of Sciences, a reviewer of various research journals and a member/life member of many national/international professional societies/organizations.