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An Introduction to Graphene Materials

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Abstract

Graphene, an allotrope of carbon, is the thinnest compound known to human which is a single layer (monolayer) of carbon atoms, tightly bound in a hexagonal honeycomb lattice. Nanosize graphene is known to possess large surface area and shows promising properties in terms of mechanical, electrical, chemical, and magnetism. Graphene and its derivatives are an exciting replacement for the existing nanomaterials, and so, graphene is discovered to be useful in the application of energy conversion and storage, sensing, electronics, photonics, and biomedicine. In this introductory chapter, the potential implementation of graphene and its nanocomposites, along with the characterization techniques employed for graphene, is briefly discussed. We hope this review can inspire more innovative insights into this emerging topic in energy materials.

Keywords: graphene, nanocomposites, devices, electrochemical properties, synthesis

1. Introduction

In recent years, a new material called graphene has emerged in the regime of advanced nanomaterials and is being extensively explored by the scientists and engineers. Graphene is a two-dimensional (2D) allotrope of carbon, wherein sp^2 -hybridized carbon atoms are covalently bonded in a hexagonal lattice to form a single sheet of atoms [1]. It has been realized that graphene happens to be the basic building block of other carbon allotropes such as graphite, single-walled/multi-walled carbon nanotubes, and fullerenes. Monolayer graphene is a perfect 2D material owing to its thickness ranging to a single sheet of carbon atoms. It could exist in bilayer or few layer configurations as well. However, as the numbers of layers increases, it transforms to graphite. Graphene has gained immense popularity in the scientific field due to its fascinating properties such as metal-like conductivity, superior chemical stability, optimum blend of high mechanical strength and flexibility, excellent transport properties with very high charge mobility ($200,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), zero energy band gap, low optical absorption, and a high specific surface area ($2630 \text{ m}^2 \text{ g}^{-1}$) [2–4]. These outstanding characteristics make graphene increasingly demanding in a plethora of applications such as photocatalysis, supercapacitors, batteries, solar devices, light emitting diodes, hydrogen storage, sensors, and so on [5–9]. Graphene could also be incorporated in ceramics, metal oxide semiconductors, or conducting polymers to enhance the performance of the host materials by the synergistic effects. These applications offer exciting

new opportunities for scientists to devise new strategies and methods for the synthesis and applications of graphene.

The synthesis of a high-quality graphene to be suitable for any kind of application has always been very critical so far, as there is a stringent limitation on its thickness keeping its adhesion, transparency, and continuity unhampered on larger areas. As an example, graphene could be synthesized by exfoliation of graphite flakes (such as HOPG or Kish graphite) or through the annealing of polar SiC surfaces at high temperature of 1200°C. However, these methods face the major limitations of nontransparency and lesser amount of graphene deposition on the substrate [10]. Hence, in recent years, numerous methods have been designed and utilized for efficient synthesis of graphene without letting its special properties getting deteriorated. The chemical vapor deposition (CVD) technique is one of the techniques being successful in synthesizing graphene at 1000°C from hydrocarbon gases like CH₄ and has become one of the popular methods to prepare transparent and uniform graphene thin film on the metal substrates. It is an inexpensive technique for the high-throughput growth of graphene on larger areas. However, it needs one extra step to transfer graphene film to the arbitrary substrates which needs more efforts and becomes tedious. Another variant of this method is known as hot filament chemical vapor deposition (HFCVD), wherein the precursor gases are heated to a higher temperature of around 1500–2000°C with the help of filaments made up of refractory materials such as tungsten. Due to a higher temperature, it is possible to achieve the complete decomposition of precursor gases and initiate the pyrolytic reactions to attain a complete phase formation of the material to be synthesized on the substrate of choice. It is an emerging technique to synthesize high-quality graphene with only a few reports in the literature [11]. However, graphene-like carbon (GLC) thin films could be successfully synthesized using this technique. Herein, the decomposition reaction is initiated among precursor gases like hydrocarbon (CH₄) gas, hydrogen (H₂), and argon (Ar) under the vacuum conditions by flowing them over hot filaments. The carbon species thus condenses onto the desired substrates, kept close to the filaments, and requires phase if formed [12], as shown in **Figure 1**. Further the GLC thin film could be either directly used or transferred onto different substrates for its utilization in a particular application. As presented in **Figure 2**, these films, when tested as a counter electrode in dye-sensitized solar cells (DSSC), showed a relatively high conversion efficiency of ~4.3% [12] and ~6.94% [13]. It is also presented in **Figure 3** that the GLC-Ni nanocomposite films synthesized by the combination of HFCVD and DC sputtering presented a moderate conversion efficiency of ~3.1% [14].

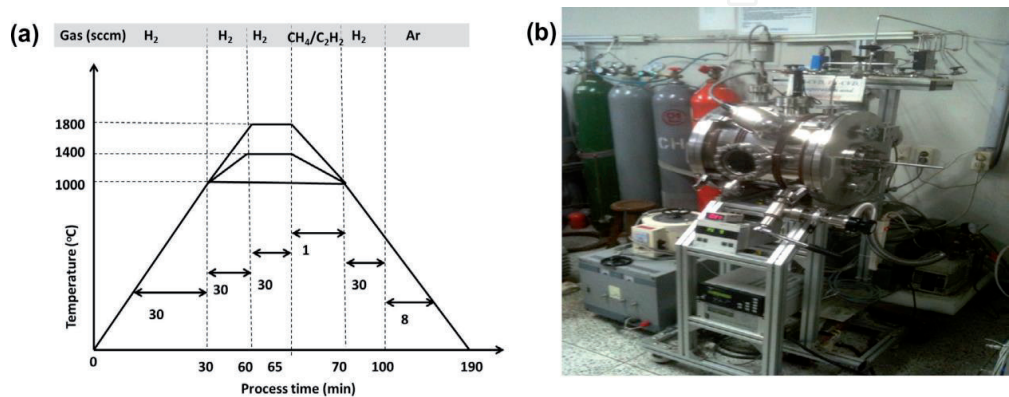


Figure 1. (a) Schematic illustration showing the parameters for the growth process of graphene-like thin film on FTO glass substrate by HFCVD and (b) photograph of HFCVD system [12].

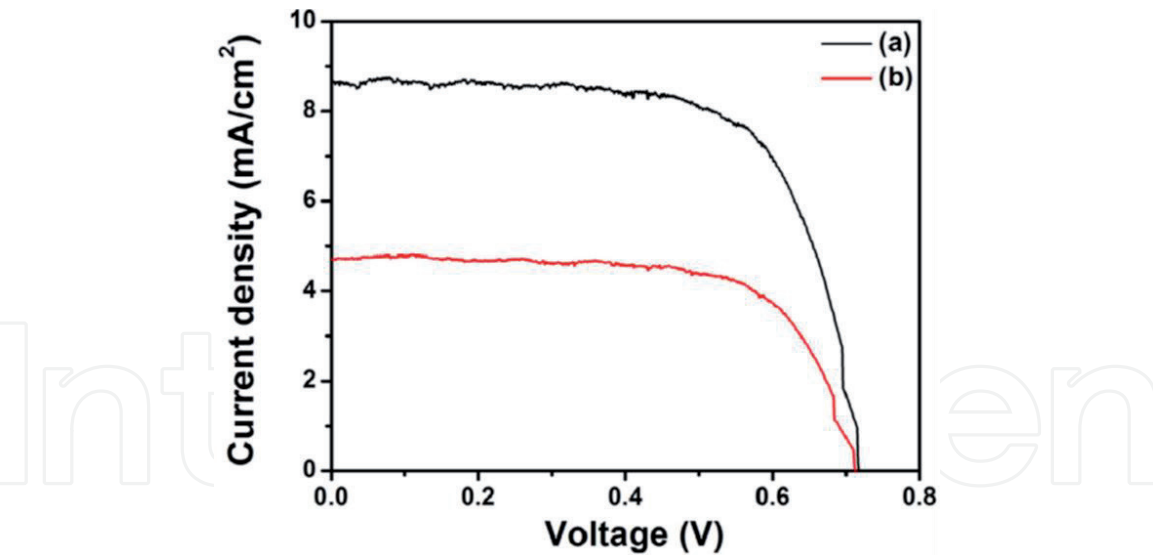


Figure 2.
J-V curves of the DSSCs fabricated with graphene-like thin film counter electrodes obtained from (a) CH_4 and (b) C_2H_2 precursor gases [12].

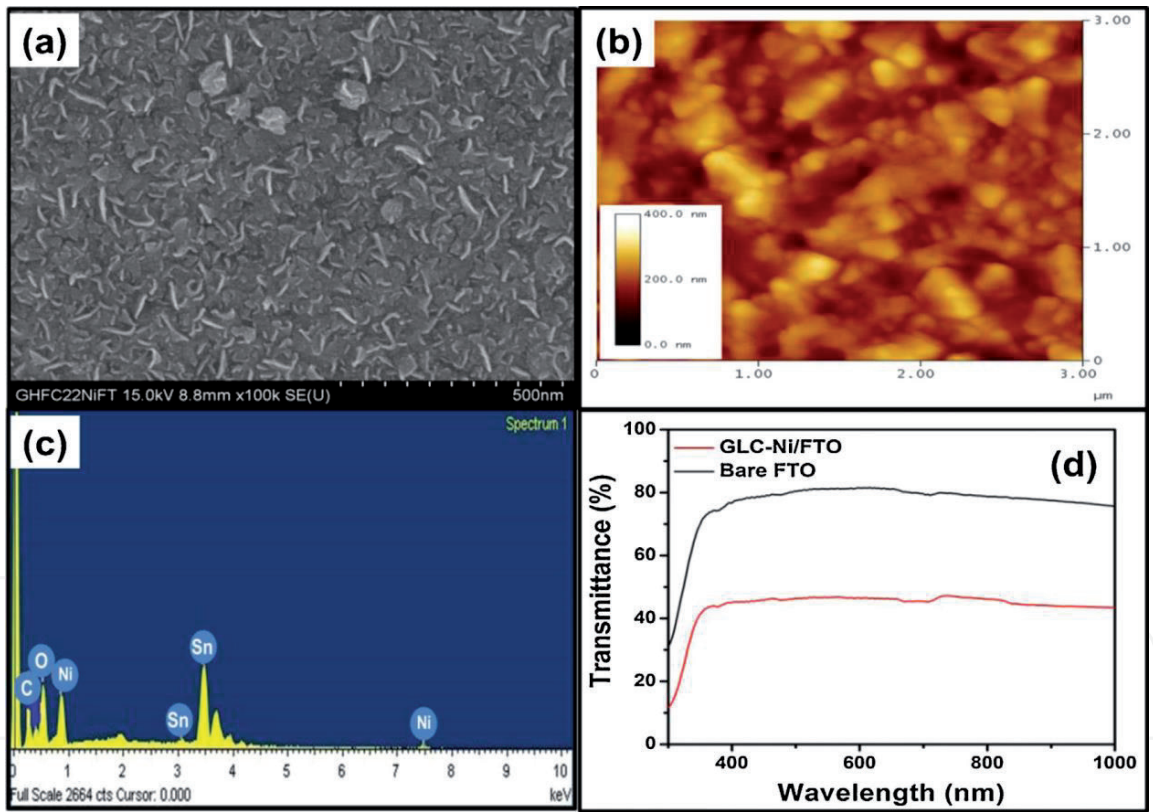


Figure 3.
(a) FESEM, (b) AFM, (c) EDS, and (d) UV-vis spectra at transmittance mode of GLC-Ni/FTO thin film [14].

Graphene could be synthesized by the chemical-based method known as Hummers and Offeman method, in which the standard graphite powder is mixed with sulfuric acid at $\sim 0^\circ\text{C}$ and then potassium permanganate is added to the reaction suspension which raises the temperature to $\sim 20^\circ\text{C}$. Thereafter, deionized water is added with vigorous stirring which further raises the temperature to $\sim 98^\circ\text{C}$ with subsequent addition of hydrogen peroxide. At first graphene oxide (GO) is obtained after rinsing and drying the precipitates. After reducing this product using hydrazine monohydrate with subsequent washing and drying, graphene oxide gets transformed to graphene. Further, the as-synthesized graphene could be used to

make a nanocomposite with polyaniline by a method known as chemical oxidative polymerization of aniline monomer. The composite thus formed could be used in the photocatalytic degradation of rose bengal dye which could serve as an environmental remedy against hazardous industrial effluents [15]. The electrochemical synthesis of as-prepared graphene oxide with aniline monomer was performed and applied as electrode material for the detection of hydrazine chemical. The high sensitivity of $\sim 32.54 \times 10^{-5} \text{ Acm}^{-2} \text{ mM}^{-1}$ with response time of 10 s was achieved by Ameen et al. [16]. The graphene oxide was also used for the formation of nanohybrid by using metal oxide such as zinc oxide (ZnO) through the hydrothermal process, carried out at $\sim 90^\circ\text{C}$ for 12 h. Uniform distribution and mixing of ZnO particles and graphene sheets were seen, as shown in **Figure 4**. The synthesized ZnO-GO nanohybrid was utilized as an efficient photocatalyst for the 95% degradation of crystal violet (Cv)-dye in 80 min, as displayed in **Figure 5**. The fast Cv dye degradation

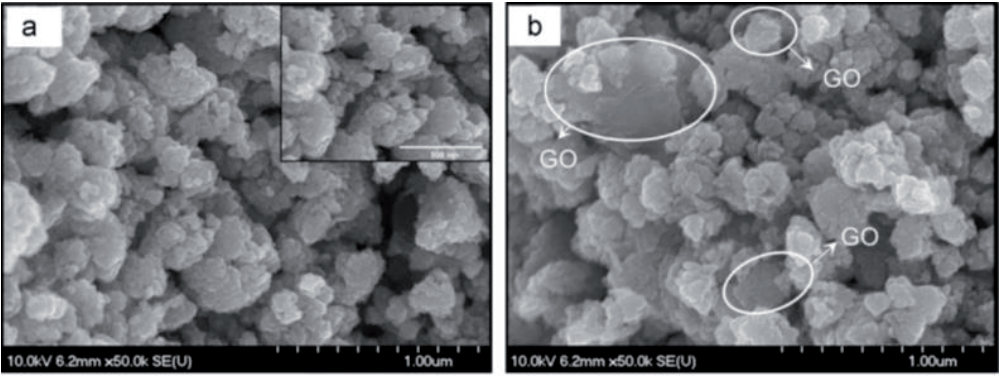


Figure 4.
FESEM images of (a) ZnO nanoparticles (b) ZnO-GO nanohybrid [17].

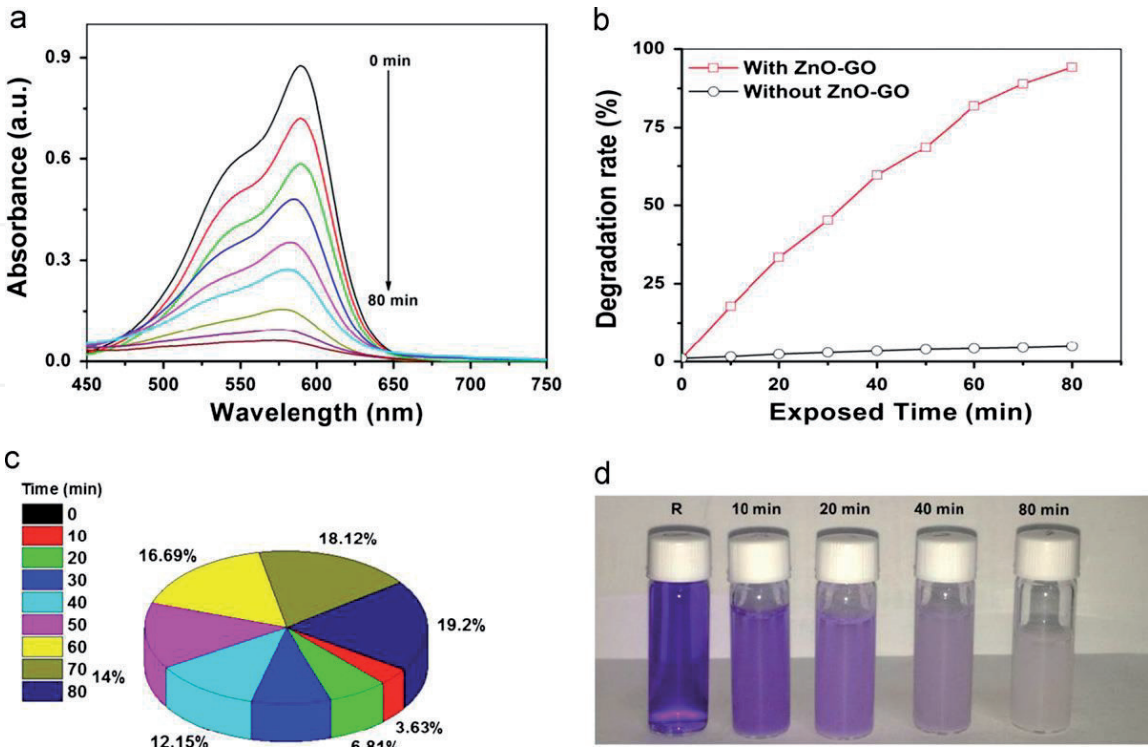


Figure 5.
(a) UV-vis absorbance spectra of decomposed Cv dye solution over ZnO-GO nanohybrid under light illumination, (b) the degradation rate (%) versus exposed time, (c) Cv dye degradation pie chart as a function of exposed time, and (d) the photographs of decomposed Cv dye solution before and after the photocatalytic reaction [17].

over ZnO-GO nanohybrid photocatalyst was attributed to GO as supporting material which enhanced the absorption capacity and suppressed the recombination of photo-generated charge carriers [17]. According to another study, GO was electrophoretically deposited on fluorinated tin oxide at 50 V in 30 s, and the GO deposited specimens were further engrafted by the chemically synthesized ZnO quantum dots using spin-coating technique. The electrode thus prepared, which successfully sensed ethyl acetate with substantially high sensitivity of $\sim 16.035 \text{ mA mM}^{-1} \text{ cm}^{-2}$ [18]. Graphene was also be used in the modification of buffer layer to fabricate small-molecule organic solar cells. After the addition of graphene, the solar cells exhibited an improved power conversion efficiency of $\sim 3.63\%$. This improvement could be ascribed to the reduction in the series resistance as well as better interfacial contacts between the layers brought about by graphene [19].

Graphene being a two-dimensional material also acts as a solid lubricant and offers the unique properties against friction and wear which are not observed in other materials. Graphene exhibits impressive tribological properties owing to its high chemical stability, mechanical durability and easy shear capability of its densely packed and atomically smooth surface. Since, it is ultrathin even with multilayers, it could be applied to nanoscale or microscale systems such as microelectromechanical systems (MEMS) and nanoelectromechanical systems (NEMS) with oscillating, rotating, and sliding contacts to reduce stiction, friction, and wear [20].

The studies illustrated above demonstrate the potential of graphene as an emerging material applicable in almost all the developing fields, and hence, it has attracted pivotal importance in the new age technology and innovation. Through this, this chapter exhibits the vast ambits of graphene with a hope to attract scientists and engineers to contribute into its challenging domains.

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