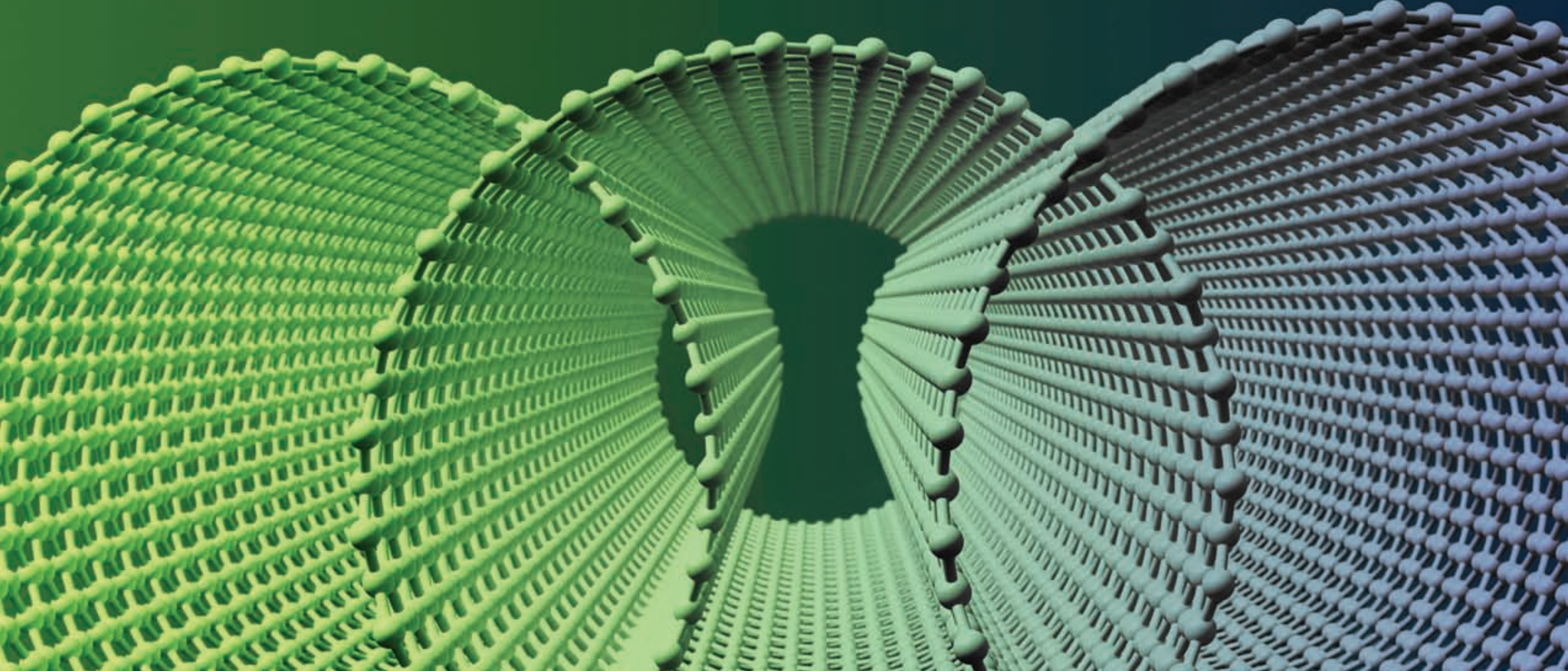
SYNTHESIS, APPLICATION AND FUTURE PERSPECTIVES OF SMART NANO-MATERIALS

PART 1



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Synthesis, Application and Future Perspectives of Smart Nano-materials

(Part 1)

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Synthesis, Application and Future Perspectives of Smart Nano-materials - *(Part 1)*

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FOREWORD

In the 21st century, the recent advances in nanoscience and nanotechnology attracted the discovery of advance novel materials with multiple functionalities. These advanced nanomaterials (NMs) have received considerable attention due to their significant properties, such as chemical composition, small particle size, shape, specific surface area, and solubility. Among the various nanomaterials, smart nanomaterials can be impetus by external factors such as the techniques used for fabrication, temperature, pH, pressure, particle size and shape, pore size, environment, and vicinity, which induce the new kind of functional properties. Therefore, the literature discusses the recent advancement in smart nanomaterials and synthesis procedures that create unusual functional material characteristics and furnish a great opportunity for a larger span of application of these materials.

The book “Synthesis, Application and Future Perspectives of Smart Nano-materials”, edited by Laxman Singh and R.N. Rai, addresses multiple aspects of Smart Nano-materials and their advanced applications in various areas such as energy, sensing, pharmaceuticals, food science and technology, biomedical health, sensing, cosmetics and dermatology, gas, oil, energy, wastewater and environment, textiles, agriculture and many more. The Smart Nano-materials possess excellent electrical, sensing, mechanical, thermal, optical and catalytic properties. In this book, the Editors collected comprehensive literature from all over the world about the latest applications, classification of smart nanomaterials, novel fabrication techniques for achieving good functional properties, *etc*. The authors have put very good efforts into bringing together researchers, professor, and scholars from different parts of the world to contribute a timely and comprehensive picture of smart nanomaterials. Their expertise and good academic and research credentials in the diverse fields of nanomaterials for energy, biomedical, and environmental applications have helped significantly in compiling and editing the chapters and preparing the book. The book has the potential to serve the community interested in smart nanomaterials and their advancement applications and the latest synthesis process.

I want to wish all the best to the publishers, editors, and contributors for great success. I hope the readers of the book and the policymakers and other stakeholders will find it valuable for further research and commercialization aspects of smart materials, their properties, synthesis techniques and applications.

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PREFACE

Smart materials are a family of materials that can significantly change their electrical, catalytic, thermal, optical, mechanical, or magnetic properties in a controllable manner by external factors such as atmospheric pressure, humidity, temperature, biochemical response, stress, pH, electromagnetic waves, electric or magnetic field, light, moisture, *etc.* These materials help to remove the barriers between functional and structural materials, which can lead to a significant revolution in materials science for modern science and technology development for a wide range of industrial applications, such as energy materials, magnetic energy, sound energy and mechanical energy, transducers, sensors and actuators, artificial muscles, and electrically active polymers (EAP). Smart nanomaterials are the foundation of many advanced applications, and this book outlines the emerging technological advances, innovations, applications, latest synthesis techniques, and factors affecting the properties of these materials. The book covers the most important aspects of chemistry, physics, and biology, as well as the synthesis of smart nanomaterials. The book "**Synthesis, Application, and Future Perspectives of Smart Nanomaterials (Part 1)**", edited by "**Laxman Singh and R.N. Rai**", addresses the multiple aspects of new smart nanomaterials and various advanced fabrication synthetic methods, which will satisfy the desire and thirst of academicians, researchers, and technologists in the field of nanoscience and nanotechnology. This book contains a total of six chapters that have been written by academic research & development experts in their respective fields of nanoscience and nanotechnology to explore the topic of our book. Chapter 1 covers chemocatalytic, electrocatalytic, and photocatalytic use of new nanomaterials for HER reaction. Chapter 2 discusses core-shell metal/carbon nanomaterials for microwave absorption and optical limiting applications. Chapter 3 presents a systematic development in the synthesis of CQDs and their applications. Chapter 4 covers the synthesis of nanomaterials and their wide range of applications. Chapter 5 discusses the various nanostructured metal oxides and their electrochemical behavior for supercapacitor applications. Chapter 6 provides a brief literature review on the synthesis of TiO_2 nanostructure by various methods and its applications.

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CHAPTER 1

Smart Nano-materials for Catalytic Hydrogen Evolution Reactions

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Abstract: Cumulative demand for energy needs enormous growth in more secure and diversified energy sources with high energy generation capacity and successful strategies to reduce greenhouse gas emissions. Amongst various energy approaches, they are constructing a system using hydrogen (H_2) as the primary carrier that can facilitate a secure and clean energy future. The development of technologies that meet desired performance and cost requirements for the safe and reliable storage and transportation of hydrogen produced from various sources and intended for diverse uses is crucial for establishing a future hydrogen economy. Hydrogen is one of the effective, renewable, and environmentally benign sources of alternative energy. Electrocatalytic and photocatalytic water splitting, along with the Chemocatalytic process from chemical sources using suitable nanomaterial based catalysts, have shown great proficiency for hydrogen evolution and are believed to be a promising avenue to reach the goal of future hydrogen economy. Smart nanomaterials, including metal nanoparticles (NPs) and nanoclusters (NCs), have been extensively investigated for the catalytic hydrogen evolution reaction (HER). Moreover, the crucial properties of nanomaterials, such as porosity, active sites, morphology, shape and size of NPs, chemical compositions, metal-support interactions, and metal-reactant/solvent interaction in nanomaterials, are the major factors affecting the performance of catalytic HER. In the current chapter, we discuss the state-of-art design of various carbon and MOF based/derived nanocatalysts along with their performance for hydrogen evolution from Electrocatalytic, Photocatalytic and Chemocatalytic reactions.

Keywords: Catalyst, Chemocatalytic, Carbon nanotubes (CNTs) and graphene, Electrocatalytic, Energy, Hydrogen, Hydrogen evolution reactions, Metal organic frameworks, Noble metal, Photocatalytic, Non-noble metal, Porous carbon, Smart-nanomaterials.

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INTRODUCTION

Driven by rising standard of living and growing population worldwide, global energy consumption has dramatically increased in the last few decades and is expected to increase in the future. The continuous increase in energy consumption and rapid depletion of fossil fuels has led to serious energy crises and demands to switch over to alternative sources of energy such as rain, tides, waves, geothermal heat, converting biomass to energy, solar energy, and last but not least hydrogen energy [1, 2]. Hydrogen is the cleanest renewable energy source and is considered an alternative to fossil fuels. Finding effective hydrogen-based energy technology is one of the major challenges facing major limitations in storage and transportation because it cannot be practicable to pump into tanks as easily as gasoline. However, the storage of hydrogen in the form of compressed gas or cryogenic liquid is the most mature technology at present, but it faces major drawbacks in transportation because only a small amount of hydrogen can be stored in a reasonable volume, which makes the hydrogen storage more challenging. Therefore, the development of a safe and efficient hydrogen-based energy technology capable of conveniently producing hydrogen under normal conditions is highly desirable [1 - 5].

Hydrogen production from water splitting by the electrocatalytic or photocatalytic hydrogen evolution reaction (HER) is a promising strategy for clean and secure energy generation [6 - 8]. This technique has several advantages in that water is a no-cost natural source and can easily produce hydrogen by the catalytic water splitting under normal conditions in the presence of suitable nanomaterials without any infrastructural restrictions. In this technique, only environmentally preferred H_2 and O_2 are formed [9]. Besides the water splitting, another promising technique is chemocatalytic HER in which the chemicals containing high hydrogen content *i.e*., formic acid (FA), hydrazine Hz), hydrazine borane (HB) and ammonia borane (AB), can produce an excess amount of hydrogen in the presence of appropriate catalyst under mild conditions [10]. These techniques provide a facile way for the storage and transportation of hydrogen with low potential risk and minimum investment. The development of hydrogen as a fuel is crucial because of the notably higher combustion energy (122 kJ/mol) of H_2 over gasoline or any other fossil fuels [11]. For HER, precious metals such as platinum (Pt), iridium (Ir), palladium (Pd) and ruthenium (Ru) based nanomaterials exhibiting excellent catalytic performance have been extensively investigated [12]. Commercially available 20% Pt/C is the most frequently applied material as a benchmark catalyst for the electrocatalytic HER. Similarly, various nanomaterial-based catalysts have also been developed for the catalytic HER from water and other chemical sources [6 - 11]. Relatively higher costs and lower abundance of noble metals have restricted the commercialization of these nanomaterials as catalysts on a higher scale. In this way, various research groups are actively engaged in developing cost-effective smart nanomaterials by reducing the noble metal loading or using non-precious metals with enhanced catalytic activity for HER. Recently, the research on designing and developing highly active non-noble metal nanocatalysts derived from metal–organic frameworks (MOFs) and carbon materials such as carbon nanotubes (CNTs), graphene, carbon fiber, carbon nitride, and activated porous carbon has paid much attention (Fig. **1**) [13 - 17]. This chapter aims to summarize the role of smart nanomaterials in the development of hydrogen as an alternative energy source *via* efficient techniques such as electrocatalytic, photocatalytic, and chemocatalytic HER. Here, we mainly focus on the state-of-the-art advances of smart nanomaterials, processing and mechanisms of the catalysts for HER, and the prospects for the opportunities and challenges of nanocatalysts for hydrogen generation in the future.

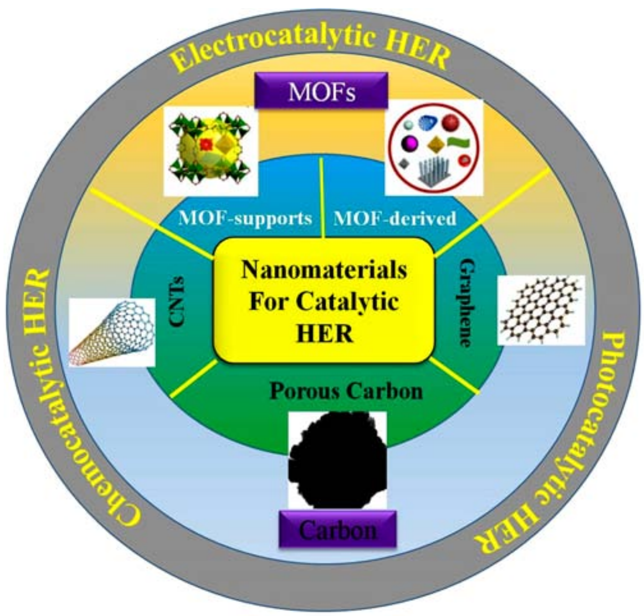

Fig. (1). A schematic diagram showing the nanomaterials derived from various MOFs and carbon sources for the catalytic hydrogen evolution reaction.

HYDROGEN EVOLUTION REACTION (HER)

Electrocatalytic HER

Electrocatalytic-driven water splitting that produces clean H_2 has been widely considered as a capable method for future sustainable and renewable energy portfolios [18]. Electrocatalytic HER occurs at the surface of an electrode in different steps, as shown in Eqs. **1-6** and Fig. (**2**). The first step, where the hydrogen atom (H*) adsorbs the electrode surface (M) by the reaction of a proton

CHAPTER 2

Multifunctional Core-Shell Metal/Carbonaceous Smart Nanomaterials For Microwave Absorption And Optical Limiting Applications

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Abstract: This chapter focuses on core-shell type carbon-coated metal nanoparticles, which possess distinct properties that can be manipulated to enhance their interactions with electromagnetic radiation. The synergism at the magnetic metallic core and carbon shell interface plays a vital role in augmenting the optical response of these nanoparticles. Consequently, it becomes crucial to develop synthesis strategies that optimize the defects at this interface. In this chapter, we provide a detailed description of a cost-effective pyrolytic synthesis approach and present mechanistic studies on the microwave absorption (at GHz frequencies) and optical limiting behavior of the synthesized core-shell nanostructures. The pyrolysis synthesis strategy offers a low-cost method for producing the core-shell nanoparticles. By carefully controlling synthesis parameters, we achieve precise control over the structure and composition of the nanoparticles. Moreover, we investigate the defects and their distribution at the interface, as these defects significantly influence the optical properties of the nanostructures. Furthermore, we explore the microwave absorption capabilities of the synthesized core-shell nanostructures at GHz frequencies. By characterizing their absorption behavior, we gain insights into their potential applications in microwave technologies, such as EMI shielding and stealth technology. Additionally, we examine the optical limiting behavior of the core-shell nanostructures, which refers to their ability to attenuate intense light and protect optical devices from damage. Through comprehensive optical characterization and analysis, the mechanistic insights on the optical limiting behavior of the synthesized nanostructures are elucidated. The findings evolve the understanding of light-matter interactions in these nanostructures and pave the way for their potential applications in various technological fields.

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Keywords: Attenuation of intense light, Core-shell, Carbon shell, Defect optimization, EMI shielding, GHz frequency, Interface engineering, Low-cost fabrication, Light-matter interactions, Laser protection, Magnetic metallic core, Microwave absorption, Non-linear optics, Optical characterization, Optical limiting, Optical devices, Pyrolysis, Stealth technology, Synthesis strategies, Smart nanomaterials.

INTRODUCTION

Electromagnetic (EM) radiations exhibit a transverse wave nature. They consist of electric and magnetic fields which vary over time and are perpendicular to the direction of wave propagation. The electromagnetic spectrum encompasses a range of frequencies, from the shortest to the longest, and each frequency regime corresponds to a specific range of photon energy. As a result, different types of waves interact differently with various substances. When an EM wave interacts with matter, it gives rise to a range of fascinating phenomena, broadly categorized as absorption, transmission, and reflection, which fall under the domain of light-matter interactions [1 - 4]. These light-matter interactions have broad implications across various fields and disciplines. The diverse phenomena observed when electromagnetic waves interact with matter, coupled with the influence of magnetic and dielectric properties, highlight the rich domain of light-matter interactions and their significant implications across multiple scientific and technological domains. They play a crucial role in areas such as optics, photonics, materials science, and engineering. By studying and harnessing these interactions, researchers can develop innovative technologies, devices, and materials with enhanced properties and functionalities. Additionally, understanding the behavior of electromagnetic waves and their interaction with matter is fundamental to advancing fields like telecommunications, energy harvesting, sensing, and imaging. Optical interactions with matter include diffraction, interference, refraction, and scattering, which can be observed through spectroscopic tools that quantify the extent of these interactions. Moreover, electromagnetic waves can influence materials with magnetic or dielectric properties, leading to magneto-optic or opto-magnetic effects [5, 6].

At the nanoscale, materials exhibit remarkably different properties compared to their bulk counterparts. Nanomaterials can be classified based on their shapes, sizes, and physicochemical properties, conveniently categorized as 0D, 1D, 2D, and 3D nanomaterials [7]. The size of particles also influences various properties such as melting point, color, fluorescence, electrical conductivity, magnetic permeability, and chemical reactivity. As particle size changes, these properties exhibit distinct behavior, offering opportunities for tailoring materials with desired characteristics. Quantum effects dominate in such systems, where particles ranging from 1-200 nm can only be observed under an electron microscope, unlike larger particles visible under an optical microscope. Nanoparticles are particularly interesting for studying optical processes due to their surface plasmon resonance characteristics [8, 9]. The size-dependent optical processes are attributed to the tunability of the particles' optical band-gap (E_g), which increases as the particle size decreases. When photons interact with a particle, electrons are excited from the ground state to higher energy levels. These excited electrons can relax to the ground state or an intermediate lower energy state, releasing energy through processes such as fluorescence or photoluminescence. Energy transfer to adjacent particles through inter-system crossing may also occur during these optical processes. Such optical phenomena fall within the realm of linear optics, where the principle of superposition applies. The linear optical properties have wide applications in everyday life [10]. In linear optics, the polarization of a material is directly proportional to the electric field, whereas in non-linear optics, this relationship becomes more complex. Non-linear optics is a branch of optics that focuses on the study of light propagation and interaction in materials where the response of the polarization density is non-linear with respect to the electric field of light [11]. Non-linear optical (NLO) phenomena occur when a laser interacts with a material, leading to the generation of new frequencies and altered optical properties. NLO has a wide range of applications in fundamental research and practical technologies, contributing to advancements in various fields of science and engineering. Additionally, properties such as melting point, color, fluorescence, electrical conductivity, magnetic permeability, and chemical reactivity depend on the particle size.

Core-shell nanoparticles represent a special category of nanomaterials that have garnered widespread attention due to their unique properties and applications [12]. As the name suggests, core-shell nanomaterials consist of two parts: an interior "core" and outer "shell(s)." Extensive research has demonstrated that core-shell configurations outperform simple systems composed of individual components, often exhibiting entirely new properties resulting from synergistic interactions between the two. Such systems can also function as smart nanomaterials, responding to stimuli like light, electric fields, magnetic fields, pH, and more [13 - 16]. The design of core-shell structures can be tailored by modifying the constituents or adjusting the thickness ratio of the core and/or shell, allowing for a wide range of possible configurations [17]. By tuning both the core and shell components, an exciting array of customized systems can be generated. These core-shell nanoparticles offer exciting possibilities for high-performance applications. They exhibit excellent electromagnetic interference (EMI) shielding capabilities, allowing them to mitigate electromagnetic disturbances effectively. Additionally, they possess remarkable microwave absorption properties, making them ideal for applications requiring efficient absorption of microwave radiation.

CHAPTER 3

Design, Synthesis and Processing of Carbon Quantum Dots as Smart Nanomaterials

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Abstract: The outstanding optical characteristics, including photoluminescence, photobleaching resistance and light stability of carbon quantum dots, have been increasingly being used in more and more fields, including ideal crudesubstantial for creating sensing materials during the last few years. Carbon quantum dots, which are, in general, tiny carbon nanoparticles (<10 nm in size), have been developed either by "Top-down" or "Bottom-up" approaches, with further modification during the preparation or post-treatment. Majorly, the synthesized carbon quantum dots show high potential towards biomedicine, optronics, catalysis and sensors and are rather dissimilar from those of the bulk material's characteristics. This chapter highlights the techniques involved in design and preparation of high-quality carbon quantum dots. The summary of the reported strategies and techniques for their preparation will hopefully provide a valuable insight for relevant work.

Keywords: Arc-discharge method, Bottom-up method, Carbon dots (CDs), Carbon quantum dots (CQDs), Carbon nanodots (CNDs), Chemical oxidation method, Carbonization method, Electrochemical method, Electron beam irradiation method, Graphene quantum dots (GQDs), Hydrothermal/solvothermal method, Laser ablation method, Microwave assistant pyrolysis method, Synthesis of CQDs, Top-down method, Template method, Ultrasound assisted method.

INTRODUCTION

A strategy, along with the synthesis of quantum dots (QDs), was developed in the early 1980s by Alexey Ekimov in solid (glass crystals) and by Brusin liquid state as a new type of semiconductor and luminescent engineered nanomaterials with a

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characteristic diameter of 2–10 nm [1 - 7]. Groups 2 to 4 and 3 to 5, including Zn, Ag, Cd, Pb, Hg, Ln, Se, P, and Te elements contained in a compound, exhibit the tendency to form QDs. The distinctive optical and electric characteristics like size-tunable light emission, high brightness, narrow emission range and photostability, semiconductors, and QD have emerged to be important functional materials. The presence of extra atoms on the surfaces, due to the 3-dimensional truncation of QDs, makes it unique in properties compared to the bulk materials [8]. Over the last two decades, the developments of high quality QDs resulted in many compounds displaying applications in areas of demand like telecommunication lasers, light-emitting diodes (LEDs), photovoltaics, photoconductors and photodetectors, biomedical and environmental purposes, catalysis and many more [9]. The strong fluorescent property of QDs arises from a large range of versatile element ratios present in the nanoparticles [10]. Consequently, the bandgap is associated with the nanocrystallite size since it stands on the number of atoms that create the band. QDs have an energy bandgap that increases with decreasing particle size and wavelength [11]. QDs show exceptional luminescent characteristics like intake of white light and afterward re-emit certain colours in limited nanoseconds and exhibit extensive continuous absorption spectra, fine emission and very prominent light stability [12]. After minimizing the toxicity of QDs, these materials are used in biomolecule (BM) sensing and imaging-guided targeting, like cancer imaging [13 - 16]. The composition of the core of cadmium selenide in CdSe/ZnS quantum dots ranging from 10 to 50 atoms in diameter and 100 to 100,000 (approx.) atoms in total, used specially as secondary antibody conjugates [17]. The CdSe QDs provide protection against photo-oxidation through the improvement of the fluorescence quantum yield by ZnS or CdS layer around the QD [18]. Among the reported QDs, carbon-based QDs (CQDs) are the special classes of carbon nanoparticles with sizes of particles below 10 nm and having stable optical and electronic properties with unique characteristics such as chemical-stability, alluring fluorescence, water-solubility and magnificent photostability which diverge from bigger particles due to quantum mechanics. CQDs are also recognized by different abbreviations such as carbogenic nanoparticles, carbon dots (CDs), carbon nanoparticles (CNPs), or carbon nanodots (CNDs). In general, a carbon quantum dot can be categorized as graphene quantum dots (GQDs), CQDs/ CDs, CNDs/CNPs and carbonized polymer dots (CPDs) based on the carbon core structure, the surface groups, and the properties of the carbon (Fig. **1**) [19].

In 2004, Xu *et al*. [20] first disclosed fluorescent CQDs during refinement of single-walled carbon nanotubes obtained from the arc-discharge soot. With the rapid expansion of the carbon-derived quantum dots with interesting characteristics with benign, plentiful and inexpensive behaviour, the applications of these nanomaterials have progressively become an expanding target as a novel nanocarbon member (Fig. **2**) [21]. Further, high stability, good biocompatibility, and low toxicity of CQDs make it a good target for wastewater treatment [22, 23].

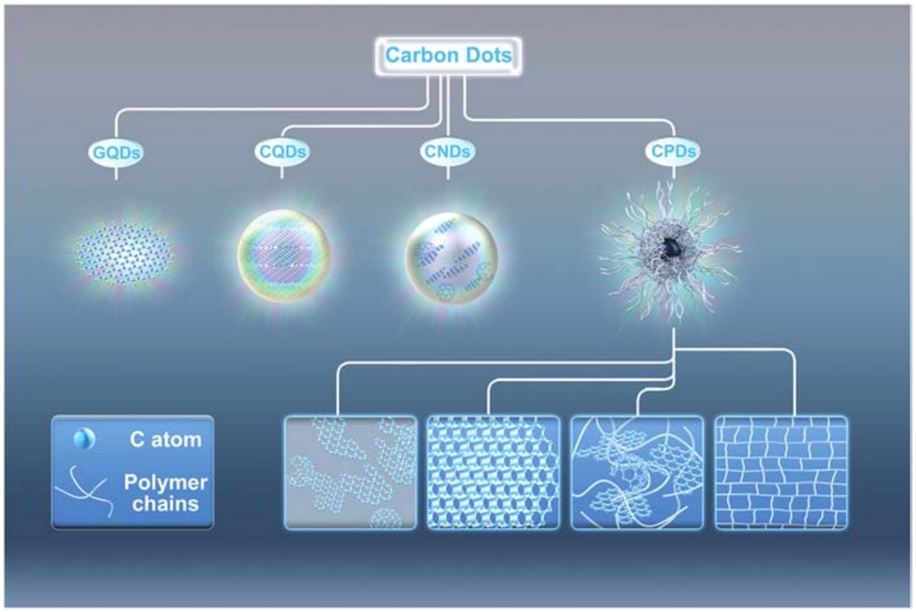

Fig. (1). Different types of carbon dots. (reprinted/reproduced from Ref [19]. Copyright © 2019, The Authors. Published by WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim)

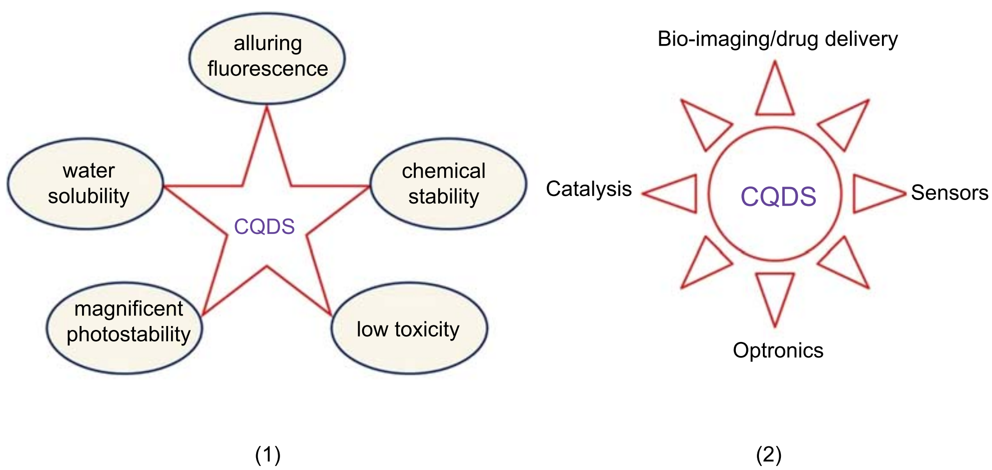

Fig. (2). Properties (1) and applications (2) of CQDs.

Two kinds of synthetic methods [24] *viz*. top-down and bottom-up approaches were applied for the preparation of CQD from organic molecules (Fig. **3**).

CHAPTER 4

Nanomaterials and their Various Applications

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Abstract: In the present review, the concept of nanochemistry and its applications has been lucidly dealt. The idea of miniaturization of materials for harnessing the benefits of size-dependent properties started in the middle of the last century. Due to their tunable physical and chemical properties along with versatile potential applications nanomaterials are technically more advanced than their bulk counterparts. On the basis of size, shape, composition and origin, nanomaterials can be classified. Technological operations throughout the world are mainly controlled by science and engineering. Nanomaterials have opened a new beginning and contributed to various fields of modern science and technology. Nanotechnology fields are evolving that could generate a global market for mineral, non-fuel commodities and agricultural products. Presently, Nanotechnology is characterized as a revolutionary discipline in terms of its influence on industrial applications. Nanotechnology offers probable solutions to several problems using emanating nano techniques. The review covers from definition to classification, various available ways for the synthesis of nanomaterials. It also deals with a wide variety of applications for nanomaterials.

Keywords: Applications of nanomaterials, Biomedical uses, Classification, Characterisation techniques, Electronic application, Energy applications, Environmental remediation, Everyday materials, Future transportation, Future opportunities, Nanomaterials, Nanoparticles, Nanorods, Nanowires, Quantum dots, Speciality of nanomaterials, Synthesis of nanoparticles, Types of nanomaterials.

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INTRODUCTION

Richard P. Feynman, in his talks to the American Society in Pasadena (Dec 1959), explored lots of possibilities that were afforded by the miniatures. He stated that if the things can be made into small scales, they can perform better and save time and space. He revealed that instead of reproducing the pictures and all the other information in its present form, we can write the content in codes dots and dashes to represent various letters [1]. When the word “nanomaterial” was not in existence, Feynman claimed that he did not know how to create things on a small scale. If anyhow it can be made with little elements, such as little wires with 10 or 100 diameters, and the circuits should be a few thousand angstroms, which would be easy to handle. This field was untouched and unknown at that time. He wanted to do something in this field, but at that time, he was not able to do anything due to unknown grounds [1, 2].

Robert F. Curl, the Nobel Laureate, said that Indians were using nanotechnology in earlier times as the sword of Tipu Sultan was one of its examples. The sword was made up of ultra-high carbon steel, also known as Damascus steel. They were extraordinarily strong but flexible enough to bend from hilt to top. The major component of this sword was Wootz steel. The sword was very hard in nature because the nanoparticle of carbon was embedded in the steel. The carbon embedded sword had a very sharp edge [3].

Lycurgus cup [4] is another example of gold and silver nanoparticles from the 4th century. The cup shows dichroism. When a white light reflects on it, it looks green in colour and when a white light is transmitted to it, it looks red. This effect can be obtained by dispersing colloidal gold and silver nanoparticles throughout the glass. The prefix ‘nano’ has found increasing applications in different fields in the last decade. For the public and even for nonexperts, nanoscience, nanomaterials, nanochemistry, and nanotechnology are the few ‘nano’ containing words that can be easily found in newspapers, scientific reports and popular books. The Latin word *nanus* means *dwarf,* which actually signifies very small. The dimension of nanomaterials lies in the range of 1 to 100 nm *i.e.* in the nanometer scale. These are the cornerstones of nanoscience and nanotechnology. These are the tiny materials with higher potential. They can exist in different forms, such as particles, tubes, powders, coatings, *etc*. Nanomaterials can be metals, ceramic, and polymeric or composite materials. The word composites means that it is made up of two or more than two different parts. The dimension of at least one phase must be in the nanometer range [5 - 7]. In other words, composites are a mixture of two or more than two materials that are mixed in the best proportion of the properties of both materials, which can obtain new characteristic properties that the individual constituents cannot have. In the last 20 years, the development of polymeric nanocomposites has become very important. In these composites, one of the materials comprises the dimensions in the order of 10^{-9} m. The output or the final product should not be in the nanometer range, it can be in the range of micro scale or in the macroscopic size [8]. Surface structures with high resolution of these materials have been identified by using scanning tunneling microscopy and scanning tunneling microscopy since 1980 [9]. By using modeling and simulation, characterisation and prediction of properties can be easily done. Nanocomposites are environment friendly that is why they propose new technologies and business opportunities for different types of sectors like aerospace, automotive, electronics and biotechnology industries.

Nanotechnology is the science of very small. Depending on size variations, the molecules show a variety of surprising and interesting results. The potential applications of nanomaterials by using nanoscience and nanotechnology in the biomedical field are remarkable where traditional methods have been restricted. Generations and applications of nanomaterials at macromolecular, atomic and molecular scales [10] are described in nanotechnology.

TYPES OF NANOMATERIALS

Nanomaterials are classified into two groups depending on their origin:

Nanomaterials that have been made Non-intentionally

This kind of nanomaterials occurs naturally in the environment. Different human activities or volcanic eruptions can produce these types of materials without intention, *e.g.*: nanoparticles produced by diesel combustion, even some of the biological components like DNA and protein.

In living organisms, so many activities occur at the nanoscale level. Natural nanomaterials like proteins and other molecules are also used by our human body to control several processes of the body.

Intentionally made Nanomaterials

These are the nanomaterials that are produced through a defined fabrication process, such as engineered nanomaterials (ENMs). ENMs are materials designed at the nanoscale level to take advantage of their small size and novel properties, which are not seen in their big molecules or bulk counterparts. Today, different commercially available products, such as sunscreen, cosmetics, electronics *etc*., are manufactured using ENMs. Based on usage and applications, nanomaterials can also be categorised, as shown in Table **1**.

CHAPTER 5

Nanostructured Metal Oxide-based Positive Electrode Materials for Electrochemical Supercapacitor Applications

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Abstract: Supercapacitors are recognized as a potent device for posterity. It is crucial to take into account the energy and power densities of the supercapacitor. Modern fabrication techniques and the development of better electrode materials will be enabling the supercapacitor to operate at high power and energy densities. Supercapacitors have much attention devoted because of their distinctive traits like high power, long cycle life and environmentally benign nature. They bridge the high-powered conventional capacitors and high energy batteries. There is an enormous scope to improve the energy densities of electrochemical supercapacitors without sacrificing their high-power densities. In this view, a research community has been working extensively to improve the advancement of supercapacitors with various nanostructured materials. A lot of effort has been made recently to enhance the quality and performance of supercapacitors. Activated carbon products with high surface area and porous nature are commercialized. Research communities are looking for an alternative and superior material to replace the commercially available activated carbon material. To match the energy storage quality and performance of commercialized carbon, a variety of alternative materials are available. Various materials, including metal oxide, polymers, and other carbon allotropes, are competing to replace commercially available carbon, but they fall short in terms of performance or cost of manufacture. Nanostructured metal oxides rank among the best materials.

In this chapter, the various nanostructured metal oxides and their electrochemical behaviors as, the positive electrode is critically analyzed from both research and applications perspectives. Here, concise descriptions of various nanostructured metal oxides and their behaviors as positive electrode for supercapacitor applications are explored.

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Keywords: Asymmetric Supercapacitors, Cycling stability, Cyclic voltammetry, Chronopotentiometry, Energy storage, Electrical double layer capacitance, Energy density, Faradic reaction, High Oxidation state, Nanostructured materials, Pseudo capacitance, Power density, Porous materials, Positive electrode, Redox, Rate performance, Specific capacitance, Supercapacitors, Specific surface area, Transition Metal oxides.

INTRODUCTION

The rise in population and urbanization around the world has resulted in high energy demand. The research community is attempting to develop renewable energy sources due to the quick exhaustion of fossil fuels and greenhouse effect brought on by greenhouse gas emissions, such as solar, wind, and hydroelectric electricity that are clean, abundant, and never get exhausted [1, 2]. However, these renewable energy sources are sporadic. As a result, significant effort is being put into developing effective energy storage systems to store excess energy created by renewable energy sources and use it when needed later. Capacitors, supercapacitors, batteries, and fuel cells are the four basic energy storage systems accessible. Because of their high power and energy densities, supercapacitors and batteries occupy an essential position. It is considerably easier to improve the energy density of supercapacitors rather than improve the power density of batteries; researchers are experimenting with various materials to improve the energy density of supercapacitors without sacrificing their power density [3, 4]. The materials investigated for supercapacitors are broadly classified into three types: carbon materials, metal oxides, and polymer-based materials [5]. Carbon materials store charges electrostatically and behave like electric double layer capacitors (EDLC), while metal oxides and polymers store charges electrochemically and behave like pseudocapacitors [6]. Still supercapacitors need to improve their performance and future requirements in hybrid electric vehicles and other electronic materials by tuning the nano sized functional materials. Nanomaterials and nanostructured materials have figured prominently in the evolution of several essential technologies in recent years [7 - 9]. In addition to the size, nanomaterials differ from bulk materials in that they could have unique physical properties that open up new possibilities for a range of technical applications. The electrode materials for electrochemical supercapacitor applications should have a large surface area, and nanostructured materials provide a large surface area and better charge accessibility over their surfaces. High capacity is expected from the nanostructured materials containing high surface area materials with more electro-active sites. So, the high surface area with more mesopores and, greater accessibility of electrolyte ions and greater stability makes the nanostructured materials as prospective electrode materials for energy storage applications [10 - 12]. Pseudocapacitive materials, metal oxides and polymers deliver higher capacitance through their characteristic redox reactions with various ions, which pertains to higher capacitance than the DLC with carbonaceous materials [13 - 15]. Metal oxides override the polymer electrode materials because of their ease and cost-effective preparation methods and large-scale productions. Transition metal oxides are characterized by both organic and aqueous electrolytes however aqueous electrolytes are extensively studied because of their low cost and not having to deal with any complicated conditions [16 - 18]. The goal of this chapter is to summarize nanostructured metal oxides as positive electrode materials for supercapacitor applications with improved electrochemical performance and enhanced energy density. Its improvements as a potential alternative for commercially available carbon materials are the goal of this chapter.

Types of Supercapacitors by Its Energy Storage Mechanism

Based on the energy storage mechanism, supercapacitors can be Electric double–layer capacitors and pseudocapacitors [6].

Electric Double – Layer Capacitors

The charge storage in electric double-layer capacitors is solely electrostatic; the charge is stored between the electrode and electrolyte interfaces. The amount of electrostatic charge accumulation is determined by the surface area of the pores and the accessibility of ions. Generally, EDLC is formed by carbon-based materials like activated carbon (AC), carbon nanotube (CNT) graphene, and so on. The carbon materials that possess low electrical resistance will behave as EDLC. In EDLC, an electrolyte-soaked permeable membrane separates two electrodes, each of which forms an electrode-electrolyte interface and is referred to as a half-cell. Asymmetric full cell or symmetric supercapacitors were made by joining two half-cells separated by a permeable membrane. In symmetric supercapacitors, an electrode or half-cell is connected with another by a series connection, so the total capacitance of the supercapacitors is calculated by the equation (1).

$$\frac{1}{C_{Total}} = \frac{1}{C_1} + \frac{1}{C_2} \tag{1}$$

Where, C_{Total}, C_1 and C_2 are the total capacitance of the symmetric supercapacitors, half-cell capacitance of the first and second electrodes.

CHAPTER 6

A Brief Review of the Current Scenario on the Synthesis and Application of TIO_2 Nanoparticles

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Abstract: TiO_2 nanomaterials can be synthesized in various types of structures, such as nano-powder, nano-films, nano-rods, nano-crystals, *etc*., by various methods such as biological, precipitation, hydrothermal, electrochemical, solvothermal, spray pyrolysis, co-precipitation, micro-emulsion, solution-combustion, and sol-gel, *etc*. Each method has unique importance, merits, and demerits. Such as biological method is an eco-friendly method and avoids toxic chemicals in the preparation of TiO_2-based nanomaterials. The co-precipitation technique is very convenient and easy, but its control over size distribution is not good, which results in coarser particles instead of nanoparticles. The micro-emulsion method facilitates good control over the particle size by the ratio of surfactant to water, low reaction temperature, and short processing time. The sol-gel method has high homogeneity in crystals, better tuning over the shape and size of the crystals with reasonable preparation cost. The hydrothermal and solvothermal processes have good chemical uniformity and a higher probability of synthesizing unique metastable structures at minimum reaction temperatures but nanomaterials synthesized *via* these methods are not stable for application at the higher temperature. The electrochemical technique facilitates a multifaceted and minimum temperature method to synthesize TiO_2 nanoparticles with good control over crystallite size, better yield, and negligible environmental effect. To synthesize the nanostructures of TiO_2, liquid phase processing is the most convenient method since it gives better homogeneity in the product with good control over shape and size. In this chapter, short literature regarding the synthesis of TiO_2 nanostructure by various methods and its applications are discussed. Moreover, the regeneration of used TiO_2-based nanoparticles is also reported.

Keywords: Anatase, Air treatment, Crystal shape, Crystal size, Dye-sensitized solar cell, Nanoparticles, Nano-films, Nano-rods, Photocatalysis, Photodegradation, Reuse, Regeneration, Rutile, Semiconductors, Solar device, Synthesis, Titanium dioxide, Titania, TiO_2, Water treatment.

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INTRODUCTION

As a photocatalyst, nanomaterials are used very frequently in the photocatalytic process since nanomaterials have a huge surface area, a high number of reactive atoms, and vacant reactive sites. Among various nanomaterials, TiO_2 has achieved great attention in the last three decades due to its great physio-chemical stability, non-toxicity, high chemical stability, and minimum cost [1, 2].

TiO_2 has wide applications in various products such as electrochemical electrodes [3], paint-pigments [4], sunscreen lotions [5], capacitors [6], solar-cells [7] and toothpaste [8], *etc*. Three different phases of titanium dioxide, namely anatase, rutile, and brookite, are found [9]. Each phase has unique properties in terms of morphology, crystal structure, stability, bandgap energy, particle size, *etc*. These properties of TiO_2 nanomaterials depend on their synthesis route. The various routes are applied for the preparation of titanium dioxide based photocatalysts, like as sol-gel [10, 11], chemical vapour deposition [12, 13], hydrothermal [14, 15], micro-emulsion route [16, 17], *etc*. In this article, literature regarding the synthesis technique of TiO_2 photocatalyst is discussed.

SYNTHESIS TECHNIQUE OF TIO_2 NANOPARTICLES

Biological Method

In this technique, nanoparticles are synthesized with the help of micro-organisms, including bacteria (*Pseudomonas deceptionensis, Weissella oryzae, Bacillus methylotrophicus, Bhargavaeaindica, etc*.), fungi (*Neurospora crassa, Actinomycetes),* and yeasts (*Yarrowia lipolytica* NCYC 789, *Rhodosporidium diobovatum,* Extremophilic yeast), *etc*. Micro-organisms have the ability to reduce metal salts to metal nanomaterials with narrow size distribution and low polydispersity due to various reductase enzymes [18].

Cui *et al*. synthesized the biometric mesoporous titanium dioxide using yeast cells as templates. The synthesized TiO_2 structure has the majority of the anatase phase and light conductive carbon. The structural analysis revealed that the synthesized TiO_2 sample has a hierarchical mesoporous structure with a pore size between 4.7 and 11.3 nm. They also reported excellent electro-catalytic activity of bio-templated mesopores titanium dioxide air electrodes for O_2 reduction in alkaline solution [19].

Jha *et al*. reported a biosynthesis of TiO_2 nanoparticles by reproducible microbes (*Lactobacillus* sp. and *Sachharomyces cerevisae*). The synthesized nanoparticles had a particle size range from 8-35 nm. They reported that the pH and partial pressure of hydrogen (rH^2) or redox potential of the culture solution play an essential role in the biosynthesis technique of titanium dioxide nanoparticles [20].

Kirthi *et al*. prepared TiO_2 nanoparticles *via* the bacterium *Bacillus subtilis*. The dominant anatase phase of TiO_2 nanoparticles was produced by abundantly available microbes *Bacillus subtilis*. The size of synthesized nanoparticles was 66-77 nm with a spherical shape [21].

Dhandaoani *et al*. synthesized microbial-mediated TiO_2 nanoparticles by *Bacillus subtilis* and used them to destroy bacteria within a biofilm through H_2O_2. The synthesized photocatalysts had an anatase phase with a particle size range from 10-30 nm. They reported that the biogenic TiO_2 nanoparticles act as a promising photocatalyst due to the formation of hydrogen peroxide in the region of titanium dioxide biofilm interfaces to put down the germination of water-based biofilm [22].

Solution Combustion Method

This technique is also called combustion synthesis (CS) [23]. Kingsley *et al*. additionally modified this method by incorporating it with a wet chemical method and renamed it solution combustion synthesis (SCS) [24, 25]. In this method, an exothermic reaction beginsunder heating and goes through self-sustained expansion. It is a simple and economical technique for nanomaterials synthesis. Nano-structures of ceramics, composites, alloys, and inter-metallic can be prepared *via* solution combustion technique [26]. This process has the following steps: (**i**) initial heating (**ii**) keeping the content for 3-5 min at 350°C (depending on the precursor) (**iii**) grinding and calcination. Since this technique uses a solution methodology, it has possibilities of liquid chemical methods, like stoichiometry, regulation, and the appropriate doping quantity [27]. In the combustion process, a higher temperature confirms the occurrence of the desired phase composition. A considerable amount of gas formation during solution-combustion synthesis restricts the enlargement of particle size and permits the development of nanosized products [28]. In the solution-combustion method, various metal salts like NO_3, SO_4, and CO_3 are utilized as starting material [24]. In contrast, for the combustion reaction, $C_6H_8O_7$ [29], NH_2CONH_2 [30], $C_2H_5NO_2$ [31], $C_2H_{12}O_6$ [32], and $C_{12}H_{22}O_{11}$ [33] are taken as the fuels.

Rajeshwar and Tacconi synthesized the TiO_2 fine powder *via* the solution combustion route. The $TiOSO_4$ or $TiO(NO_3)_2$ was taken as a precursor, whereas urea and thiourea were used as fuel. The TiO_2 powder that was synthesized *via* this route had an anatase phase of TiO_2 with a bandgap energy of 2.40-3.10 eV. They reported that urea inhibits the development of the rutile phase during the

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