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Graphene/Nanoparticles Composites synthesis and Application

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Abstract
The development of graphene/nanoparticles composites materials is currently the issue of tremendous research interest. Graphene sheets possess surface defects and oxygen functional groups, which make them ideal templates for synthesis of semiconductor and metal nanoparticles. To date graphene have created an immense research interests because of its excellent electronic, optical, mechanical, and thermal properties, graphene has shown great promises in a wide range of applications such as photovoltaic application, energy storage devices, photocatalytic hydrogen evolution, and gas sensing application. Enhanced properties are expected in these graphene/nanoparticles composites, which arise from the synergic effect of the graphene sheets anchored nanoparticles. In this review, after introduction on the properties and the various synthesis methods of graphene/nanoparticles, we will discuss the application of graphene/nanoparticles composites specially graphene/semiconductor nanoparticles composites, in fields of Photovoltaic application, energy storage, Photocatalytic hydrogen evolution and gas sensing application.

Keywords: *Graphene Sheet; nanoparticles; composites application*

1. Introduction

Graphene sheet is the amazing monolayer of sp^2-bonded carbon atoms arranged in honeycomb structure, has attracted extensive interest in recent years and emerged as the most intensively studied material [1]. Graphene is a gapless semiconductor with unique electronic properties and its electron mobility can reach 10,000 $cm^2 V^{-1} s^{-1}$ at room temperature and has a micrometer-sized 2D plane with large π–π conjugation [2]. The bandgap within graphene sheet can be opened by reducing the dimensions of the graphene sheets to the nanolevel [3] or by introducing dopants [4]. Recently nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures. It exhibit size and shape dependent physical and chemical properties which make them suitable in application of various fields. Nanomaterials have a large surface to volume ratio than their conventional bulks state. Also at the nanolevel, quantum effects can become much more important in determining the materials properties. At the nano level, properties like electrical conductivity and mechanical strength are not the same as they are at bulk level. Its electronic structure changes dramatically [5]. Hence, at the present day it is very necessary to synthesis and studies the nanomaterials and its composites. Recently scientists decorated various semiconductor/metal nanoparticles on graphene sheet. Composites especially graphene based provide an important milestone to improve the overall performance. Because, hybrids have versatile and tailor-made properties with performances superior to those of the individual oxide nonmaterial. To date, various kinds of nanopaticles have been synthesized and decorated on graphene, which include SnO_2 [6], TiO_2 [7], and Al_2O_3 [8]. But, these materials have some limitations (e.g., TiO_2 has a limited photoactivity with the radiation provided by solar light [9] that can be potentially overcome by the use graphene as platform to these materials.

The extremely large surface areas graphene is very useful to decorated nanoparticles. Graphene/nanoparticles composites obtained the energy-band alignment, for example it is possible to obtain PV devices with excellent performance [10]. Also, the efficiency enhancement of charge separation and transfer in the composites can play a very important role in improving PV response. In spite of the efficient nanomaterials based devices, their fabrication processes are simple and the energy they produce uncompetitive compared to traditional nonrenewable energy sources (e.g. coal, natural gas, hydropower, etc.). Hence, surface functionalization of graphene is required to improve the

This review first gives an account of graphene and a general overview of nanoparticles, followed by a short description to synthesis of graphene/nanoparticles composites and then the recent application on the graphene/nanoparticles composites.

2. An Overview Graphene/Semiconductor nanoparticles composites Synthesis.

Now a days graphene, has received considerable attention because of its unique properties, including high thermal conductivity (~ 5000 W m^{-1} K^{-1}), high electrical conductivity (10^8 S m^{-1}), and large specific surface area (2.63 × 10^6 m^2 kg^{-1}) [1]. Nanoparticles research is currently an area of intense scientific research, due to a broad variety of potential applications. Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic structures.

Size-dependent properties are observed such as quantum confinement in semiconductor particles, surface Plasmon resonance in some metal particles. The optical properties exhibited by nanoparticles are quite different from there bulk counterpart. The reason behind this change in properties is mainly due to the change in surface Plasmon resonance. When the size of nanoparticles is smaller than the wavelength of incident radiation, a surface Plasmon resonance is generated and which very useful in photovoltaic application.

These section overviews the major and most popular graphene/nanoparticles synthesis methods, such as in situ growth approach, electrochemical deposition, Sol-gel process, hydrothermal approach and solution mixing method have been developed for fabricating the graphene/nanoparticles composites. In this review, we will focus on the synthesis of graphene/nanoparticles composites, specifically the semiconductor nanoparticles, and their applications.

Bearing in mind its superior electron mobility and high specific surface area, graphene improve the photocatalytic performance of semiconductor nanoparticles such as TiO_2, where graphene can act as an efficient electron acceptor to enhance the photo induced charge transfer and to reduce the recombination of the photo generated electron holes [11, 12].

2.1 In-situ growth approach

One of the commonly used methods to prepare graphene/semiconductor nanoparticles composites is the in-situ growth approach, by direct reaction of the graphene sheets and the semiconductor nanoparticles in solution. For example, Nemade *et al*. [13] prepared graphene/SnO_2 composites by using in situ approach. The composites were prepared into three steps. First, $SnCl_4$ and NaOH were dissolved in distilled water in two separate beakers with a molar ratio of 1:4 and chemical solution was put in an ultrasonic bath for 2 h. Second, graphene was mixed in solution placed in oven to dry at 373 K. Here the graphene is synthesized by electrochemical exfoliation method. Accordingly, four samples were prepared by altering the proportion of graphene from 0.4 to 1.6 wt. %. Third, the dried products were sintered in a quartz tube at 473 K for 8 h under a nitrogen atmosphere. Lambert *et al.* [14] reported in situ synthesis of composites comprised of flower-like anatase TiO_2-graphene oxide by the hydrolysis of TiF_4 in the presence of aqueous dispersions of GO.

In another report, Cao *et al.* [15] reported graphene/CdS composites as optoelectronic materials by mixing GO and Cd $(CH_3COO)_2$ in dimethyl sulfoxide (DMSO), and then sintering the solution in autoclave at 180° C for 12 hours. Here, the DMSO acts as both the solvent and the sulfur source, and the hydrothermal process has led to both the formation of the CdS nanoparticles and the graphene. Such in situ growth approach has also been applied to synthesize ZnO [16], In_2O_3 [17] Bi2O3 nanoparticles [18] and MnO_2 nanoneedles [19] on graphene sheets.

Through a different route Nemade *et al.* [20] employed in another report Sb_2O_3/graphene composites. The preparation of composites could be divided into two steps: First prepared Sb_2O_3 nanoparticles and graphene sheets separately. First in two separate beakers, $SbCl_5$ and NaOH dissolved in demonized water of resistivity not less than 18.2 MΩ/cm with molar ratio 1:5. Second, graphene sheets were synthesized by electrochemical exfoliation method. Mixed solution placed in oven to dry at 100°C for 5 hours. Then the Sb_2O_3 nanoparticles were decorated on graphene sheet.

2.2 Electrochemical deposition

Electrochemical deposition is an efficient method to prepare graphene/semiconductor nanoparticles composites, such as ZnO, Cu_2O, and CdSe nanoparticles as compare to wet impregnation, microwave irradiation, micro emulsion. Electrochemical deposition method is widely used employing different methodologies, such as cyclic voltammetry, potential step deposition and double-pulse.

Ren *et al.* [21] were dispersed multilayer structures of graphene in a nickel plating solution by using a surfactant with a magnetic stirring method. Nickel/graphene composites were formed on target substrate. For composites Graphene nanosheets were mixed into nickel nanoparticles through a plating process. In this process graphene nanosheets were uniformly dispersed in the nickel nanoparticles, and the oxygen radicals present in the graphene were reduced during the electrodeposition process.

Golsheikh *et al.* [22] fabricated cubic phase silver nanoparticles, silver nitrate as precursor decorated on rGO composites was electrodeposited on ITO by a cyclic voltammetry method. Enzymeless electrochemical sensor using Ag/rGO composites deposited on ITO exhibited notable electrocatalytic activity for the reduction of H_2O_2. Purna *et al.* [23] reported ZnO bi-pods on rGO for optoelectronic applications, ZnO nanoparticles were directly grown on the rGO films by single-step electrodeposition method. Bi-pod morphology was observed for ZnO electrodeposited on rGO sheet by pulsed current electrodeposition. The obtained ZnO/rGO composites show large potential for highly transparent optoelectronic devices.

2.3 Sol-gel process

Sol-gel process, is usually conducted under mild conditions (such as low temperature and atmospheric pressure) and do not have high requirements on equipment. Mirzaei and Davoodnia reported the microwave assisted sol-gel synthesis of MgO nanoparticles and their catalytic activity in the synthesis of Hantzsch 1, 4-dihydropyridines [24].

Botta *et al.* [25] study the photocatalytic efficiency of pure and Fe-containing ZrO_2 semiconductors nanoparticles in transformation of substrates nitrite, EDTA and Cr (VI) and compared with that of TiO_2 (Degussa P-25) by sol gel method. Sui *et al.* [26] reported Sn-doped TiO_2 composites by sol–gel synthesis with high aspect ratios. Wojtoniszak *et al.* [27] used sol-gel method to prepare the TiO_2/graphene composite via the hydrolysis of titanium butoxide in graphene oxide (GO) containing ethanol solution. The reduction of GO to graphene was realized in the post heat treatment process.

Farhangi *et al.* [18] prepared Fe-doped TiO_2 nanowire arrays on the surface of functionalized graphene sheets using a sol-gel method in the green solvent of supercritical carbon dioxide. In the preparation process, the graphene nanosheets acted as a template for nanowire growth through surface -COOH functionalities.

2.4 Hydrothermal approach

The hydrothermal process, one of the conventional methods for synthesis of semiconductors, is another effective method rather than co-precipitation method for the preparation of semiconductor materials with graphene. In this process, semiconductor nanoparticles are loaded on the graphene oxides sheets, which are reduced to graphene.

Zheng *et al.* [29] synthesized graphene/zinc oxide composites using a hydrothermal method and used as electron acceptors in poly-(3-hexylthiophene) based bulk-heterojunction organic photovoltaic cells. The power conversion efficiency of this type solar cell is strongly depended on graphene-ZnO weight %. So, it is expected that graphene could be a good candidate for the acceptor material in photovoltaic applications. Zhang *et al.* [30] also have examined the H_2S sensing applications of highly aligned SnO_2 nanorods on graphene three-dimensional (3D) array structures synthesized by a straight forward nanocrystal seeds-directing hydrothermal method

Song *et al.* [31] have demonstrated a cataluminescence gas sensors application of graphene sheets decorated with SnO_2 nanoparticles, synthesized by hydro- thermal assisted an in situ synthesis route. Duan *et al.* [32] studied the photoanode performance of Sn-doped TiO_2 synthesized by the hydrothermal method. Feng *et al.* reported the synthesis of MnO_2/graphene composites by a facile one-step hydrothermal method and examined its shape-controlled supercapacitive properties [33]

2.5 Solution mixing method

Solution mixing is a simple method to prepared graphene/semiconductor composite solution mixing is started with an ultrasonic mixing and then UV-assisted photocatalytic reduction of GO. Paek *et al.* [34] synthesized SnO_2/graphene composites; SnO_2 sol prepared by hydrolysis of $SnCl_4$ with NaOH, and then prepared graphene dispersion was mixed with the sol in ethylene glycol. Kuila *et al.* [35] reported graphene/polymer composite by solution mixing method. The tensile strength and sharp increase in electrical conductivity observed in dodecyl amine modified graphene.

Zeng *et al.* [36] fabricate a highly transparent composite film of zinc oxide (ZnO)/poly (methyl methacrylate)-co-poly (styrene) (PMMA-PS) with the novel UV-shielding properties. Nanoparticles were prepared by phase-transfer of ZnO suspension in hexane to nanoparticles dispersion in toluene with surface modifier. The dispersion had the complete transparency as a solution. Transparent "solution" mixing method to fabricate a highly transparent nanocomposite film of zinc oxide (ZnO)/poly (methyl methacrylate)-co-poly (styrene) (PMMA-PS) with the novel UV-shielding properties. While transparent "solution" containing nanoparticles was prepared by phase-transfer of ZnO NPs suspension in hexane to NPs dispersion in toluene with surface modifier.

Geng *et al.* [37] mixed graphene oxide sheets and the CdSe nanoparticles modified with pyridine to produce graphene-CdSe quantum dots composites. They thought that pyridine ligands could provide p-p interactions for the assembly of CdSe nanoparticles capped with pyridine on GO sheets.

3. Graphene/Semiconductor nanoparticles composites application

3.1 Graphene/Semiconductor nanoparticles composites for photovoltaic application

Currently, the graphene/semiconductor nanoparticles composites are mostly employed in photovoltaic applications. This PV cell with improved the absorption of solar radiation and charge carrier transport using semiconductor nonmaterial's which have responsible to increased in power conversion efficiency. In the present day it is very necessary to understand the basic mechanism of PV cell, let us take an example of bi-layer PV cell. In a bi-layer devices structure consists of a transparent conductor, a photoactive layer and the electrode [38]. The photoactive materials namely donor and acceptor are sandwiched between the transparent conductor and the electrode. PV cells containing graphene/nanoparticles composites as active materials have been studied extensively [39-41]. The most commonly indium tin oxide (ITO), with its work function of 4.4-4.5 eV, is used as the transparent conductive electrode. ITO is brittle and limited as a flexible substrate [42]. To overcome this drawbacks recently various researcher replace ITO by grapheme as a transfer ant conducting electrode has a work function of 4.5 eV [43]. The whole structure was made on a supporting substrate.

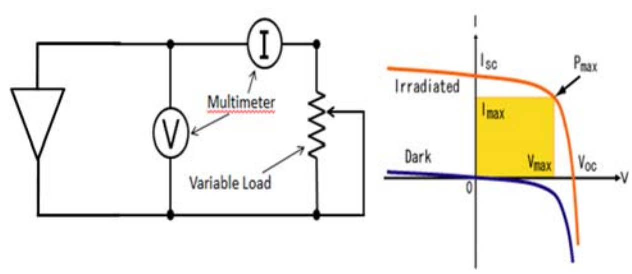

Fig 1: I-V characteristics of a photovoltaic cell

In photovoltaic devices, grapheme sheets have been mostly used as charge acceptors [44], transparent electrodes [45, 46], and charge transport bridges, For example, Using graphene as a novel charge acceptor, Guo *et al.* [47] developed quantum dots solar cells with the multilayered graphene-quantum dots device structure and energy level alignment. The resulting device exhibited an incident power conversion efficiency 16% and a photoresponse 10.8 A/m^2 under 1000 W/m^2 illumination. This achievement represents significant progress in the development of high-performance quantum dots solar cells. Further research efforts in this area could lead to even higher efficiencies. Radich *et al.* [48] reported the graphene-based transparent electrodes for photovoltaic cell. Yang *et al.* [49] reported graphene as 2D bridges into the nanoparticles electrodes of dye-sensitized solar cells. Bridges brought a faster electron transport and a lower recombination, together with a higher light scattering. The total conversion efficiency was 6.97%, which was increased by 39%, comparing with the nanocrystalline titanium dioxide photoanode, and it was also much better than the 1D nanomaterial composite electrode.

Khare *et al.* [50] reported the nanocomposite based on reduced graphene oxides and zinc oxide for applications of photovoltaic cell by dip coating chemical casting methods on a glass substrate. Composite is a promising nanomaterial to play a major role in photovoltaic or solar cell to improved efficiency. Graphene/TiO_2 can be used in both DSSC and quantum dots solar cells (QDSC). DSSC could alternate traditional silicon solar cells in the future, since they have high photon-to-electron efficiency and low cost [51]. Tang *et al.* has reported rGO/TiO_2 indiun tin oxides as photoanode for DSSC. The increase of electron transport manifested in an increase of the short-circuit current density. They achieved a power conversion five times higher than pure TiO_2 [52].

3.2 Graphene/Semiconductor nanoparticles composites for energy storage devices:

The surface properties of graphene can be adjusted via chemical modification, which offers wonderful opportunities for the development of functionalized graphene-based materials [53]. Such graphene-based materials show unique electronic and optical properties, which make these materials attractive for many potential applications including energy storage [54].

A new simple route to prepare N-doped graphene/SnO_2 sandwich papers was developed by Wang *et al.* [55] for high-performance lithium-ion batteries. Cao *et al.* [56] have also reported graphene supported Ag nanoparticles prepared by a solvothermal approach for enhanced electrochemical performance in lithium-ion batteries. Lian *et al.* [57] have reported a gas liquid interface synthesis approach, which has been developed to prepare SnO_2/graphene nanocomposites and focused on the high reversible capacity of SnO_2/graphene nanocomposites as anode materials for lithium-ion batteries. Li *et al.* [58] have reported the graphene/SnO_2 composites as electrochemical supercapacitors application. Li *et al.* [59] further demonstrated the graphene/MnO_2 composite papers as flexible supercapacitor electrodes.

Zhai *et al.* [60] reported 3D MnO_2/graphene composites based symmetric supercapacitors with large areal capacitance for high-performance. He *et al.* [61] fabricated the 3D graphene/MnO_2 composite networks as ultralight and flexible supercapacitor electrodes. In addition to this He and his co-worker explored the excellent electrochemical performance of graphene/MnO_2 composite based symmetrical supercapacitor.

3.3 Graphene/Semiconductor Nanocomposites for Photocatalytic Hydrogen Evolution

Photocatalytic hydrogen evolution is a long-standing goal for researchers since it can help to supply the growing worldwide energy demand because of its environmental friendliness. The urgent demand for clean and renewable alternative energy recourses has recently triggered research on hydrogen evolution approaches, especially photocatalytic hydrogen production from solar energy via semiconductor nonmaterials. The graphene due to its large specific surface area possesses more active adsorption sites and photocatalytic reaction centers, which is capable for highly enlarge the reaction space and enhance photocatalytic activity for hydrogen evolution [62]

Zhang *et al.* [63] firstly reported the photocatalytic activity of TiO_2/graphene nanocomposites for hydrogen evolution. Composites are synthesized using a sol-gel method using tetrabutyl titanate with different weight % graphene oxide (GO) as the starting materials. The nitrogen atmosphere affects photocatalytic activity of composites and demonstrates graphene is a very promising candidate for development of high performance photocatalysts. Furthermore zhang synthesize chemically bonded TiO_2/graphene sheets nanocomposites using a one-step hydrothermal method. Composite shows 1.6 times larger photocatalytic hydrogen evolution for 2.0 wt% graphene than that of Degussa P25 [64].

Chen *et al.* [65] reported different reduction degree of RGO (reduced graphene oxide) synthesized via a direct hydrothermal process in $ZnIn_2S_4$ for hydrogen evolutions. The result shows that the RGO in RGO/$ZnIn_2S_4$ composites influenced their performance for photocatalytic hydrogen evolution.

Jia *et al.* [66] reported N-graphene loading as a cocatalyst in CdS nanoparticles; N-graphene/CdS composites enhanced photocatalytic hydrogen evolution from splitting water under visible light irradiation. Due to this N-doped graphene as a protective material for CdS as well as to other semiconductors and thus promote their potential application for hydrogen production by using solar energy.

3.4 Graphene/Semiconductor nanoparticles composites for gas sensing application

Gas sensor interacts with a gas and measures the concentration of gas in its surrounding area. Semiconductor nanoparticles used for detecting toxic gases and work via a gas sensitive film. The sensitive film reacts with gases, activate the device when toxic levels are present.

Nemade *et al.* [67] fabricated and evaluated carbon dioxide (CO_2) and liquid petroleum gas (LPG) sensor based on few-layered graphene (FLG) using electrochemical exfoliation method. The FLG sensor exhibited good sensing response not only for LPG but also for CO_2; sensor shows excellent stability at room temperature for both LPG and CO_2 as shown in figure 2. Yoon *et al.* [68] reported CO_2 sensing with FLG. Recent study has established the detection of molecules by pristine graphene, attracting great research interest from both the scientific and engineering communities.

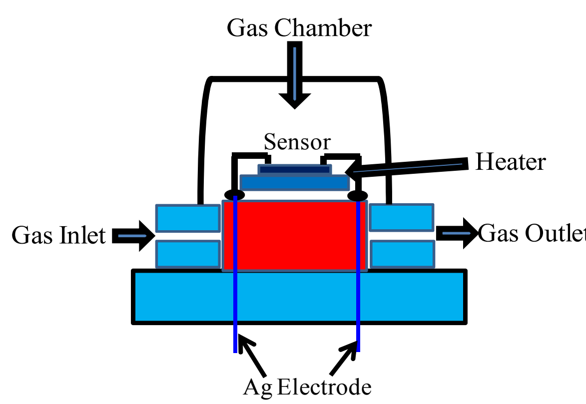

Fig 2: Gas sensing by few layered graphene

Also, graphene surface anchored nanoparticles can provide greater usefulness in gas adsorption and sensing processes [69, 70]. Nemade *et al.* [71] reported graphene/Y_2O_3 composite for CO_2 gas sensing at room temperature. The composite prepared by mixing 20 wt% graphene synthesized by electrochemical exfoliation of graphite into the 1 g Y_2O_3 in acetone. The sensing films by screen-printing on glass substrate shows excellent stability with optimum sensing response. Nemade *et al.* [72] fabricated gas sensor based on graphene/ZnO composite for LPG sensing. The composites 60 wt % graphene/ZnO sensor exhibits the highest sensing response than pure state of graphene and ZnO nanoparticles.

4. Conclusion

As discussed herein, several processes have been used for graphene/nanoparticles synthesis, and its utilization in different components of next generation in various fields was confirmed. To date, graphene/nanoparticles are applied in photovoltaic cells, energy storage devices, photocatalytic hydrogen evaluation, and gas sensensing application, owing to its versatile properties such as optical, electrical, and mechanical properties. The graphene into the nanocomposites mainly acts to promote the separation of charge carriers and transport of photogenerated electrons. The performance of composites is highly dependent on the semiconductor nanoparticles and their morphologies and surface states. Therefore, the development of novel composites is required. Nevertheless, there are still many challenges and opportunities for graphene/based nanoparticles nanocomposites especially semiconductor nanoparticles and they are still expected to be developed as potential application to address various environmental and energy-related issues.

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