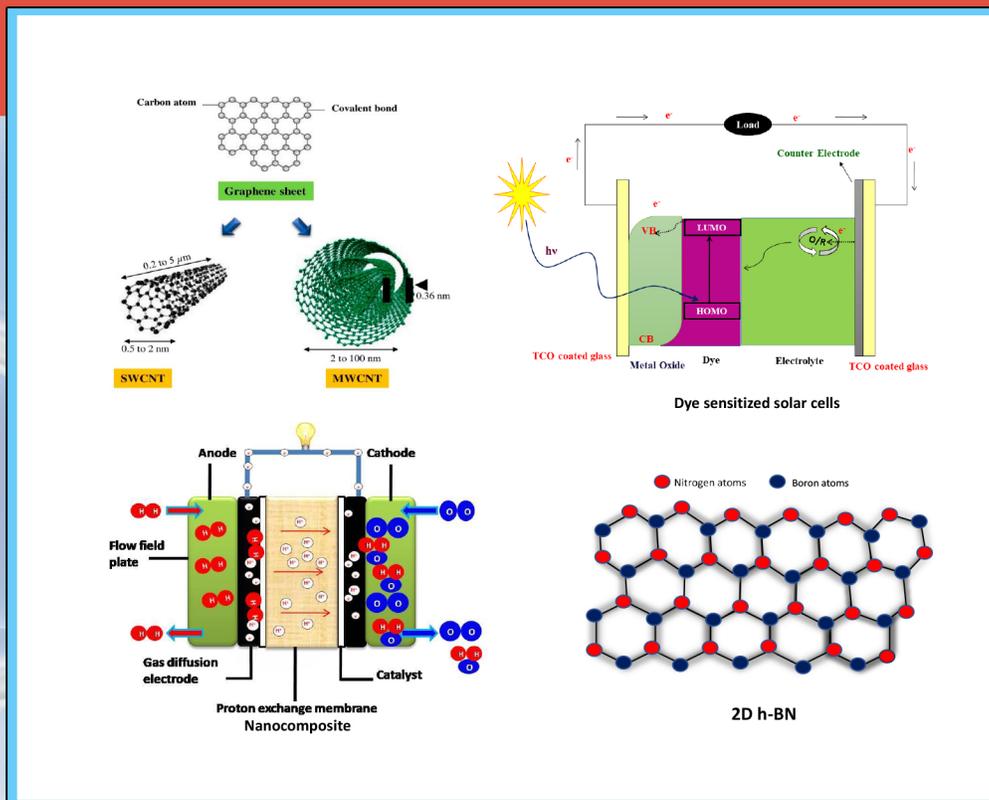


APPLICATIONS OF NANOMATERIALS IN ENERGY STORAGE AND ELECTRONICS



Editors:
Gaurav Manik
Sushanta Kumar Sahoo

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**Current and Future
Developments in Nanomaterials
and Carbon Nanotubes**

(Volume 3)

***Applications of Nanomaterials
in Energy Storage and Electronics***

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FOREWORD

In the 21st century, depleting fossil fuel resources and environmental concerns have created huge challenges in meeting adequate energy production and storage. Undoubtedly, the ground-breaking nanotechnology may be the only solution to meet the demands of mankind in the future by producing a secure, green and sustainable energy. Carbon-based and other advanced functional nanomaterials have enormous potential to produce and save energy through effective and sustainable approach, and also to support suitable applications in the field of opto- and bio-electronics.

This unique book by the editors (Dr. Manik and Dr. Sahoo), comprising about fifteen chapters presents an excellent overview and current state-of-the-art future generation nanostructured materials like carbon nanotubes, carbon nano onions, nanowires, graphene, 2D boron nitride, metal oxides, quantum dots, metal organic frameworks (MoFs) *etc.* and their respective nanocomposites. Such materials find great applications with regard to efficient storage of energy like solar, hydrogen and electrochemical energy. These materials find enormous applications in fuel cells, supercapacitors, bio-sensors and opto-electronic nano-devices, ferroelectric liquid crystal nanocomposites for optical memory, future display devices and electronics. Considering these aspects, I believe that the book shall find great use in the scientific and engineering community.

It is notable that the book chapters have been contributed by several researchers from premier institutes who carry extensive experience and knowledge in the relevant fields. Further, the book is well edited, quite consistent and focused on enrichment of the knowledge of the readers. This is an excellent masterpiece for students, academics and industry researchers.

This book shall, therefore, be an impactful addition in the area of application of next generation nanomaterials in the field of energy storage and electronics. The reported work will be important to many groups of researchers and industry experts across the globe, including, but not limited to, those working in materials science, chemical engineering, biotechnology, polymer science, physics, chemistry and renewable energy.

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PREFACE

Nanotechnology is one of the research areas most focused on the development of a new class of nanomaterials that offer enhanced material or product performance by exploiting synergism. Due to the growing demand in the area of energy and electronics, nanomaterials and their hybrids have shaped the research in the relevant fields with remarkable attention as advanced multifunctional materials with desired efficiency, higher durability and improved stability.

Currently, the applications of nanomaterials in the field of energy harvesting, storage and opto-electronics are booming, which has resulted in an upsurge in the number of publications, patents and technology transfers worldwide. Despite this, relatively only a few books have focused on nanomaterials applied to energy and electronics. Therefore, the editors found it an opportunity to edit a book on “*Current and Future Developments in Nanomaterials: Applications in Energy Storage and Electronics*”. We hope that the present book will immensely benefit scientists, engineers, academic researchers, research scholars and post graduate students working in the area of nanomaterials. This book consists of 15 chapters that describe the recent advancements in synthesis and applications of nanomaterials in energy harvesting and storage, and also technology in the field of opto-electronics for next generation devices. Some of the chapters summarize the recent progress in applications of nanomaterials like Carbon Nanotubes, Metal Oxides, and Graphene oxides-based hybrids in solar energy harvesting using recent Photovoltaic Technologies. Similarly, some of the chapters review the fundamentals and state-of-the-art developments in Nanowires, Graphene Quantum Dots, Boron nitrides, Carbon Nano Onions and Metal Organic Frameworks leading to the fabrication of Supercapacitors, Bio-sensors, Lithium ion batteries and Hydrogen storage applications. Further, a few chapters discuss the next generation fuel cells using Polymer Nanocomposites, Ferroelectric Liquid Crystal Nanocomposite and Opto-electronic Nanomaterials for optical memory and displays devices.

The editors are extremely thankful to the esteemed and experienced contributors of all chapters and also the Bentham Science Publishing team for their kind support. We hope that the content presented herewith in a simple and concise form shall serve as a comprehensive guide to benefit the readers and elevate their knowledge in this increasingly advancing area.

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CHAPTER 1**Carbon Nanotube Based Nanomaterials for Solar Energy Storage Devices****Ravi Prakash¹, Sunil Kumar^{1,2} and Pralay Maiti^{1,*}**¹ School of Materials Science and Technology, Indian Institute of Technology (BHU), Varanasi 221005, India² Department of Chemistry, L.N.T. College (B.R.A. Bihar University), Muzaffarpur-842002, India

Abstract: Carbon nanotubes (CNTs) and their nanocomposites are used in various products and technologies due to their unique characteristics. For their future implementation, the manufacturing of CNTs with appropriate specifications has gained momentum in the area of nanoscience and technology. Conventional phase change materials used in solar thermal energy storage have low thermal conductivity. CNTs are used to prepare phase change materials with high thermal conductivity to solve this issue. This chapter addresses the synthesis, structure, and properties of CNTs. The different varieties of solar energy storage systems used to store solar radiation are also discussed. Further, we explain the phase change materials (PCMs) as suitable solar thermal energy storage systems and discuss the methods to prepare CNT-based nanomaterials for use as a heat transfer fluid (HTF) after using the CNTs based PCMs in solar storage systems. CNT based nanomaterials as a heat transfer fluid significantly increase the effective receiving efficiency, thermal conductivity, and absorption coefficient of such storage systems.

Keywords: Arc discharge, Carbon nanotubes, Chemical vapour deposition, Electrolysis, Graphene, Heat transfer fluid, Laser ablation, Multi-walled carbon nanotubes, Nanomaterials, Nanotechnology, Phase change materials, Photovoltaic, Single walled carbon nanotubes, Solar cells, Solar energy storage devices, Solar radiation, Thermal conductivity, Sonochemical, Specific heat capacity.

INTRODUCTION

The production of renewable energy, consumption, and storage are major global challenges for researchers [1 - 3]. Solar energy devices that convert solar energy directly into electrical energy are called solar cells [4, 5]. There are significant

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research and development efforts underway to improve the device efficiency and lower the fabrication cost [3, 4, 6 - 8]. Photovoltaic devices are already used in the current era, but the devices suffer from insufficient durability and higher expense for fabrication. Further, solar energy production is mainly dependent on weather conditions; that is why solar power generation is irregular and unpredictable. Moreover, the energy requirement is considerably high in the daytime, and solar energy is available only for a small number of hours, creating the problem of maintaining a balance between the requirement and supply [9]. These two factors are the driving force behind the development of efficient solar energy storage devices, which may help reduce the fluctuation arising from the generation side and provide the possibility of performing auxiliary services. Energy storage systems are thus increasingly reducing the mismatch between need and supply and improving the work capability and reliability of energy systems which play a crucial role in conserving the produced energy [10, 11]. The conventional mechanism of the solar energy storage device is to convert the solar energy into electrical energy through solar panels and then store it in batteries, but it suffers from the issue of high manufacturing costs. In recent years, some research groups have introduced phase change materials (PCMs) as an alternative method for solar energy storage [12]. Since then, the developments of phase-change materials have become a hot research topic. The solar thermal energy storage devices are fabricated using PCMs due to their excellent stable form during phase transition.

In this method, the solar energy is converted into thermal energy using the PCMs and stored in a storage tank, which acts as a thermal battery [12 - 14]. Nanotechnology is an important field in the development of modern technology and attracts researchers in all fields. Carbon nanotubes are prime members of the research and development in nanotechnology. CNTs are classified into two categories (Fig. 1) based on a number of layers present in the structure; (1) single-walled carbon nanotubes (SWCNTs) and (2) multi-walled carbon nanotubes (MWCNTs). The physicochemical properties are shown in Table 1. CNTs possess high thermal, mechanical, and electrical characteristics, making them suitable for developing smart composite materials used in energy storage devices, field emitters, sensors, and so on [15]. This chapter deals with CNT-based nanomaterials, their synthesis, properties, and applications in solar energy storage devices. CNTs have been used in various technologies, depending on their attractive electrical, mechanical, and thermal properties [16]. They are primarily used in electronics [19], transistors, and display technologies, owing to their electrical properties [20, 21].

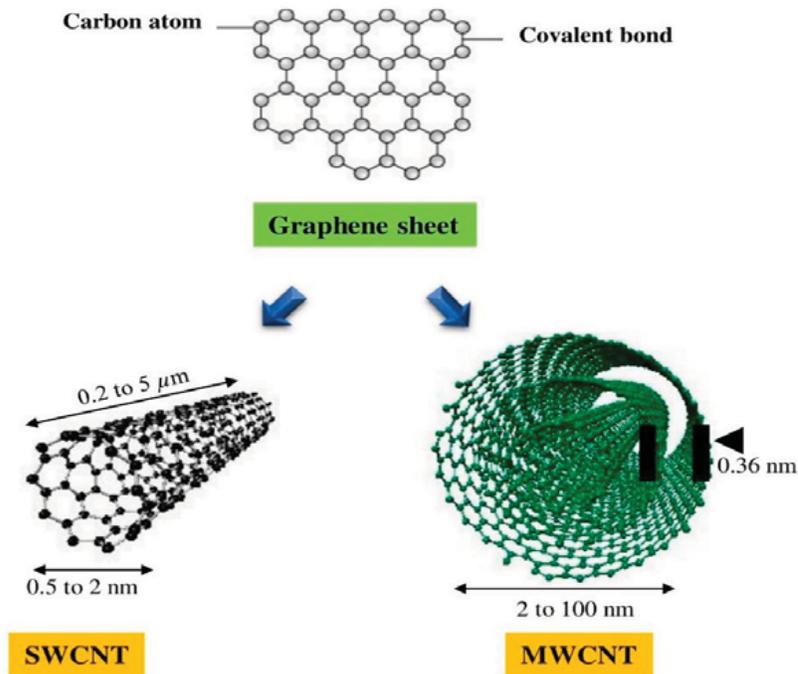


Fig. (1). Conceptual diagram of SWCNTs and MWCNTs; Reprinted with copyright permission from Ref [17, 18].

CARBON NANOTUBES

Carbon nanotubes contain sp^2 hybridisation and assume different structures with graphite as a well-known example. Graphene is a 2-dimensional (2D) single layer of graphite in the list of carbon nanomaterials. Graphene is stronger than diamond because it contains sp^2 hybridisation, which is stronger than sp^3 hybridisation in a diamond.

The sp^2 hybridized carbon can form open and closed cages with honeycomb structures [22] and Kroto *et al.* [23] discovered such kinds of structures. Carbon nanotubes are large molecules of pure carbon that are long, thin and tube-like, about 1-3 nanometres in diameter, and hundreds to thousands of nanometres long.

CHAPTER 2

Recent Advances on Carbon Nanostructure-Based Biosensors

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Abstract: Carbon-based nanostructured materials have derived substantial attention as novel functional materials towards the fabrication of various biosensing platforms owing to their interesting physicochemical and optoelectronic properties, as well as desired surface functionalities. These nanomaterials provide increased and oriented immobilization of biomolecules along with maintaining their biological activity in view of their lower cytotoxicity and higher biocompatibility. The integration of carbon nanomaterials with biosensing platforms has provided new opportunities and paved the way for the efficient detection of various biomolecules and analytes. These nanostructured materials-based biosensors have improved biosensing characteristics, including broader linear detection range, lower detection limit, better selectivity, and higher sensitivity. This chapter summarizes the results of different electrochemical and fluorescent biosensors related to various nanostructured carbon materials, namely carbon nanotubes (CNTs), graphene and its derivatives (reduced graphene oxide (rGO), graphene oxide (GO), graphene quantum dots (GQDs) and carbon dots (CDs).

Keywords: Biosensor, Carbon dots, Carbon nanotubes, Electrochemical, Fluorescent, Graphene, Graphene oxide, Graphene quantum dots, Heteroatom doping, Nanomaterial, Nanostructured, Reduced graphene oxide, Surface functionalization.

INTRODUCTION

The interest in developing advanced biosensors accompanied by nanostructured materials is rapidly increasing over the last two decades. With the advent of nanoscience and nanotechnology, these biosensors can provide various desirable

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characteristics, including higher sensitivity, good selectivity, low cost, faster response, miniaturization, portability, simple operation, and accurate detection [1 - 6]. Among the various types of nanostructured materials, carbon nanomaterials have aroused enormous scientific attention toward creating biosensing platforms because of their fascinating functional, optical, electronic, physiochemical, mechanical, catalytic, and biocompatible properties [7, 8]. Additionally, these nanomaterials possess strong adsorption ability, larger surface area, greater electron-transfer kinetics, ease of surface functionalization, enabling the oriented immobilization of biomolecules, providing enhanced analytical performance with desirable biosensing characteristics [1, 9, 10].

The family of nanostructured carbon materials includes fullerene, carbon nanotubes (CNTs), graphene and its derivatives (GO, rGO), nanodiamond, carbon dots (CDs), carbon nanofibers, and graphene quantum dots (GQDs), *etc.* [11, 12]. The graphite with sp^2 hybridization and diamond with sp^3 hybridization are the two commonly known allotropic forms of carbon [13]. These nanostructured materials are classified according to the geometrical structure of the particles (spheres, ellipsoids, horns, rods, sheets, foams, or tubes) and dimensionalities (0D, 1D, 2D, and 3D). For instance, Fullerenes 0D form of carbon possesses spherical or ellipsoidal nanoparticles [14], whereas CNTs 1D form of carbon contains tube-shaped particles [15]. Interestingly, carbon-based nanostructured systems can lead to the development of novel bioanalytical technologies, advantageous for detecting various infectious and non-infectious diseases [16, 17]. The surface properties of carbon nanomaterials can be easily tailored, facilitating them to conjugate with different diagnostic or imaging agents toward the development of next-generation biosensors [1].

As stated by the International Union of Pure and Applied Chemistry (IUPAC), the biosensor is “a device that utilizes specific biochemical reactions mediated by isolated organelles, whole cells, tissues, immunosystems or enzymes for detecting chemical compounds or analytes generally *via* optical, thermal or electrical signals” [18]. Basically, a biosensing system comprises three key components: a bio-recognition element, also known as a bioreceptor that selectively recognizes the target analyte, an immobilization matrix wherein biomolecules are immobilized, and the transducer that converts the input biological signal into a measurable output signal [19, 20]. The nanostructured materials can be used as an immobilization matrix in the electrochemical biosensors to integrate the biomolecules with a transducer surface. Owing to strong adsorption ability and a larger surface-to-volume ratio, these nanomaterials offer increased biomolecule loading and maintain immobilized biomolecules’ functionality. Moreover, these materials provide faster electron transfer kinetics between the electrode surface and active sites of biomolecules, prevailing the fabrication of an efficient

biosensing platform [21]. Alternatively, owing to the inherent photoluminescent and interesting optical (absorption in UV or NIR regions) properties, carbon nanomaterials (CDs and GQDs) are utilized as energy donor species for the fabrication of fluorescent biosensor [7]. On the other hand, graphene-based layered materials have been used as energy acceptor species or fluorescence quencher to detect various analytes [22].

In this chapter, efforts have been made to present the recent advancements over the last decade in carbon nanostructured-based biosensors. This chapter's application is restricted to electrochemical and fluorescent biosensors based on various nanomaterials, including CNTs, graphene, GO, rGO, CDs and GQDs. The first section focuses on CNTs based biosensors. The second section outlines graphene and its derivatives-based biosensors. The third section explores the recent advancements pertaining to CDs and GQDs based biosensors.

CNTS BASED BIOSENSORS

CNTs are the 1D allotropes of carbon and were discovered by S. Iijima in 1991 [15]. CNTs can be classified into two dichotomies: multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs). SWCNTs are the single graphene sheet rolled into a cylinder, whereas MWCNTs are the stacked concentric graphene sheets, having 0.34 nm interlayer spacing and rolled into a cylinder. The basic structure of CNTs can be chiral, armchair, or zigzag, described by a vector (n, m) that decides the chemical and physical characteristics of CNTs [1]. In general, CNTs possess a unique sp^2 -hybridized carbon surface, higher thermal and electrical conductivity, high surface area, high mechanical strength, and excellent chemical stability [2]. Besides, CNTs provide the ease to functionalize with numerous targeting ligands and polymers (functional groups) through noncovalent or covalent interactions [1]. In line with this, Farias *et al.* reported the carboxylic functionalized MWCNT (MWCNT_f) based electrochemical biosensor toward the sensitive detection of flutamide (an anticancer drug) in urine and pharmaceuticals samples using the cyclic voltammetry (CV) technique. The presence of MWCNT_f presented an improved catalytic ability to reduce or oxidize the flutamide [23]. In another work, Nasrabadi and the team demonstrated the electrochemical biosensor based on fullerene functionalized ionic liquid (1-butyl-3-methylimidazolium tetrafluoroborate) and CNT for the quantification of diazepam in real samples (tablets, urine, and serum). Enhanced electrocatalytic behavior toward the reduction of diazepam was observed with a limit of detection (LOD) of 87 ± 2 nM and a linear detection range of 0.3–700.0 μ M [24]. Nishimura and co-workers reported the sulphuric acid (H₂SO₄) functionalized SWCNT-based flexible electrode for dopamine detection with an improved LOD of \sim 100 nM compared to the non-functionalized

CHAPTER 3

Carbon Nano-Onions: Synthesis, Properties and Electrochemical Applications

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Abstract: Carbon nano-onions (CNOs) or multilayered fullerenes have received considerable attention in diversified research areas such as supercapacitors, fuel cells, batteries, photovoltaics, and biosensors due to their unique physicochemical, optical, catalytic, and electronic properties. These structures were first observed in 1992, and ever since, a considerable amount of research on their physical properties and development of CNOs based supercapacitors and sensors has been successfully witnessed. CNOs are prepared *via* different experimental techniques, and their structural and physical properties often rely upon the fabrication process or parameters. This chapter presents an overview of different methods that have been adapted to prepare CNOs and their novel properties with a focus on the fundamental curvature morphology effects. A comprehensive discussion on the potential applications, citing recent research, is provided. The challenges and the potential directions of CNOs-based materials with an eye to develop highly efficient and long-term stable CNOs-based energy storage devices and sensors are also addressed.

Keywords: Anode materials, Carbon nano-onions, Carbon nanomaterials, Fullerenes, Flame-assisted synthesis, Glucose sensors, Immunosensors, Lithium-ion batteries, Raman spectra of CNOs, Supercapacitor electrodes.

INTRODUCTION

Nanostructured carbon materials have been a subject of interdisciplinary research since Curl, Kroto, and Smalley discovered the fullerene 'C₆₀' in 1985 [1]. Gradually, several other carbon-based nanostructures have been found, including carbon nanotubes (CNTs) [2], carbon nanohorns [3], nanodiamonds [4], graphene [5], and graphene quantum dots (GQDs) [6]. In 1992, Ugarte [7] discovered multi-shell fullerenes composed of concentric shells of carbon atoms known as carbon nano-onions (CNOs). He noticed that an irradiation process causes *in-situ*

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structural modification of amorphous carbon into spherical-shaped CNOs with a diameter of less than 50 nm. In this process, an intense electron beam causes graphitization and curling of the amorphous carbon. Typically, the distance between each fullerene layer is found to be 0.335 nm, which is almost the same as the distance between two graphitic planes [7].

Recently, the CNOs have received enormous interest due to their potential industrial applications in catalysis, supercapacitors, sensors, etc [8 - 14]. Subsequently, synthesizing CNOs of the desired size with a simple and economical approach becomes the core research theme for numerous researchers. To date, several approaches for producing CNOs have been identified, including thermal annealing of nanodiamonds, arc-discharge in water between two graphite electrodes, chemical vapor deposition (CVD) and plasma radiation, etc [14 - 18]. However, most approaches are limited to solid-state strategies that necessitate relatively high energy-assisted conditions. Recently, a flame-assisted pyrolysis method has been reported to synthesize CNOs using vegetable oils and clarified butter as carbon precursors [19, 20]. Furthermore, the flame-based pyrolysis method renders CNOs in gram scale yields with well-controlled chemical, structural and morphological properties. This chapter encompasses the recent advances in the synthesis and characterization of CNOs, and their structural, physical, and chemical properties and potential applications.

PRODUCTION AND STRUCTURAL PROPERTIES OF CNOS

The most widely used method to produce CNOs is align="center"annealing nanodiamond (ND) particles at high temperatures under high vacuum conditions [21, 22]. Fig. (1) depicts a summary of the selected structural and chemical properties of CNOs derived from nanodiamonds at different annealing temperatures [23]. In brief, the graphitization of nanodiamonds began on the surface at 600 °C and eventually proceeded to the core of the NDs. The conversion of sp^3 to sp^2 occurred in the temperature range from 900 °C to 1100 °C and was followed by the graphitization of amorphous carbon. However, it has been discovered that the NDs are completely transformed into CNOs at temperatures above 1600 °C. Further increase in annealing temperature and annealing time of NDs resulted in polygonal-shaped CNOs. This research also revealed that increasing the annealing temperature of NDs from 1100 °C to 1900 °C increases the ratio of sp^3 carbon to sp^2 carbon atoms in the as-produced CNOs from 0.39 to 1. Simultaneously, the increase in the annealing temperature, particularly above 1700 °C, causes an increase in electrical conductivity up to 4 S cm^{-1} due to more sp^2 carbon formation [23, 24]. The carbon shells of CNOs become more graphitic with increased sp^2 carbon content, leading to an increase in electrical conductivity. Even though the CNOs have a lower conductivity than

graphite and graphene, it is comparable to carbon black ($1\text{--}2\text{ S cm}^{-1}$) and activated carbon (0.5 S cm^{-1}) [25]. A recent study found that annealing in the argon atmosphere rather than vacuum condition results in few-layer graphene flakes between the carbon onions, which improves electrical conductivity [26].

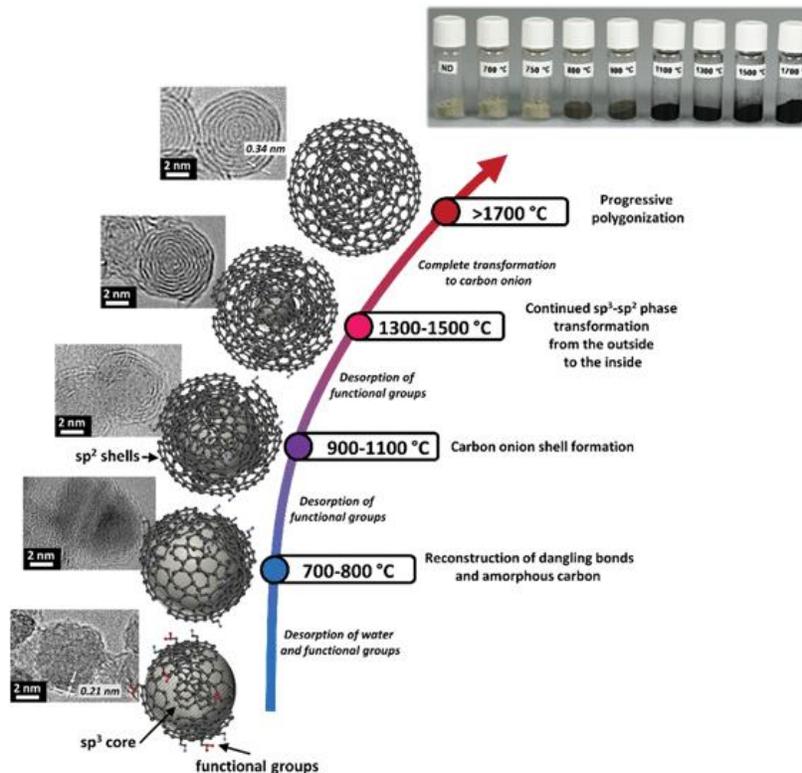


Fig. (1). Structural, and chemical properties of CNOs obtained *via* high-temperature annealing of NDs. Transmission electron micrographs (TEM), digital photographs, and schematic representation of intermediate stages of NDs depending on the annealing temperature during the transformation from NDs to CNOs [23]. (Reprinted with or reproduced from the permission from Royal Society of Chemistry ref.23).

CNOs are also synthesized using the arc-discharge method [27], which involves passing a high voltage and current through two graphite electrodes immersed in water. This process produces hollow-CNOs with 20–30 graphitic layers with particle diameters ranging from 15 to 25 nm. Chemical vapor deposition (CVD) was also deployed to synthesize spherical-shaped CNOs with diameters ranging from 5 to 50 nm [28, 29]. Furthermore, CNOs were efficiently and cost-effectively prepared by the pyrolysis of propane [30] and plastic wastes [31].

Recently, the CNOs have been produced *via* a flame-assisted pyrolysis of vegetable oils and clarified butter [20]. The flame naturally creates a high-

CHAPTER 4

Graphene Based Hybrid Nanocomposites for Solar Cells**Sachin Kadian^{1,2}, Manjinder Singh¹ and Gaurav Manik^{1,*}**¹ *Department of Polymer and Process Engineering, Indian Institute of Technology Roorkee, Roorkee, Uttarakhand, 247667, India*² *Department of Electrical and Computer Engineering, University of Alberta, Edmonton, AB T6G 1H9, Canada*

Abstract: Over the last few years, due to its exceptional two-dimensional (2D) structure, graphene has played a key role in developing conductive transparent devices and acquired significant attention from scientists to get placed as a boon material in the energy industry. Graphene-based materials have played several roles, including interfacial buffer layers, electron/hole transport material, and transparent electrodes in photovoltaic devices. Apart from charge extraction and electron transportation, graphene protects the photovoltaic devices from atmospheric degradation through its 2D network and offers long-term air or environmental stability. This chapter focuses on the recent advancements in graphene and its nanocomposites-based solar cell devices, including dye-sensitized solar cells (DSSCs), organic solar cells (OSCs), and perovskite solar cells (PSCs). We further discuss the impact of incorporating graphene-based materials on the power conversion efficiency for each type of solar cell. The last section of this chapter highlights the potential challenges and future research scope of graphene-based nanocomposites for solar cell applications.

Keywords: Bulk heterojunction, Carbon nanotubes, Dye-sensitized solar cells, Electron transport layer, Graphene, Graphene oxide, Graphene quantum dots, Hole transport layer, Organic solar cells, Open circuit voltage, Perovskite solar cells, Reduced graphene oxide.

INTRODUCTION

The rapidly increasing demand for clean energy, led by the escalation of high-speed, wearable, and portable optoelectronic devices, has accelerated the development of advanced techniques to combat unprecedented challenges.

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For decades, sunlight has been explored as a safe, clean, and economical source of energy that could generate electricity deprived of creating any environmental issues. In this, photovoltaic materials aid the conversion of solar energy into electricity through the photovoltaic effect, and thus, a solar cell is also known as a photovoltaic cell [1]. Further, the structure and properties of these photovoltaic materials can be tailored with the help of nanotechnology to develop highly efficient devices. Therefore, several new technologies, materials, and synthetic approaches have been discovered and continue to be implemented. Recently, due to graphene's attractive characteristics, including high carrier mobility, good optical transparency, zero-band gap, and desired mechanical strength, graphitic materials have been extensively explored for solar cell applications [2]. More specifically, due to the several functional groups including carbonyl, carboxylic acid, hydroxyl, and epoxy, reduced graphene oxide (rGO) and graphene oxide (GO) have been practically employed as attractive derivatives of graphene to synthesise graphene-based nanocomposites [3, 4]. Furthermore, the existing oxygen-containing groups facilitate more active sites for further functionalization of several other molecules, organic and inorganic moieties on GO, to develop novel nanocomposites with desired properties [5, 6]. Despite these several attractive characteristics of graphene, its commercial applications for the fabrication of next-generation optoelectronic devices rely on its optical response [7, 8]. Therefore, research on the synthesis of zero-dimensional (0D) fluorescent graphene sheets (*i.e.*, graphene quantum dots) has recently gained significant attention to compile the state-of-the-art involvement of graphene-based materials in the development of advanced photovoltaics and other optoelectronic devices [9, 10].

Herein, we discuss the progress of graphene and its nanocomposites in solar cells such as dye-sensitized solar cells (DSSCs), organic solar cells (OSCs), and perovskite solar cells (PSCs) amidst their cell configuration, working principles, and challenges of individual device. Next, the performance of advanced solar cell devices prepared after incorporating the graphene-based nanocomposites as active layers, electrodes, electrons, and hole transport layers is demonstrated and compared with the performance of commercially available conventional solar cell devices. Also, the role of graphene-based nanocomposites in solar cell devices is emphasized by comparing the most compelling outcomes. Decisive insights into the existing problems and future scopes of graphene and its nanocomposites in photovoltaic applications are discussed in the last section.

APPLICATION OF GRAPHENE AND ITS NANOCOMPOSITES IN OSCS

In pursuit of developing novel solar cell devices, this section will systematically discuss the significance of graphene and its nanocomposites as an electrode,

electron-transport layer (ETL), and hole-transport layer (HTL) in OSCs devices.

Graphene-based Materials as Electrode in OSCs

The materials used as OSCs' electrodes are needed to be highly conductive and transparent. Thus, Fluorine tin oxide (FTO) and Indium tin oxide (ITO) have widely been used as electrodes in commercially available OSC devices. The transmittance and resistance of ITO are 80% and 10-15 Ω/sq , respectively, on a glass substrate, while on the polyethylene terephthalate substrates, the resistance varies from 60 to 300 Ω/sq [11]. Nevertheless, ITO has several limitations such as high sensitivity towards acidic and basic media, difficulty in patterning, high manufacturing cost due to inadequacy of indium, and its brittle nature. These issues signify that the solar cell market is still looking for a promising material having high conductivity, acceptable transparency, desired flexibility, and good chemical stability. Metal nanowires, metallic grids, oxides, and carbon nanotubes have been studied as a suitable substitute to replace the transnationally used electrodes [12 - 15]. However, because of their poor transparency, the power conversion efficiency of resulting solar cell device align="center"was not enhanced, and thus, all these materials were unable to replace the ITO. Recently, graphene and its nanocomposites have been explored in OSCs as new electrode material [16 - 19]. Park and colleagues reported that the OSCs prepared from anode and cathode electrodes of graphene exhibited 6.1% and 7.1% power conversion efficiencies (PCE), respectively [20]. Wang *et al.* reported that graphene prepared from chemical vapor deposition (CVD) exhibits higher conductance and transparency than Hummer's method [21]. The higher conductance and transparency align="center"are ascribed to the presence of sp^3 -carbons and structural defects in the graphene synthesized *via* Hummer's method, which affects the π -bond connectivity and, thus, its electron transfer capability. In contrast, graphene sheets prepared from the CVD method demonstrate high conductivity with large and controlled sheet align="center"size, resulting in comparatively higher performance of OSCs. In general, the performance of OSC devices mainly depends on the transmittance, conductance, and thickness of thin films of graphene. Further, Gómez-Navarro *et al.* reported that the morphological defects present in GO and rGO sheets help in light transmittance. Hence, GO based electrodes display higher transmittance than those of CVD graphene [22]. Later on, Liu *et al.* prepared a four-layer CVD graphene with 90% transmittance and used the same in fabricating a flexible photovoltaic device as a top transparent electrode [23]. Because of the slow air diffusion through layered graphene, the as-prepared device exhibited slower degradation of organic materials with high stability and thereby demonstrated that a few layers of graphene are beneficial over a single-layer graphene.

New Frontiers of Graphene Based Nanohybrids for Energy Harvesting Applications

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Abstract: Graphene has gained recognition within the research community owing to its fascinating properties in the plethora of energy-related applications. The properties include high thermal and electrical conductivity, greater mechanical strength, optical translucency, intrinsic flexibility, massive surface area, and distinctive two-dimensional structure. Graphene is highly competent in enriching the functional performance, endurance, stability of many applications. However, still ample research diversity will be desirable for graphene commercialization in energy sectors. This intuitive scrutinization reconnoitered the talented employment arena of graphene in various energy storage and harvesting fields. The amplification of the versatile applicability of graphene and comprehensive perception regarding pros and cons of graphene based nanohybrids could critically pinpoint current constrictions by upgrading its characteristics performance. The chapter provides an insight into the unique features of graphene and amalgamation with nanomaterials to enlighten its various energy-related applications, including supercapacitors, biosensors, solar cells, batteries. With the breakneck miniaturization in the employment of graphene in various energy-relevant applications, it is crucial to epitomize align="center" and figure out the progressive momentum of graphene and its nanohybrids in several energy-related application territories.

Keywords: Batteries, Conductivity, Energy storage, Energy harvesting, Fuel cell, Graphene, Nanomaterial, Nanohybrid, Surface area, Sensor, Supercapacitor, Solar cell.

INTRODUCTION

According to the Paris settlement signed by 2015, the foremost objective was to cogitate reasonable ways of contending environmental fluctuations by recognizing

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the unconventional form of energy generation [1]. In the light of environmental sustainability of tackling energy, the fossil artifacts impacted profoundly for usage in energy harvesting regime. Depletion of fossil fuels is now alarming for the emerging energy harvesting and storage process. Renewable energy is a copious cradle of energy and alternative for minimizing the ozone layer depletion caused by the emission of fossil products [2, 3]. Meanwhile, solar energy and wind energy are remarkable and in dynamic phases, irregular alteration of phases requires the integrative approach with energy storage and converting device in a cost-effective manner [4]. Recent trend align="center" in energy storage and sustainable development is underway to explore more effective, sustainable energy harvesting systems through fuel cell technology [5]. Likewise, dye synthesized solar cells (DSSCs) are also alluring energy conversion tools. Graphene align="center" is a two dimensional (2D) single graphitic sheet-like morphology that align="center" possesses remarkable and fascinating properties *e.g.*, extraordinary conductivity, good electrocatalytic efficiency, mechanical stability, and solar radiation absorptivity [6]. It offers phenomenal concert in different application meadows such as sensors, catalysis, adsorption as well as energy storage and conversion. Integration of nanomaterials within the graphene matrix provides enhanced mechanical strength and electrical conductivity of the nanocomposites. Additionally, these nanocomposites illustrated superior thermal stability and electrochemical activity, as well as gas barrier properties [7].

For instance, the accumulation of graphene in these composites enriches the propagation of the electrolytic substance through its outward facet and caters electrically conductive ionic paths for dynamic nanomaterials decorated on it [8]. By designing graphene based nanohybrids, the distinctive properties of graphene and dynamic nanomaterials and their good synergism can be exploited, thereby significantly showcasing the perspective of graphene-based nanohybrids in various energy-related applications.

UNIQUE FEATURES OF GRAPHENE

Graphene, a crystalline allotrope of carbon, is well-advised as the advanced type of carbon nanomaterials owing to its two-dimension solitary leaf of a carbon atom within a hexagonal networking arrangement [9]. Two dimensionally oriented honeycomb lattice of graphene is a unit cell of all dimensional varieties of carbonaceous materials resembling 0D (fullerene), 1D (carbon nanotube) and 3D (graphite) showing zero band gap semi-conductor with extraordinary charge carrier kinesis (up to $10^6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) at relativistic speed $\approx 10^6 \text{ m s}^{-1}$ [9, 10] (Fig. 1). Due to its peculiar structural features *e.g.*, quantum Hall effect (QHE), bipolar electric field effect and electron wave propagation, graphene has acquired tremendous superiority for a wide variety of energy-related applications,

e.g., energy harvesting applications [11]. The underlying cause behind the relevancy of graphene in fabricating energy devices lies in its huge surface area, extraordinary electrical mobility and extended electron channeling network. Nonetheless, the architecture of graphene governs the definite surface area of graphene structure. Nevertheless, the major drawback includes agglomerates or restacking due to strong π - π stacking, which somehow confines the pristine usage of graphene materials as electrode material in energy devices [12]. Besides that, in semiconducting bilayer graphene, charge transporters comply with parabolic energy dispersal and unveil tunable zero band gap. The electronic and electrochemical features of graphene are intensely influenced by edge configuration [13, 14]. This can be diversified by the unique architectural framework of graphene molecule, which strongly mutates the threshold energies and forces within its circumference. Hence, an edge to edges force can be achieved by termination or doping with nitrogen, boron, and functional groups including oxygen, hydrogen, metals using oxygen gas plasma hydrogenation process [14, 15]. Interestingly, peculiar characteristic thermal conductivity is identified within a solitary layer of graphene due to acoustic phonons [16, 17]. These phenomena encourage the significance and utility of graphene in the burgeoning of nanoelectric energy devices futuristically [18].

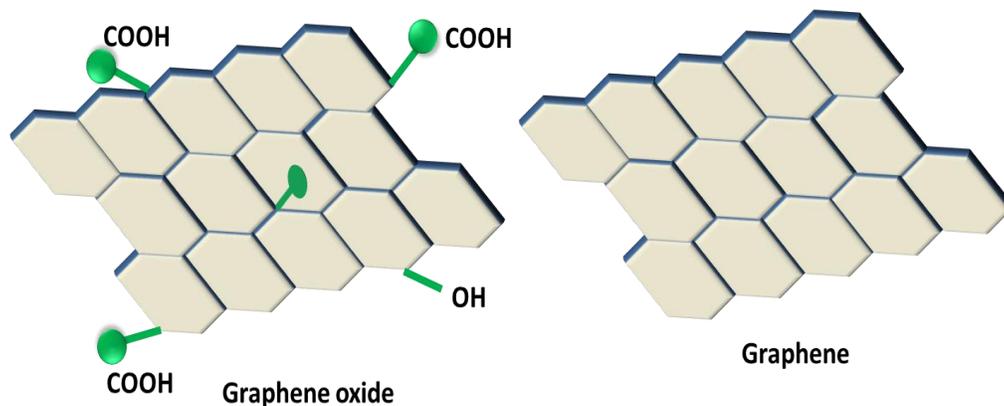


Fig. (1). Structural representation of graphene oxide and graphene.

FABRICATION OF GRAPHENE AND ITS VARIOUS ASSEMBLY

Two strategies were adopted to yield graphene are classified as top-down and bottom-up approaches. Bulk graphite material is the pivotal precursor of single and multilayer graphene. In the top-down approach, exfoliation of graphitic oxide from bulk graphite material can be achieved by mechanical and chemical ways [19]. Fig. (2) displays a probable synthesis spectrum of graphene and its

Metal Oxide Based Nanocomposites for Solar Energy Harvesting

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Abstract: In recent years, the development of industrialization and the increasing population has increased energy consumption across the globe. So, there is a need for green and sustainable energy generation from solar cells with greater efficiency. Photovoltaic (PV) technology with improved performance is going to be a gamechanger in resolving the energy crisis in an eco-friendly and more sustainable manner. Widely used silicon (Si) based PVs are relatively expensive due to strong requirements for the high purity of crystalline semiconductors. The Si wafer cost covers 50% of the total cost of the align="center"module. In this regard, metal oxide-based semiconductors are stable and environment-friendly materials that are used in photovoltaics as photoelectrodes in dye solar cells (DSCs), quantum dot sensitized solar cells, and build metal oxide p–n junctions. This chapter comprehensively discusses the most recent progress in metal oxide semiconductors in alternative type solar cells, in particular dye-sensitized solar cells (DSSC).

Keywords: Bandgap, Dye-sensitized solar cells, Efficiency, Electron mobility, Metal oxides, Nanorod and nanotube, Photoanode, Semiconductor.

INTRODUCTION

An increase in energy consumption and global warming as a result of the depletion of fossil fuels has prompted a search for alternative energy sources, particularly renewable energy resources, to address the energy crisis. Therefore, the research and development of clean energy resources like solar radiation, tide, wind, geothermal, and biomass energy as an alternative to fossil fuels have become a major task for modern science and technology. Among this wide variety of renewable energy projects developments, utilization of solar energy is the most

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promising one as future energy technology because of its ease of availability and easy conversion to other forms of energy [1]. The solar energy is readily available source align="center"across the globe, but efficient utilization still remains a challenge. The conventional p-n junction type solar cell based on single crystal silicon has been widely used to date. The manufacturing cost of a silicon wafer is still relatively expensive due to the strong requirements of the high purity of crystalline semiconductors. The Si wafer cost covers 50% of the total cost of module cost, so improvements in costs, applicability and sustainability are to be addressed [2]. One way of reducing this major cost component is by replacing Si wafer with semiconductor thin films deposited onto the supporting substrate like glass, plastic, *etc.* [3 - 8]. Such films may have purely inorganic materials such as polycrystalline silicon, amorphous silicon, cadmium telluride and copper-indium-diselenide, or contain organic materials as an important part of the device [9 - 12]. Many efforts have been made for the development of potentially cheaper thin film-solar cells. But these thin film solar cells are still in the pre-commercial phase because of their higher capital cost per unit output for thin film manufacturing facilities.

Metal oxides based nanomaterials are unique materials because of their electronic structure, physical, and electromagnetic properties [13]. The metals are useful materials, especially where they can be used as adsorbents and photocatalysts as well as for the align="center"manufacturing of environmental monitoring devices and dye sensitized solar cells. In 1991, Gratzel extended the concept of PEC solar cell to a novel solar cell based on a dye sensitized porous nanocrystalline TiO_2 as a photo anode [14, 15]. Generally in a dye sensitized solar cell, a photon absorbed by a dye molecule gives rise to electron injection into the conduction band of nanocrystalline semiconducting metal oxide materials such as TiO_2 , ZnO , *etc.* used because of their high surface areas. Voltage generated under illumination corresponds to the difference between quasi-fermi level in the oxide and the redox potential of the electrolyte or work function of the hole conductor [16]. The main advantage of photoelectrochemical solar cells is that it is insensitive to defects in the structure. The scheme of DSSC align="center" is shown in Fig. (1).

PHOTOANODE MATERIALS

Titanium Dioxide (TiO_2)

In DSSC, the right selection of photo anode materials is important to achieve better solar conversion efficiency. Generally, TiO_2 nanoparticles based photo anode is being used in DSSC by most researchers as its conduction band edge lies slightly below the excited energy level of many dyes. It also provides better electrostatic shielding to the injected electrons from the oxidized dye molecule

due to its higher dielectric constant ($\epsilon = 80$) and can prevent the recombination before reduction of the dye. More than 60% of the research reports of DSSCs are based on TiO_2 , because of their easy availability, electrical, optical, chemical stability and biocompatibility. The efficiency of TiO_2 photo electrode based DSSCs has been reported to be 8% more than that align="center"of liquid electrolytes. There are various methods that have been used for the synthesis of TiO_2 in different morphologies. F. Sauvage *et al.* prepared crystalline TiO_2 beads with mesoporous structure (size 800 nm) using sol-gel followed by solvothermal method. The solar conversion efficiency obtained was about 7.20%, which was higher than standard Degussa P25 TiO_2 (5.66%) [17]. Another similar work also reports the preparation of mesoporous beads with more than one dye and obtained efficiency of 10.5% [18].

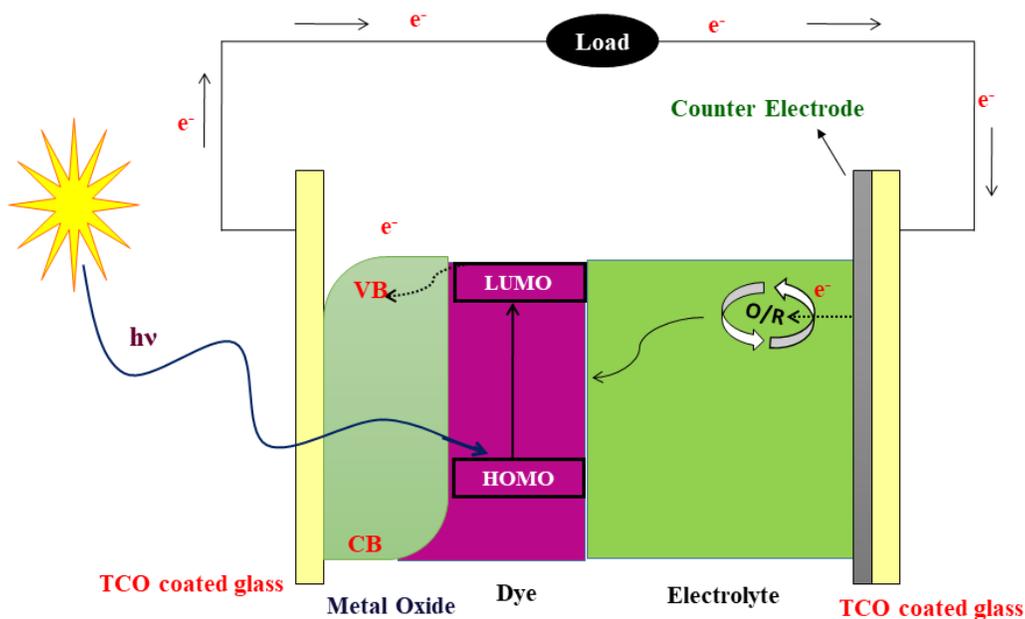


Fig. (1). Schematic diagram of Dye sensitized solar cells.

The mechanism of light absorption in nanoparticle and mesoporous structure is depicted in Fig. (2). However, the mesoporous nanostructure still shows lower electrical conductivity and their pores facilitate recombination reactions at the electrode. In this connection, a new approach of nanowires has been introduced that achieved promising results as compared to mesostructured materials [19]. J. Fan *et al.* synthesized TiO_2 nanowire and reported a solar conversion efficiency align="center"of about 9.40% [20]. The improved photo conversion efficiency of nanowires arises due to their higher surface area. For further enhancement in

Two-dimensional Functionalized Hexagonal Boron Nitride (2D h-BN) Nanomaterials for Energy Storage Applications

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Abstract: The conservation of energy and the materials utilized for its storage have gathered a wide range of interest nowadays. Two-dimensional hexagonal boron nitride (2D h-BN), often termed as ‘white graphene’, exhibits various interesting properties and hence, acts as a promising future candidate for energy sustainment and storage. This material assures exquisite thermal and chemical stability, high chemical inertness, exotic mechanical strength, and good optoelectrical properties. 2D h-BN undergoes physical and chemical modulations, and their properties could be tuned, making them more appropriate for energy storage applications. They could also be incorporated with other 2D materials like graphene, molybdenum disulphide (MoS₂), *etc.*, to improve their properties. It is thus thoroughly and systematically studied for its further usage in field effect transistors (FETs), UV detecting devices and emitters, photoelectric and microelectronic devices, tunnelling devices, *etc.* The comprehensive overview provides an insight into 2D h-BN and its synthesis routes developed within the past years. The different major properties exhibited by 2D h-BN are also reviewed. Hybridization and doping processes are also discussed. Functionalised h-BN and its utilisation in different energy storage applications are elaborated and reviewed. This review chapter will give a quick glance and perspectives on 2D h-BN and its extraordinary characteristic features that could enhance their usage in energy conversion, storage, and utilisation applications.

Keywords: Doping, Electrolytes, Energy storage, Functionalised h-BN, Hexagonal boron nitride (h-BN), Honey-comb arrangement, Hydrogen storage, Secondary batteries, Solar energy, Supercapacitors, Technical advancements, Thermal stability.

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INTRODUCTION

Recent incessant utilization and consumption of global energy have led to the origin and development of new advanced sources of energy such as solar, hydrothermal, biomass, geothermal, wind, and nuclear energy. Energy storage is the process of capturing and storing energy produced once and maintaining it for future energy demands, usage, and production. The two challenges that are commonly faced are energy storage and conversion of the energy produced. Traditional energy storage devices are vulnerable to natural conditions; hence conventional methods and equipment need to be developed to obtain high efficiency and standard performance. Its application includes rechargeable and renewable batteries, supercapacitors, biofuels, flywheels, *etc.* The major drawbacks experienced in energy storage devices are thermal explosion (thermal runaway) that limits the operational working and safety, working efficiencies, scale and lifespan, cost and availability of raw materials for designing, and environmental hazards caused. Substantial research is carried out by researchers and scientists for the prominent utilisation of nanomaterials in energy storage applications to construct a proficient power absorption and storage material with high thermal conductivity, specific capacitance, and corrosion resistance.

The extraordinary behavior and properties of two-dimensional(2D) nanomaterials offer a wide and attractive platform for them to be used in energy storage applications. Few thick atom crystals with ultra-thin thickness, usually of nanoscale are referred to as 2D materials [1]. 2D materials offer high specific area, thermal stability and innumerable other properties, and hence, can be implemented in energy reserving applications. Different 2D nanocomposites have been identified and evaluation studies were carried out for this application which includes graphene [2], hexagonal boron nitride, transition metal oxides [1 - 3], transition metal dichalcogenides [2, 4] and transition metal carbides and nitrides (MXenes) [5 - 9]. 2D nanomaterials offer high capacitance rates and exorbitant specific surface area. 2D inorganic nanomaterials depict pseudocapacitance and could be modified by doping and chemical functionalisation. These materials also show fast transport of ions, thereby enhancing expansion and contraction of layers. A fast ion adsorption mechanism is seen between the nanosheets of 2D channels that fabricates the energy storage application of 2D nanomaterials accredited by the edge in water molecules followed by an accelerated enlargement and confinement of multifaceted and bendable layers of 2D nanomaterials.

The resilience of 2D nanomaterials, favourable mechanical and packing density properties, high volumetric capacitance make them appropriate for the designing and manufacturing energy storage devices. Zero-bandgap graphene shows suitable electrical conductivity and hence, could be applied to fabricate electrically

conducting supplements that are free from electrodes. Electrical conducting properties are not shown by most of the 2D materials, thus hampering their further usage in energy storage fields [4]. Atomic layer numbers and the crystal structure is directly persuaded by the electronic structure of 2D nanomaterials. Different methods are implemented to enhance the electrical conductivity by varying 2D nanomaterials and their electronic structures. One of the major problem faced is to impose the full potential of 2D materials in storing energy by preventing restacking of nanosheets which averts full utilization of surface area domains and obstructs the electrolyte access. This difficulty could be intercepted by reconciling the morphology of nanosheets. Different synthesis techniques were developed to produce nanosheets in leveled, twisty or wrinkled shapes, that when placed with current collectors ease the ion movements.

The 2D materials could be incorporated with other materials to form a basic building material for a series of hetro- or hybrid structures that could facilitate manufacturing of new materials with improved properties. This adaptable nature of 2D materials offers the probability to engineer new frameworks that could be used for an expansive range of applications. Hexagonal boron nitride and other transition metal oxide nanomaterials could be integrated with electrically conducting graphene's to form a heterostructured composite to enhance the energy storage properties [10, 11]. Establishing new nanomaterials and intercalation of large molecules could overcome the problem of restacking.

In this review, we provide a summary on functionalised hexagonal boron nitride and its applications in energy storage fields. The properties of this 2D material will be highlighted and an elaboration of their use in energy storage applications will be focussed. The structural, morphological, electrical, mechanical and thermal studies are analysed from different research papers and are explained. A general survey of energy storage and conversion applications is evaluated and proof-read with newly penned review articles. Designing and fabrication of electrode structures, device layout, and manufacturing methods are considered. The different possibility of utilising this material in energy storage applications, future perspectives and challenges faced are identified and elaborated based on the literatures studied and recommendations are made for future research.

HEXAGONAL BORON NITRIDE (H-BN)

Hexagonal boron nitride is a compound included under group III-V elements comprised of an equal number of nitrogen and boron atom layers in a honeycomb lattice arrangement under sp^2 hybridisation, where the layers are organised by van der Waals forces.

CHAPTER 8**A Concise Summary of Recent Research on MOF-Based Flexible Supercapacitors****Ankita Mohanty^{1,2} and Ananthakumar Ramadoss^{1,*}**

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Abstract: This book chapter elucidates the recent works accomplished in the platform of flexible/wearable supercapacitor devices based on metal-organic frameworks (MOFs) electrodes. Comprehensive insight into various types of supercapacitors, the advantage of MOF-based supercapacitors among them, classifications of MOF-based flexible supercapacitors concerning their building blocks, and recent research accomplished with their pros and cons are illustrated. Finally, the performance assessment, strategies to improve efficiency, and future perspectives are briefed.

Keywords: Aspect ratio, Composites, Conducting polymers, Current collectors, Energy storage, Flexible, Gel-electrolyte, Metal-organic framework, Nano structure, Organic linker, Supercapacitor.

INTRODUCTION

The exponential growth of industrialization and the increasing population highly mandate the realization of sustainable energy storage devices. The intermittency of renewable energy sources and excessive utilization of fossil fuels align="center"has conceived a worldwide energy deficiency issue. Moreover, various electrochemical energy storage devices are being able to achieve this energy demand. Rechargeable batteries, fuel cells and capacitors are widely used as efficient energy storage devices; however, their poor power density, cycle life, and environmental hazard nature are the major bottlenecks in their application.

Supercapacitors are considered trending electrochemical energy storage systems owing to their special attributes like superior power density , excellent cycling

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stability, and nature safety [1]. Modern society is adopting wearable and flexible smart electronic devices as essential gadgets in day-to-day life.

Flexible supercapacitors are being proven to be quite reliable for the construction of efficient wearable or portable electronic devices [2, 3]. Light-weight, leakage-proof packaging, portable size, and high flexibility with good performance are the explicit features that make flexible supercapacitors stand out among other traditional electrochemical energy storage devices [4].

Predominantly, supercapacitors act upon two different types of charge storage behaviours, *i.e.*, pseudocapacitors and electric double-layer capacitors (EDLCs) [1]. The EDLC type supercapacitors undergo an arrangement of double layers of charges over the electrode surface. In contrast, pseudocapacitors include the faradaic oxidation-reduction reaction of the electrode and electrolyte ions [5]. Transition metal oxides (TMOs) [6, 7] and conducting polymers [8] obey pseudocapacitive behaviour while carbon-based materials show EDLC nature [9]. Novel materials like MXenes [10], layered double hydroxides [11], metal-organic frameworks (MOFs) [12], *etc.*, depict battery-like behaviour and are used in hybrid supercapacitor devices. A hybrid supercapacitor device reflects both sustainable energy density and optimized power density by exploiting the merits of both supercapacitor and battery like electrodes in the same system [1]. MOFs are treated as excellent hybrid supercapacitor electrode materials because of their structural tunability, huge surface area, high aspect ratio with excellent porosity [12]. They can be of different structures and dimensions (1D, 2D and 3D) depending on the selection of organic linkers and metal ions [13]. Usually, pristine MOFs reflect poor electrical conductivity due to the existence of insulating organic linker chains [12, 13]. Unlimited assignment of organic linkers and metal ions avails MOFs with various structures, varying porosity, and huge internal surface area [12, 14]. Therefore, mostly MOFs are used as templates to derive various metal oxides, metal sulfide, metal carbides, layered double hydroxides or carbon materials, *etc.* [15]. MOFs can also be converted into carbon materials when treated at very high temperatures under an inert atmosphere [16]. All these admirable properties of MOFs are utilized towards the application of design and assembly of wearable and smart electronic devices [12].

As yet, MOFs have not reached state of the art. However, much laboratory-scale research work is accomplished and proves the potentiality of MOFs in the assembly of flexible supercapacitor devices [17, 18]. The proper understanding of the requirements and mechanism of a flexible supercapacitor will pave the way towards real time application on an industrial scale. In this book chapter, recent research works based on MOFs for flexible supercapacitors are summarized systematically with their design, synthesis mechanism, performance evaluation,

etc.. A brief idea about flexible supercapacitor, its importance, and requirements are discussed in the below section.

FLEXIBLE SUPERCAPACITOR DEVICE

A flexible supercapacitor device consists of positive and negative electrodes, separated by a separator and sandwiched *via* an electrolyte between them. There is no significant difference between a flexible supercapacitor device and a conventional supercapacitor device in terms of charge storage mechanism. The only uniqueness of a flexible supercapacitor device is the total flexibility of the device. That means the device can work in all bending, twisting, rolling conditions retaining its original performance [4]. Another advantage of this device is very light-weight and align="center"portability. Therefore, these devices are highly preferred in fabricating portable and wearable smart electronic devices, including fitness bands, glucose sensors, smartwatches, wireless earphones *etc.*.

A flexible supercapacitor device necessitates the flexibility of all of its components. Thus, a flexible supercapacitor device must have (i) a flexible current collector, (ii) free-standing active electrode and (iii) a sol-gel polymer electrolyte [4]. Various flexible substrates such as CC [19 - 22], nickel foil [23], copper foil [24], aluminium foil [25], stainless steel foil [26], titanium foil [27], metal tapes [28], graphite tapes [29] *etc.* are used as current collectors. Compositing all these components, a flexible supercapacitor device should retain confined volume, light-weight, appreciable stability, cost-effectiveness, swift charge-discharge ability, mechanical durability, resistance to expansion and compression and excellent efficiency [4].

Accordingly, flexible supercapacitor devices need to be designed perfectly so that they should be able to achieve good energy density with cycling stability and mechanical stability. Various kinds of active materials current collectors are being utilized for flexible supercapacitor device fabrication. In this book chapter, the prime focus is on MOF-based flexible supercapacitor devices. Hence, various flexible supercapacitors based on MOF and MOF-derived active electrodes are described hereafter.

MOF FOR FLEXIBLE SUPERCAPACITOR

Metal-organic frameworks (MOFs) constitute strong covalent bonds between various metal ions and organic linkers [12]. Hence, MOFs provide huge specific surface area, high porosity, good internal surface area, the excellent surface to volume ratio *etc.* [12]. Exploiting the special features of MOFs in designing flexible supercapacitors is quite welcoming and challenging. Most of the past research on MOF synthesis includes the binder method, *i.e.*, forming MOFs in

CHAPTER 9**Advanced Batteries and Charge Storage Devices based on Nanowires****Sunil Kumar^{1,2}, Ravi Prakash¹ and Pralay Maiti^{1,*}**¹ School of Materials Science and Technology, Indian Institute of Technology (Banaras Hindu University), Varanasi-221005, India² Department of Chemistry, L.N.T.College (B.R.A. Bihar University), Muzaffarpur-842002, India

Abstract: Compositional designed electrodes exhibiting high specific capacities are of great interest towards high performance charge storage devices. Electrode surface can store charge or guest ions due to structural confinement effect. Ion storage capacity depends on the structural integrity of electrode (anode) materials of batteries. Electrolyte selection also decides the storage capacity of batteries and other charge storage devices. Volume expansion or variation can be minimized through structural variation of the electrode. The charging phenomenon proceeds through the continuous ion destruction process of adsorbed ions into semipermeable pores. Dimension controlled electrode materials possess superior ion storage capacity. The contemporary design is an effective way to improve the charge storage capacity of electrodes. Low dimension materials exhibit better charge storage capacity due to high surface density (surface to volume ratio) and efficient charge confinement. The confined dimensions (quantum confinement) play important roles in orienting the desired kinetic properties of nanomaterials, such as charge transport and diffusion. This chapter emphasizes critical overviews of the state-of-the-art nanowires-based electrodes for energy storage devices, such as lithium-ion batteries, lithium-ion capacitors, sodium-ion batteries, and supercapacitors. Ions or charges can be percolated easily through nanowire networks due to fast adsorption and diffusion. High-rate capability is intensified over large electroactive surface in an ordered nanowire electrode.

Keywords: Active electrodes, Batteries, Capacitors, Charge storage capacity, Capacity retention, Composite storage surface, Energy density, Electrolyte wettability, Electrode strain accommodation, Functionalized phase, Ion adsorption, Interfacial ion exchange, Metal-organic framework, Nanowire, Nanowire array, Nanowire nucleation sites, Redox active sites, Redox reaction, Surface penetration.

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INTRODUCTION

Today's fast-growing generations require renewable and sustainable energy to drive the life cycle. The unique shaped electrodes realize intense research to develop energy storage devices with high energy density ($\sim 100 - 200 \text{ Whkg}^{-1}$), power density ($\geq 5 \text{ kWkg}^{-1}$) and long cycle life (≥ 105 cycles) [1, 2]. Batteries and electrochemical capacitors (ECs) explore intense interest in the configurational design of electrodes to assemble highly functional and smart energy-storage devices with their high energy densities and long sustainability [3]. The devices can store energy *via* electrostatic accumulation (non-Faradic) or electrochemical reaction (Faradic reaction) [4]. The electrochemical energy storage behavior strongly depends on the structural and compositional design of the electrode materials [5]. Traditional electrode fabrication scheme requires a large quantity of binding and conducting chemicals for sustainable development of energy and device [6]. Materials with one-dimensional nanostructures have kindled great interest in the development of energy storage electrodes because of their unique properties, such as shorter diffusion distance of ions along the diameter, lesser charge/discharge time and greater electrode-electrolyte interfacial contact [6, 7]. Battery and capacitor systems are composed of anode, cathode, and electrolyte [8]. Anode and cathode are bridged by electrolytes for efficient and reversible charge transport [9]. The critical theme to improve energy storage capacity is to optimize electrical and ionic conductivities and consequently maximize the active material utilization with minimum strain in electrode [10]. The electrolyte is a source of ions that can be intercalated at the surface of the electrode. Superior electrode-electrolyte wettability offers enhanced kinetics of ion transport. The degree of reaction reversibility determines the energy efficiency and columbic efficiency of battery materials. Capacitive materials with composite structure (d-block metal oxides/sulfides and conjugated functional polymers) display higher capacitance or energy density, primarily due to continuous transmission of surface redox reactions through multioxidation state metal center. Redox-active chromophore improves storage capacity due to faster reaction reversibility. Thus, functionalities can improve redox activity on the surface of the electrode. Anodes are susceptible to storing ions or electronic charges during the charging process. The sufficient spaces between the nanowires arrays can ease electrolyte penetrating the integrated anode to increase the interfacial contact areas between electrolyte and electrode [11]. The nanoscale dimension of building blocks promotes the kinetics of ion storage due to the shorter diffusion paths [9]. In general, nanomaterials bring important improvements in energy storage devices because of their reduced size and shape, which widens the surface and interfacial contact to minimize transport and transmission path [12]. Pseudo-capacitors store

charge on the surface layer where electrolyte ions can penetrate the matrix of active materials. Size reduction can improve the charge storage capability. The oriented nanowire align="center"has vacant space to retain the large capacity variations without destroying the configuration, shape, and size of active content [13]. Nanowire arrays align="center"exhibit faster ion diffusion than the nanowire network. This is why arrays structure leads to higher capacitance with more structural balance in the continuous phase of nanowire electrode. Li-ion capacitors, typically align="center"combining the align="center"benefits of high-capacity battery type anodes and high-power capacitor type cathodes, have been realized as the most functioning devices. Nanowire serves as a structural resistance to accommodate the volume change during charging and discharging. The nanowire array structure has a tendency to segregate interfacial vacancy within neighboring 1D nanostructure. The array spaces confine electrolyte absorption causing enhancement of internal conductance and high-power performance characteristics. Moreover, the porous structure strengthens the absorption of electrolyte to facilitate reversibility of the redox reaction. Nanowires improve rate capability due to fast electron transport and insertion of ions along long dimensions [14, 15]. Nanowire arrays intensify the electrical and ionic conductivity of the electrode [16, 17]. Since, single nanowire electrode decreases its conductivity gradually, therefore, volume accommodation capacities are reduced during insertion and extraction of charges. But it resumes higher charging stability than that of other nanodimensions [3]. Metal organic frameworks (MOFs) such as zeolitic imidazolate framework-8 and zeolitic imidazolate framework-67 could easily be grown on different interfaces as a functional layer to enhance the charge storage properties [18, 19]. Surface reactions produce supercapacitance. The capacitive behavior is produced through ion exchange phenomenon at the electrode-electrolyte interface [20]. Metal oxides and hydroxides accumulate specific energy by polar sites and redox configuration. Complex metal oxides with variable valence states have a tendency to be reduced and oxidized potentially and thus better suits as pseudocapacitive electrode materials [21]. Thus, the chapter is focused on review of the structural stability of nanowire based electrodes for efficient designing of energy storage devices.

CHARGE STORAGE DEVICES

Advanced charge storage devices are Li-ion, Na-ion and Li-S batteries, which differ with each other due to differing storage ions (charge) [5]. The capacitor and supercapacitor are efficient charge storage devices. Capacitors are charge storage devices that have traditional design, and consist of two or pairs of conductors (electrodes) separated by an insulating surface. The conductors have similar and opposite charges extent on their surface with respect to the dielectric. The interfacial charge accumulation involves no change in chemical composition,

Polymer Nanocomposite Membrane for Fuel cell Applications

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Abstract: Polymer nanocomposite is a new kind of material that offers to substitute traditionally filled polymers. The nanomaterial polymer matrix inter-phase area increases drastically due to the inherent high surface-to-volume ratio resulting in remarkably enhanced properties compared to the pristine polymers or their conventional counterpart filled nanocomposites. Nanocomposites have several novel properties such as nonlinear optical properties, electronic conductivity and luminescence. Therefore, their use has been projected in many areas like chemical sensors, polymer electrolyte membrane fuel cell (PEMFCs), electroluminescent devices, batteries, electrocatalysis, smart windows and memory devices. PEMFCs embody a potential candidate for electrochemical energy generation in the twenty-first century due to their better efficiency and environmentally friendly nature. Proton exchange/Polymer electrolyte membrane (PEM) plays a vital role in the PEMFCs. Currently, PEM like Nafion and Flemions are widely used in PEMFC, which have certain drawbacks such as fuel cross-over through the membrane, low operating temperature, and high cost. The researchers from several laboratories across the globe have put their extreme effort into preparing a novel polymer electrolyte membrane with high proton conductivity, better long-term stability, improved thermal stability, high peak power density (PPD), and less fuel crossover with minimum cost. The advent of nanotechnology has brought a new scope to this research area. The hybrid (organic polymer with inorganic nanoparticle) nanocomposite membrane has developed into an exciting alternative to the conventional polymer membrane applications. It provides an exclusive blend of inorganic and organic properties and helps to overcome the drawbacks of align="center"pristine polymer membranes. In this book chapter, we have focused on different nanomaterials and their effect is analyzed in polymer electrolyte nanocomposite membranes for PEMFC applications.

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Keywords: Nanocomposite, Proton conductivity, Acid functional group, PEMFC, Water absorption, Thermal Stability, Fuel cell Performance, Ionic medium, Inorganic particle, Oxidative stability, Functionalization.

INTRODUCTION

The demand for electric power is rapidly increasing throughout the world. The traditional way of power production generally depends upon centralized fossil fuel plants, which are now less preferred for a clean and green mode of power generation technologies. Emissions from coal and other fossil fuel-powered plants release huge amounts of carbon dioxide (CO₂), greenhouse gas (GHG), and pollutants that include nitrogen and sulfur oxides. Furthermore, all forms of unified power need a grid of high-voltage transmission lines to transfer energy to the consumer's home. These transmission lines create challenges to the infrastructure for the services, known for their perceived health threats and the enormous loss of about 20% of energy depending on the distance from the source to the consumer. Sunny days are essential for getting better solar energy, but the situation becomes pathetic during long days of cloudy skies. Another option of wind energy exists which however also depends on the factors that cannot be controlled. Similarly, a suitable speed of water flow is needed for producing hydroelectric power. Thus, it is difficult to think about the renewable energy sources without consistent sun, wind, and water flow. These sources are not align="center"under the control of human beings and may not be counted as suitable align="center"or reliable sources. On the contrary, fuel cell technology has advanced to a stage where it can be considered as the probable challenger to the traditional combustion-based engine and can produce a feasible means of generating clean and green power according to demand.

A fuel cell is like a factory, which produces electrical energy as output as long as input fuel is there. There is a different classification of fuel cells based on the electrolyte used in the cells. The five major types are:

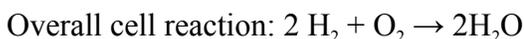
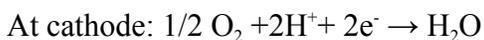
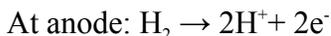
- a. Phosphoric acid (H₃PO₄) fuel cell (PAFC)
- b. Polymer electrolyte (or Proton-exchange) membrane fuel cells (PEMFCs).
- c. Alkaline fuel cell (AFC)
- d. Molten carbonate fuel cell (MCFC)
- e. Solid oxide fuel cell (SOFC)

PEMFC uses polymer electrolyte membrane as an electrolyte for proton-exchange purposes and is also called a proton exchange membrane fuel cell. However, other fuel cells use different types of electrolytes for proton transfer from anode to the cathode side of the PEM fuel cell.

POLYMER ELECTROLYTE MEMBRANE FUEL CELL

PEMFC is considered the field of interest in this chapter. PEMFC is nothing but an electrochemical device that produces electricity and water from hydrogen (H₂) and oxygen (O₂) fuels. The H₂ gas is oxidized to electron and proton (H⁺) in the presence of the catalyst, whereas the electron passes through the external load and proton passes through the polymer electrolyte.

The electrochemical half reactions are shown as follows:



Advantages of Fuel Cell

- i. It is more efficient than a combustion engine, as it produces direct electrical energy from chemical energy.
- ii. All parts of the cell are in static mode.
- iii. Lack of moving align="center"parts implies that Fuel Cells are noiseless, highly reliable and long-lasting systems.
- iv. No emission of an undesirable product such as NO₂, SO₂ and other greenhouse gases.
- v. Battery scales poorly at large size, but fuel cells range from 1watt range (mobile phone) to power plant (1 Mw).
- vi. It offers higher power efficiencies compared to traditional batteries, rapidly recharges by refueling, whereas batteries need to be plugged in for recharge or need to be thrown away or appropriately disposed align="center"of.

Disadvantages of Fuel Cell

1. Cost is the major barrier.
2. Fuel availability and storage is a bigger problem.
3. Alternative fuels such as methanol (MeOH), formic acid (HCOOH) and gasoline are difficult to use directly.
4. Operational temperature compatibility.
5. The durability hampers during start-stop condition.

Graphene-based Nanocomposites for Electro-optic Devices

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Abstract: Graphene, the most exciting carbon allotrope, and its derivatives such as graphene oxide and graphene quantum dots have sparked a flurry of research and innovation owing to their unprecedented optoelectronic properties. Graphene and its nanocomposites have been widely used in a variety of opto-electronic devices such as photodetectors, transistors, actuators, biomedical aids, and membranes. Their sp^2 hybridization state provides some extraordinary opto-electronic and mechanical properties. Chemical exfoliation of graphite into graphene and graphene oxide allows us to mix graphene nanocomposites into various layers of organic solar cells and other organic semiconductor-based optoelectronic devices, especially for roll-to-roll fabrication of large-area devices at a lower cost. Recently, these nanocomposites have also been utilized as charge transport layers and surface modifiers in perovskite solar cells and perovskite light-emitting diodes. Researchers have found that the presence of graphene, even at very low loading, can significantly improve the device's performance. In this chapter, we have discussed the application of graphene oxide, reduced graphene oxide, and doped graphene oxide in various combinations in perovskite solar cells and perovskite light-emitting diodes; these nanomaterials can be utilized either in transport layers of a multilayered device or directly incorporated in the active layers of these optoelectronic devices. These nanocomposites generally improve the device efficiencies by improving the band alignment at heterojunctions in a multilayered device by substantially reducing the trap states and the charge transfer resistance. These nanocomposites are found to achieve significantly improved device power conversion efficiency and stability of perovskite-based optoelectronic devices.

Keywords: Band alignment, Graphene-oxide, Hybridization, Low cost, Nanocomposites, Opto-electronic, Perovskite optoelectronic devices, Power-conversion efficiency, Stability, Trap-states.

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INTRODUCTION

Graphene has emerged as one of the revolutionary materials and attracted tremendous attention from all the material scientists and device engineers around the world. The world's first 2D material, graphene, was first isolated and identified by Andre Geim and Kostya Novoselov in 2004. Graphene in its purest form has some exceptional opto-electronic and mechanical properties, which makes graphene a shining star among the list of other functional materials. Due to its extremely high mechanical strength, graphene has been utilized to functionalize a variety of materials to improve their mechanical strength. The sp^2 hybridization of the carbon atoms in graphene is arranged in a honeycomb structure attached by σ and π bonds with an interatomic distance of around 0.142 nm. Graphene has extremely high charge carrier mobility in the range of 15000 – 20000 $cm^2/V.s$ at room temperature (RT) due to the delocalization of the p-electrons. In defect-free graphene sheets, electrons can move at an extraordinary speed as if there is no effective mass. In the pristine form of graphene, there is a zero-band gap in the material. However, introducing some defects or any functional group can open up a very small energy bandgap and therefore, in most applications, graphene nanocomposites such as graphene oxide (GO), reduced graphene oxide (rGO) or doped graphene is utilized in semiconducting industries. Apart from this, graphene is not used in its pure form because of its inadequate yield compared to graphene derivatives. It's easier to achieve a high production yield for the GO as compared to the purest form of graphene, subsequently, reduction of GO can lead us to the efficient production of graphene. Pristine GO is a wide bandgap, low conducting material; therefore, it cannot be useful in many applications. Several approaches have been utilized to reduce the graphene oxide and improve the electrical properties of GO; these methods include chemical, electrochemical reduction, and heat treatments. Hydrazine or dimethylhydrazine are usually used for the chemical reduction of GO. Hui-Lin *et al.* utilized an electrochemical reduction of the exfoliated GO at a graphite electrode to reduce GO in order to avoid the use of excessive reducing agents [1]. Apart from the reduction of GO, functionalization of graphene or GO could provide us with the desired optoelectronic properties of doped graphene. In this chapter, we will discuss the applications of graphene nanocomposites, namely GO, rGO and doped graphene quantum dots in perovskite solar cells (PeSCs) and perovskite light-emitting diodes (PeLEDs). PeSCs and PeLEDs have the same device structures, mainly differing in their operational conditions. These devices utilize a multilayered structure consisting of a hole transport material (HTM), an active layer, and an electron transport material (ETM), all sandwiched between two electrodes, as shown in Fig. (1). PeSCs and PeLEDs utilize an active perovskite material with the stoichiometry of ABX_3 , where A is a monovalent cation, B is a divalent cation and X is a monovalent anion. The materials which maintain the

above-mentioned stoichiometry (ABX_3) are termed halide perovskites [2]. These perovskites possess some exceptional properties, which are generally unexpected for solution-processable semiconductors. High defect tolerance [3 - 6], long carrier diffusion lengths [7 - 11], and narrow emission full-width half maxima (FWHM) [3, 12] are the characteristic features of these materials. A high-efficiency solar cell is required to maximize the photon absorption, efficient charge separation, charge transport as well as charge extraction at the electrode interfaces.

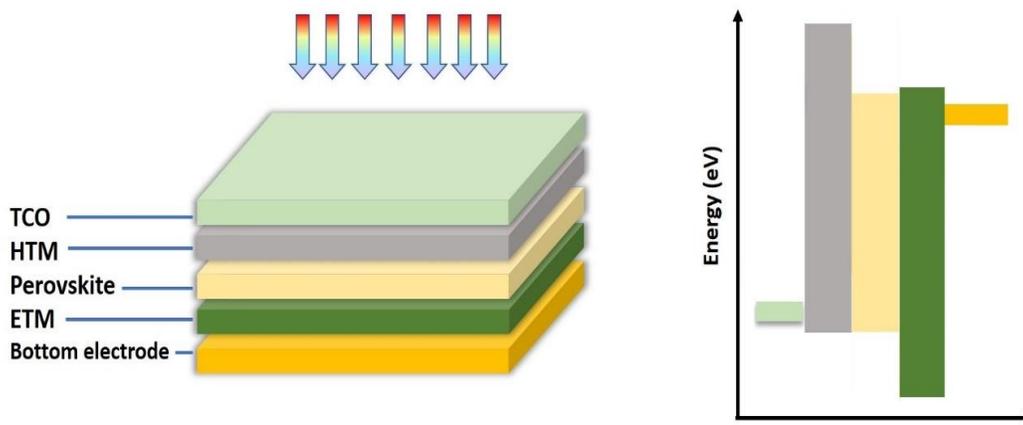


Fig. (1). Schematic diagram of (a) perovskite solar cell, (b) band diagram of a typical perovskite solar cell. (TCO- transparent conducting oxide; HTM: hole transport material; ETM: electron transport material.)

On the other hand, a light emitting diode is required to have a balanced charge injection, high radiative recombination rate and high light outcoupling efficiency. In recent years, PeLEDs have gained great attention among researchers due to high photoluminescence quantum yield (PLQY) in these materials. On the other hand, perovskite based solar cells have already achieved device efficiencies over 25%, which are comparable to the single crystal-based silicon solar cells. This extraordinary success of these materials forced the scientific community to reconsider the critical need for high temperature processable crystalline materials. This is a remarkable achievement towards large-scale production since these devices can be fabricated on a flexible substrate in a roll-to-roll manner. However, there are still many challenges to improving the operational stability of perovskites [13 - 19]. A number of graphene nanocomposites have been utilized to improve device efficiencies and stability. Large carrier diffusion lengths in perovskites can sometimes be the reason for enhanced non-radiative recombination events in perovskites, since the generated/injected charge carriers can easily diffuse towards the non-radiative sites [20]. These non-radiative sites in perovskite are generally present at the surfaces/interfaces and the grain boundaries

CHAPTER 12

Ferroelectric Liquid Crystal Nanocomposite for Optical Memory and Next Generation Display Applications

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Abstract: The dispersion of nanomaterials in ferroelectric liquid crystals (FLC) has turned out to be a promising method for fabricating optical memory devices and tuneable electro-optical materials. In a nanosuspension between FLC and nanoparticles, the presence of the dopant particles creates a synergic interaction with host FLC, which leads to the improvement of electro-optical properties. Tailoring with nanoparticles of suitable size, concentration, and compatibility results in various fascinating effects and new multifaceted composites for electro-optical devices. Adding nano-sized materials such as metallic, semiconducting, insulating or other functional species into the FLC matrix is a fertile method, giving rise to or increases in memory retention and other electro-optical properties that can replace the current electro-optical devices. These advancements depend on the harmony between the guest and host materials. This chapter gives a comprehensive overview of the present technologies and enhancements that have been acquired in nanoparticle/FLC composite systems, especially for optical memory devices and display applications.

Keywords: Composite Systems, Display Devices, Electro-Optical Properties, Ferroelectric, Ferroelectric Liquid Crystal-Nanocomposites, Ferroelectric Liquid Crystals, Insulating NP, Liquid Crystals, Metallic Nanoparticles, Nanoparticles, Optical Memory, Semiconducting Nanoparticles.

INTRODUCTION

Liquid crystals (LC), or mesogens, are an intermediate phase of matter whose properties and structures are an amalgam of both liquids and crystalline solids. It was first discovered by Austrian Botanist Friedrich Reinitzer and German scientist Otto Lehmann on cholesterol in 1888. Successfully understanding the

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fundamentals of this new phase grants Lehmann and Reinitzer the title of grandfathers of LC. The LC can be categorised or classified by their structure, composition and phase. According to the shape, there are rod-shaped (calamitic), disc-shaped, and banana-shaped (bent-core) liquid crystals. Similarly, based on their composition, they are classified as thermotropic, where mesophase is controlled solely by temperature, and lyotropic, where the concentration of solvent plays a pivotal role. Further, the mesogens are sorted based on the symmetry of the phase as chiral (Fig. 1a) and achiral [1]. The achiral liquid crystals are further divided into nematic (Fig. 1b), which possesses only orientational order, and smectic (Fig. 1c), which has a layered structure with both orientational and positional order.

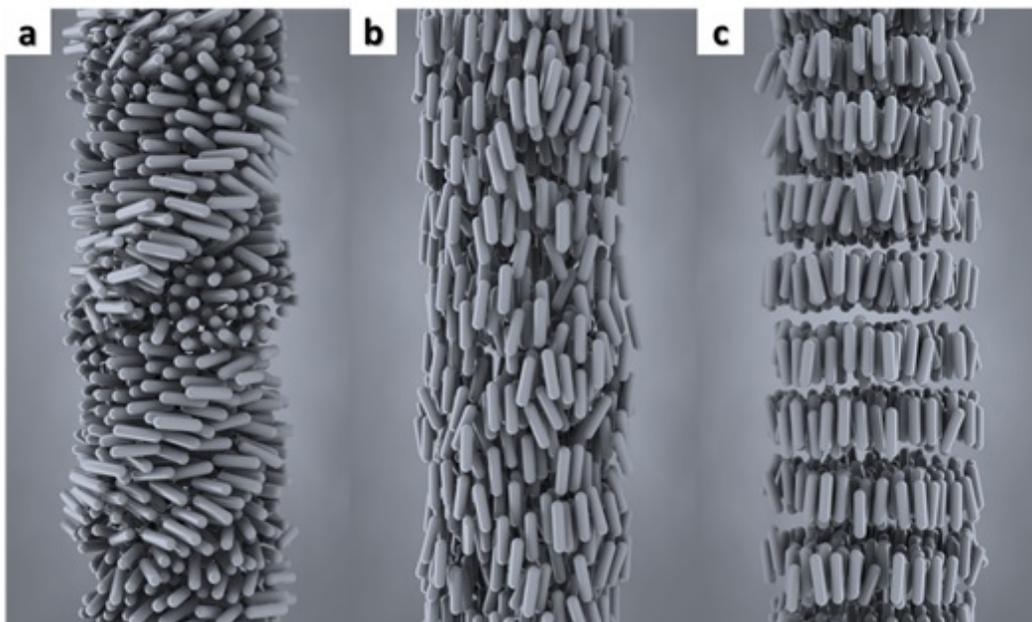


Fig. (1). (a) Chiral Nematic Liquid crystals, (b) Nematic Liquid Crystal and (c) Smectic Liquid Crystal.

Even though non-ferroelectric, ferroelectric and anti-ferroelectric mesophases constitute the chiral branch, at the moment, we are exclusively interested in the ferroelectric liquid crystals (FLC), a remarkable class of LC materials that manifest spontaneous polarisation, consequent to their lower symmetry. Despite theorizing liquid crystalline materials with ferroelectric properties having been done before [2], experimental confirmation was only provided later by Meyer *et al.* [3] by synthesizing the DOBAMBC (2-methylbutyl 4-(*-*-decyloxybenzylideneamino) cinnamate) material, the first FLC material. Nowadays, FLCs are used for multitude of applications such as flat panel displays

[4], spatial light modulators [5], optical antennas [6], and so on. The FLC, Smectic C*, has a helical structure with each molecule having a polarization perpendicular to its long axis, and thus, the net polarisation becomes zero due to the collective ordering of mesogens in each layer. FLCs can be further grouped into surface stabilized ferroelectric liquid crystals (SSFLC), deformed helix ferroelectric liquid crystals (DHFLC), and electroclinic liquid crystals (ELC). In SSFLC, the surface stabilization is obtained by making the cell thickness smaller than the pitch and net polarisation is achieved by unwinding the helix with surface interaction. The DHFLCs are short-pitched FLC where the helix deformation is achieved by application of an electric field while in ELC the electric field is applied in parallel direction to the layers to inhibit the free rotation of molecules and thus produces a net non-zero polarisation. Even though FLCs are superior to nematic with regard to fast response, viewing angle, lack of perfect alignment, domain formation, and other defects are some drawbacks of the FLC for display applications. Doping FLC matrix with materials such as nanoparticles [7], microparticles [8] or colloids [9], having a wide array of properties and dimensions, is a viable and proven method to develop more functionally advanced and stable FLC composite systems without the above-mentioned drawbacks. Within the composite system, the interaction between the molecules and the dopants should be advantageous to our need. The size compatibility, concentration, and dispersion should be proper to have an orderly alignment and avoid any agglomerations or director distortions. Considering all these, nano-dispersion in lower concentrations seems to yield better results. The development and characterization of new nanocomposite paved the way to new regimes, including the development of non-volatile electrooptic memory effect, biosensors, devices for energy storage and conversion, *etc.*

In this chapter, we review the recent advances in FLC by dispersing various nanomaterials into the host LC matrix to enhance its electro-optical properties for memory and next-generation display applications. The nanoparticles (NP) such as metallic, semiconducting, insulating, and others bring about remarkable enrichment in the performance of the FLCs when made into a composite system with FLC. Advanced electro-optical properties, memory retentions, and improved alignments are some of the virtues of these composite FLC-NP systems.

FLC-NANOCOMPOSITES FOR MEMORY APPLICATION

As discussed, the FLC-nanocomposites exhibit faster response time, lower voltage threshold, better contrast, and lasting memory effects than their pure counterpart. Now in this section, we are concentrating more on the soft memory aspects of the FLC. The bistable nature of the FLC [10] with two stable polarisation states facilitate memory applications. The FLC can store the binary 0 and 1 values as

CHAPTER 13

Next-Generation Energy Storage and Optoelectronic Nanodevices

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Abstract: Among the variety of nanostructures that have been explored as a favorable material for the application of higher energy storage devices as supercapacitors, catalysts in high-performance batteries, proton exchange membranes in fuel cells, optoelectronic devices, and so on, 2D & 3D nanostructure of graphene-based derivatives, metal oxides and dichalcogenides have received the most potential attention for building high-performance nano-devices due to their extraordinary properties. Over the past decade, several efforts have been implemented to design, develop, and evaluate electrodes' structures for enhanced energy storage devices. A significant modification has achieved the remarkable performance of these synthesized devices in terms of energy storage capacity, conversion efficiency, and the reliability of the devices to meet practical applications' demands. Light-emitting diode (LED) in quantum well or quantum dots is considered an important aspect for an enhanced optoelectronic device. This current study outlines different 3D nanostructures for next-generation energy storage devices. It provides a systematic summary of the advantages of 3D nanostructures in perspective to next-generation energy storage devices, photocatalytic devices, solar cells, a counter electrode for metal-ion batteries, and supercapacitors, optoelectronic nano-devices.

Keywords: 2D & 3D nanostructure, Counter electrode, Fuel cell, Graphene derivatives, LED, Li-ion Battery, Metal-ion battery, Nanodevices, Optoelectronic, Photocatalytic device, Quantum dots, Supercapacitor, Solar cells.

INTRODUCTION

Over the current decade, due to the large fluctuations in energy demand and supply, energy storage has become an essential area of discussion as more energy is being obtained from intermittent sources.

A conventional capacitor generally possesses a comparatively high power density

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in comparison with batteries and can rapidly discharge the power. On the other end, batteries will be able to accumulate a large amount of energy in comparison with conventional capacitors. However, batteries cannot meet the demands, such as high dynamic charge and electrode polarization resulting from energy conversion. Electrochemical capacitors (EC) are primarily used to improve the performance of batteries and fuel cells inside a hybrid vehicle for quick acceleration, electricity storage devices developed from renewable energy like solar wind energy, and allow additional power for the recovery of energy by storing energy within a solid/electrolyte interface. Those layers' critical thickness exhibits a concentration of electrolyte with adequate size in the range of 5-10 Å and capacitance of 10-20 μF/cm² for a smooth electrode [1]. The main reason behind ECs attracting customers for an extensive range of applications is illustrated in Fig. (1) by a Ragone plot.

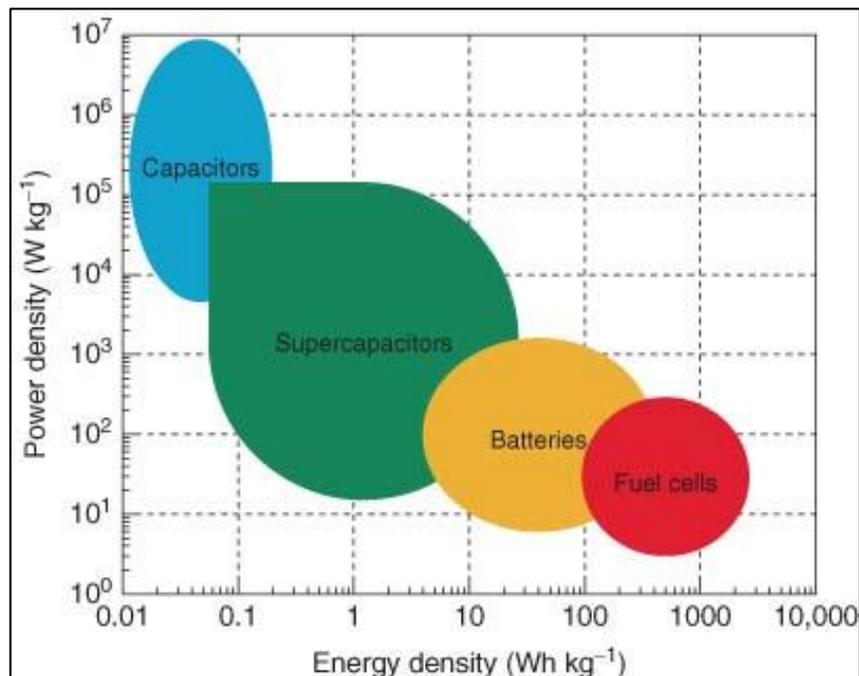


Fig. (1). Ragone plot of various energy storage systems [1].

Electrochemical double-layer Supercapacitors (EDLCs) are generally high-performance energy storage micro-devices that provide a capacitance value higher than a capacitor but with low voltage limits that channel the gap between electrochemical devices and rechargeable batteries. It consists of an electrochemical cell containing an anode, cathode, electrolyte, and a separator. The electrode composition is usually Nickel (Ni), cobalt (Co), molybdenum (M),

tungsten (W), *etc.*, which is separated by an electrolyte of basic, acidic, or neutral. The different types of supercapacitors made from different sources and for different applications are represented in Fig. (2). A rapid growth in the field of supercapacitors (2D and 3D nanostructures) was used in miniaturized microelectronics (*e.g.*, portable, wearable) and macro devices (*e.g.*, hybrid electric vehicle, sensitive automation, computer chips, automobiles, constructions equipment) due to its enhanced characteristics (high cycle life, charging and discharging characteristics, and specific power) [2]. A developed supercapacitor (SCs) of rectangular tube polyaniline structure bridges the gap between the rechargeable battery and conventional capacitor for enhanced power storage for quick charge/discharge [3], with an enhanced power density of 1091 Wkg^{-1} and a specific capacitance of 4007 F g^{-1} , which shows extreme flexibility of about 96% beneficial for energy recovery [4]. However, there is an increase in demand to develop sodium (Na) based energy storage as an alternative to large-scale energy storage [5]. A critical comparison between capacitors, SCs, and batteries for their characteristics is summarized in Table 1.

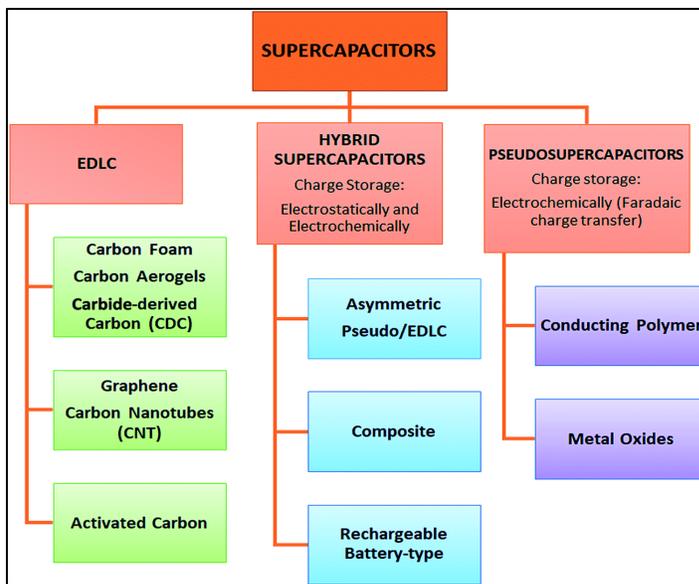


Fig. (2). Types of supercapacitors for technical applications.

Nanomaterials' Synthesis Approaches for Energy Storage and Electronics Applications

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Abstract: Nanomaterials are materials with cross-sectional dimensions varying from one to hundreds of nanometers and lengths ranging from hundreds of nanometers to millimeters. Nanomaterials either occur naturally or can be produced purposefully by performing a specialized function. Until recently, most nanomaterials have been made from carbon (carbon nanotubes), transition metals, and metal oxides such as titanium dioxide and zinc oxide. In a few cases, nanoparticles may exist in the form of nanocrystals comprising a number of compounds, including but not limited to silicon and metals. The discovery of nanomaterials has played a vital role in the emerging field of research and technology. Recently, a large amount of research efforts has been dedicated to developing nanomaterials and their applications, ranging from space to electronics applications. In this chapter, we describe the role of nanoparticles in electronics and energy storage applications, with examples including chips, displays, enhanced batteries, and thermoelectric, gas sensing, lead-free soldering, humidity sensing, and super capacitor devices. The chapter also attempts to provide an exhaustive description of the developed advanced nanomaterials and different conventional and advanced techniques adopted by researchers to synthesize the nanoparticles *via* bottom-up techniques (pyrolysis, chemical vapor deposition, sol-gel, and biosynthesis) and top-bottom approaches (mechanical milling, nanolithography, laser ablation, and thermal decomposition).

Keywords: Bottom-up Technique, Bio-synthesis, Carbon Nanotubes, Chemical Vapour Deposition, Electronics Applications, Energy Storage, Graphene, Humidity Sensor, Laser Ablation, Mechanical Milling, Nanolithography,

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Nanomaterials, Pyrolysis, Sole Gel, Spinning, Sputtering, Super Capacitor, Thermal Deposition, Thermo-electric, Top-down Technique.

INTRODUCTION

The production, storage, and utilization of energy in an optimal way are some of the important issues that are lately confronting the researchers of the world. The production of energy is not a major achievement nowadays. However, the storage and delivery of energy on demand has increasingly become even more important. Further, portable electronic devices and transportation systems are such applications where we do need to store energy appropriately. The use of energy storage devices is thus increasingly gathering importance in the field of science and technology. There are three different but important ways, such as electrical, electro-chemical, and chemical, in which energy can be stored in energy storage devices. There are large numbers of suitable materials which can be used for energy storage. However, considering the cost and energy per weight ratio of the materials, the options of suitable material for energy storage reduced drastically. Nanomaterials, such as carbon nanotubes and graphene, are suitable options for use as energy storage devices.

The high energy capacity and surface area are important parameters for the fabrication of the energy storage device. Carbon is one such lightest element used in various forms, such as carbon nanotubes (CNT's) for the fabrication of energy storage devices [1 - 5]. The single walled carbon nanotubes (SWCNTs) are not only light weight but they also attribute some other advantages, such as a large surface area of approximately $1315 \text{ m}^2 \text{ g}^{-1}$ when compared to graphite which offers it in a poor range of $10\text{-}20 \text{ m}^2 \text{ g}^{-1}$.

Nanomaterials offer drastically improved electronic conductivity in comparison with conventional super capacitor materials and conventional batteries. They also have faster ion diffusion and higher specific capacities. All these features make nanomaterials offer an encouraging solution for high power and high energy devices. After extensive research and development in the area, a library of nanomaterials with various morphologies has been explored. Some of them are zero dimensional nanoparticles such as quantum dots; one dimensional such as nanotubes, nano-belts and nanowires; two dimensional nano-sheets and nano-flakes and three dimensional porous nano-networks. These nanoscale building blocks have been combined with lithium ions for creating energy storage technology which is not achievable using conventional materials. The atoms and molecules in a nanomaterial act differently and disclose unmatched chemical, physical and electronics properties. Nanomaterials show physical properties such as reflection, absorption and light dispersion. They also show extraordinary

chemical properties such as oxidation, reduction, sensitivity, and stability towards humidity, atmosphere, heat, and light, etc. When nanomaterials are layered on a surface in the form of a solution, their reflection and adsorption properties make them a seamless choice in different applications. These properties make them ideal candidates for use in electronic, drug delivery, optical, mechanics, catalysis, bio-encapsulation and wastewater treatment, especially adsorption applications [6 - 15].

Along with the carbon nanotubes, graphene, fullerenes, carbon nano-fibres and activated carbons are also used as alternative energy storage materials [16 - 18]. Most of them are chemically inert, cheaper and light weight. They have special electrochemical, electrical, optical and mechanical properties. For example, graphene's surface area is approximately $2630 \text{ m}^2 \text{ g}^{-1}$. The large surface area of graphene makes it the most suitable choice for energy storage applications. Fig. (1) shows the classification of different types of nanomaterials.

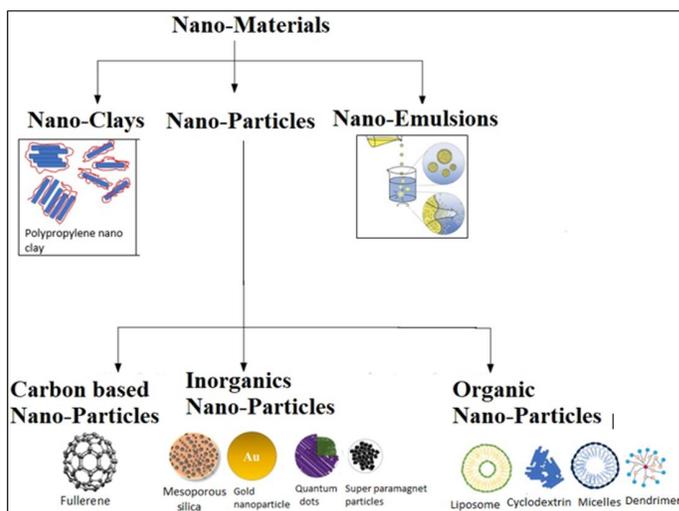


Fig. (1). Classification of nanomaterials.

The growing efforts towards clean and renewable energy drive breakthroughs in energy storage technology. Among different energy storage systems, electrochemical systems are used in portable electronic devices. Higher volumetric and gravimetric energy density is required for portable electronics devices. For stationary applications such as grid-scale energy storage, the lower capital cost is the key. The basic difference between batteries and electrochemical is in the charge storage mechanism. A battery store charge via faradic reactions, whereas electro-chemical stores charge near the surface. Hence, electrochemical systems have more specific power compared to batteries, which have a more

Nanomaterials for Flexible Photovoltaic Fabrics

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Abstract: The development of extremely flexible photovoltaic (PV) devices for energy harvesting and storage applications is currently receiving more attention by the researchers from industries. The presently available energy storage devices are too rigid and extensive and also not suitable for next-generation flexible electronics such as silicon-based solar cells. Thus, the researchers have developed high-performance, lightweight, conformable, bendable, thin, and flexible dependable devices. On the other hand, these energy storage devices require to be functional under different mechanical deformations, for example, bending, twisting, and even stretching. The nanomaterial (TiO₂, ZnO, Ag, etc.) coated fabrics also play a vital role in improving the efficiency of the solar cell (devices) to a great extent. The current chapter provides information about the development of nanomaterials-based flexible photovoltaic solar cell devices for wearable textile industry applications. The fabricated carbon ink printed fabrics such as polyester, cotton woven and nonwoven, and polyethylene terephthalate nonwoven can be used as cathode and heating sources of PV devices. The organic and flexible conductive substrate printed with carbon ink can be utilized as heating source fabrics for wearable electronics devices. The flexible substrate-based photovoltaics (PV) device is mostly used in the textile industries due to its flexibility, environmental friendliness, low cost as well as easy processability. The flexible-wearable photovoltaic devices pave the way to be used for enormous applications in various fields.

Keywords: Energy storage and harvesting, Efficiency, Flexible photovoltaic fabrics, Flexible electronics, High-performance, Lightweight, Low cost, Nanomaterials, Photovoltaic fibers, Photovoltaic fiber, Solar cell, Wearable textile industry applications.

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INTRODUCTION

Recently, flexible energy storage materials have been in huge demand by the industries. Day by day, this has increased the utilization of nanomaterials coated flexible systems which bestows higher flexibility, good electrical performance, excellent mechanical properties as well as environmental stability [1 - 3]. Nanomaterials play a significant role as active layers on the fabric substrate and nanomaterials-based flexible substrate nanodevices have been extensively exploited in different applications in the last decade compared to the available traditional planar technology [4]. On the other hand, the development of the organic transistor was fabricated on a flexible plastic substrate or thin glass substrate, mostly for electronic devices. However, they are demonstrated with poor electrical characteristics as compared to the high-performance inorganic semiconductor materials and were found to be inappropriate for other applications [5, 6]. The materials needed for the flexible electronics are depicted in Fig. (1).

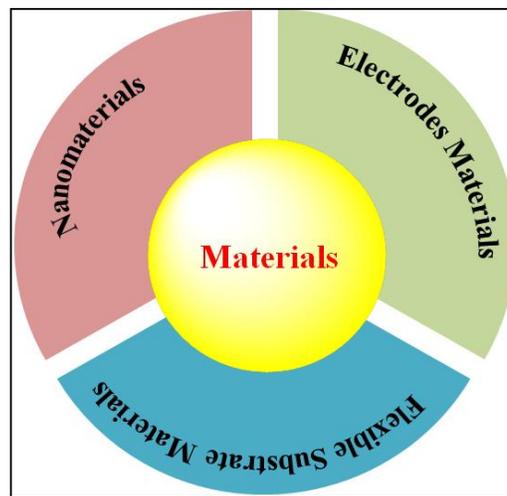


Fig. (1). Materials for flexible electronics applications.

Moreover, the use of elastomeric substrate is very limited for the deposition of the active layers on polymer substrates due to the low processing temperature and reduced performance of the fabricated electronic device. Conversely, the development of novel materials like conducting polymers, carbon-based structures, for example, metallic and ceramic composites; the nanomaterials-based electronic device can be formed on the elastomeric flexible substrate, while exploring a new electronic device field like flexible electronics. The flexible electronics focused on fabricating compatible flexible systems reveal good carrier mobility and better electrical behaviour. The nanomaterials can be utilized as an

active layer or substrate to address the restrictions of the inert system and will be immobile with the defining mechanics due to their heterogeneous low-dimensional structure.

Currently, flexible solar cells play a significant role in photovoltaics because they are weightless, tolerable to complicated deformation, can be incorporated into curve surfaces, consistent with reel-to-reel processing, proper storage and transportation [7 - 9]. These are utilized in many applications like portable or wearable electronics, power generated textiles, *etc* [10, 11]. Amorphous silicon solar cells based on flexible photovoltaic devices are available, but they are too expensive with a low bending radius. For that reason, researcher-developed novel solar cells, for example, dye-sensitized solar cells (DSCs), organic solar cells (OSCs), and perovskite solar cells (PSCs), which were found to be of great interest, especially for the low-temperature fabrication, low thickness, and color regulation. In the case of the flexible solar cell, entire functional layers are converted to flexible; particularly the electrode works as a substrate for active layers. Moreover, the interaction among the flexible electrodes and active layers by low-temperature processing is important to alter the morphology and boundary of entire functional layers while tuning the properties of the photovoltaic devices. Table 1 demonstrated the three main types of flexible substrate as a polymer (plastic), metal foil, and thin glass. Flexible photovoltaic fabrics, after the addition of MWCNT were used as a flexible wearable heating source or cathode for DSSCs.

Table 1. Advantages and disadvantages of the different flexible substrates (Koh *et al.*, 2018 [12]).

Substrate	Advantages	Disadvantages
Metal foil	<ul style="list-style-type: none"> • Rough and conformable • Low H₂O and O₂ permeation • High process temperature • Good dimension stability 	<ul style="list-style-type: none"> • Weak dimension stability • Less process temperature and chemical • Resistance • Good H₂O and O₂ permeation
Thin glass	<ul style="list-style-type: none"> • Conformable • Transparent • Low H₂O and O₂ permeation 	<ul style="list-style-type: none"> • Poor mechanical stability • Less process temperature
Polymer (e.g. Plastic)	<ul style="list-style-type: none"> • Rough • Ductile • Transparent 	<ul style="list-style-type: none"> • Weak dimension stability • Less process temperature and chemical resistance • High H₂O and O₂ permeation

This chapter deliberates the present-day research advancement on the fabrication of the nanomaterial-based flexible photovoltaic fabric cells for energy harvesting and storage applications inside the textile industry.

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