

## Review Article

# Synthesis and Applications of Semiconducting Graphene

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Semimetal-to-semiconductor transition in graphene can bestow graphene with numerous novel and enhanced structural, electrical, optical, and physicochemical characteristics. The scope of graphene and its prospective for an array of implications could be significantly outspread by this transition. In consideration of the recent advancements of semiconducting graphene, this article widely reviews the properties, production, and developing operations of this emergent material. The comparisons among the benefits and difficulties of current methods are made, intending to offer evidences to develop novel and scalable synthesis approaches. The emphasis is on the properties and applications resulting from various conversion methods (doping, controlled reduction, and functionalization), expecting to get improved knowledge on semiconducting graphene materials. Intending to motivate further efficient implications, the mechanisms leading to their beneficial usages for energy conversion and storage are also emphasized.

## 1. Introduction

Graphene has upraised far-reaching attention in very broad scientific society for its surprising electrical, mechanical, optical, and thermal properties [1]. It is an allotrope of carbon having a single layer of  $sp^2$ -bonded carbon atoms densely packed into a two-dimensional honeycomb lattice [2, 3]. Each C-atom in the structure has  $s$  and three  $p$  orbitals. Two of  $p$  orbitals ( $px$  and  $py$ ) and  $s$  orbital in the structure hybridize to form a strong covalent  $sp^2$  C-C bond. The remaining  $pz$  orbital overlaps the neighboring C-atom  $pz$  orbital to form a filled  $\pi$  orbital (valence) and the empty  $\pi^*$  orbital (conduction) [1]. Due to the structural formation graphene offers an excellent thermal conductivity, exhibits high charge mobility, and possesses high theoretical specific surface area [2, 4]. Among all these properties, the most interesting aspect of graphene is assumed to be its unique electronic properties. Graphene's electron mobility is considerably greater than silicon ( $\sim 1400 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) which is a widely used semiconductor [1]. Therefore, for the applications in postsilicon

electronics, graphene has been considered as a candidate material.

Although graphene possesses several exceptional characteristics, however, due to the absence of a substantial bandgap, its use as an electronic material for semiconducting applications is one of the greatest challenges. Graphene is basically a semimetal or a zero bandgap semiconductor [5, 6]. This semimetal characteristic of graphene does not affect its use in numerous applications but it considerably restricts its use in all other semiconducting applications where an appropriate bandgap is requisite. An identical atmosphere of the two C-atoms in the graphene unit cell is the major reason for this zero bandgap present in graphene [7]. Consequently, breaking the adjacent, in-plane lattice symmetry is the major way to open up a bandgap in graphene. This could be done by different structural and chemical alterations. For instance, if an atom substitutes the carbon atom in the structure, the symmetry in the lattice could be broken. This may result in the creation of a gap between  $\pi$  and  $\pi^*$  bands. This symmetry

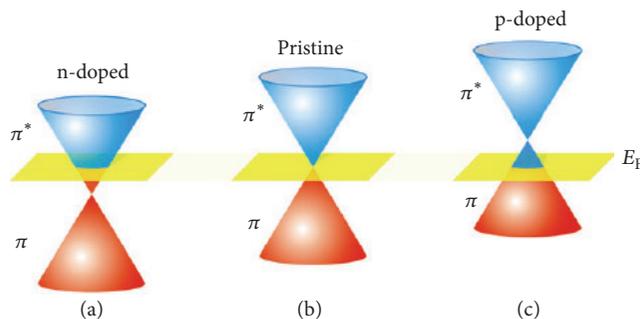


FIGURE 1: Schematic band structures of (a) n-type graphene with bandgap, (b) pure graphene, and (c) p-type graphene with bandgap (reprinted from [10]; copyright 2016, PCCP Owner Societies).

could also be broken through other means [7]. For the use of graphene in electronic devices opening a well-tuned considerable bandgap in graphene is the major challenge.

Figure 1 is the representation of the graphene band structures presented where there is a linear energy momentum dispersion relation near the Dirac point [8, 9]. The cone shaped valence band and conduction bands meet across  $K$  point. The Fermi level ( $E_F$ ) lies at the crossover point in the band structure of pure graphene with zero bandgap.  $E_F$  lies in valence and conduction band in the band structures of  $p$ -type graphene and  $n$ -type graphene, respectively, including a bandgap [10].

The surface properties of graphene are possible to be adjusted via structural alteration including chemical doping, chemical functionalization, and controlled reduction, which proposes remarkable prospects for the development of graphene-based semiconducting materials with unique electronic characteristics. These materials show advantages for numerous prospective applications, including energy conversion, energy storage, catalysis, sensing, field effect transistor, and many more because of their high power density and long lifecycle [11–14].

There are many methods that incorporate semiconducting properties into graphene, which include the preparation of graphene/nanoparticle hybrids, patterning graphene in the form of a graphene nanoribbon, nanomesh, or quantum dot. These methods have shown substantial developing and emerging interest from both theoretical and experimental viewpoints and have been reviewed in several literatures [2, 15–18]. This review focuses on converting metallic graphene into semiconducting graphene by chemical alteration of graphene through doping, controlled reduction, and functionalization. Although these newly developed methods have risen to rigorous attention in research, these methods are not classified or summarized in a single document. Hence, a methodical synopsis on these significant methods for producing semiconducting graphene and its exceptional characteristics and functions compared to graphene is greatly required. This review provides an overall context and structure on the latest advancements in the area of semiconducting graphene materials.

The conversion processes discussed in this review could be categorized into three major sections: (1) doping

of graphene through surface transfer and substitutional approach; (2) controlled reduction of graphene oxide (GO); and (3) functionalization of graphene via chemical methods. Doping of graphene with alien atoms instigates the electronic and structural distortions inside the carbon sheet leading to changes in the graphene bandgap properties. Partial reduction of GO controls the level of oxygen-containing functional group into the graphene structure. During functionalization different functionalities are grafted onto graphene by covalent or noncovalent approaches. All these methods are actually utilized for the bandgap opening in graphene and Fermi level tuning of graphene. The semiconducting graphene finds applications in many scientific fields, ranging from fuel cell, solar cell, and thermoelectric devices to supercapacitor and lithium-ion batteries. These applications are carefully reviewed in the manuscript.

## 2. Fabrication Methods

**2.1. Doping of Graphene.** A number of methods have been proposed in the literature [19–21] to modify the graphene and its electronic structure for the introduction of a substantial bandgap in it. Among all the approaches, one utmost reasonable approach is doping, which helps in tuning the bandgap in graphene. The concentration and nature of the charge carriers can be regulated by doping. For the band engineering of graphene, two major kinds of doping styles have been applied—surface transfer doping and substitutional doping. Surface transfer doping involves the adsorption of an atom into the graphene lattice structure. This incorporation of atom could shift the voltage point of graphene at Dirac point from zero gate voltage to +ve or –ve gate voltage as an outcome of  $p$ - or  $n$ -type graphene. Substitutional doping involves the replacement of carbon atoms inside the graphene lattice. The incursion of atoms into the natural graphene will unavoidably instigate the electronic and structural distortions inside the carbon sheet, leading to changes in the graphene bandgap properties. In this section, an overview of recent experimental and theoretical investigations on the doping of graphene is given, and the possible reason for the semiconducting behavior of doped graphene is explained.

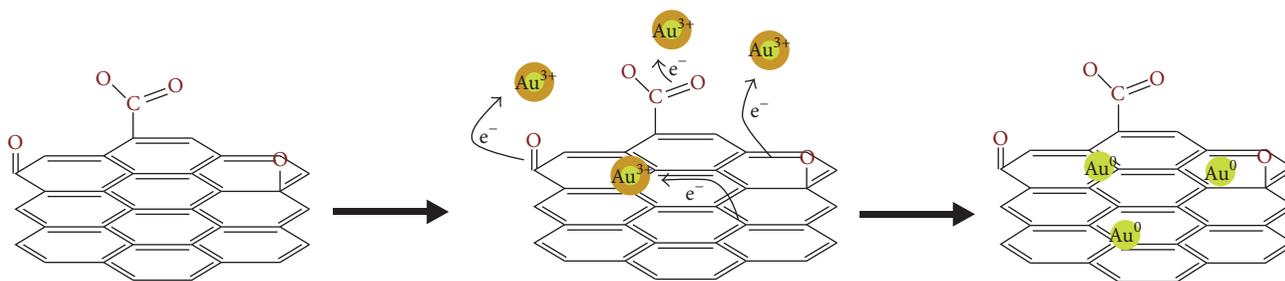


FIGURE 2: Surface transfer doping of graphene (reprinted from [24]; copyright 2009, Elsevier).

**2.1.1. Surface Transfer Doping.** Surface transfer doping of graphene could be attained through the interchange of electrons between graphene and the surface adsorbed-dopants present in graphene. Therefore, this type of doping might also be termed as adsorbate-induced doping. This type of doping does not interrupt the graphene structure and it generally can be reversible [22, 23].

For surface transfer doping of graphene, a considerable hole-doping in the graphene (with conical band structure) might be attained through the adsorption of atoms (mostly metal atoms) having high affinity for electrons. These atoms, including gold (Au), bismuth (Bi), and antimony (Sb), could be adsorbed on the surface of graphene and may modify the electronic properties in graphene [24]. Benayad et al. examined the result of Au-ion treatment on the WF and the change in electronic structure of rGOs. The relative percentage of carbon gradually decreased and the relative percentage of Au<sup>0</sup> increased markedly with increased doping concentration. This might be due to a charge-transfer from  $sp^2$  electrons to Au-ion solution. The carbon oxide species with functional groups C=O and O-C=O also contribute to donating electrons to the Au-ions and the Au-ions are spontaneously transformed into Au<sup>0</sup> by a charge-transfer from the reduced GO to the Au-ions [24] (Figure 2). Usually, the Dirac point (minimum conductivity point) of original graphene is at the zero gate voltage. This voltage point moves in graphene in the direction of positive gate voltage due to p-type doping or a negative gate voltage due to n-type doping. The adsorbed Bi and Sb atoms on the surface withdraw electrons from graphene; then the Dirac point moves in the direction of the Fermi level but does not overlap with it. However Au has the higher electron affinity and it moves the Dirac point to the vacant states, prompting the p-type doping in graphene.

It was found in the literature that the charge-transfer is motivated by the difference in work function (WF) and the chemical interactions among the metal component and graphene [25]. If the work function of metal is larger compared to the work function of graphene, graphene is expected to be doped with holes. In contrast, if the work function of graphene is larger compared to the work function of metal, graphene is expected to be doped with electrons. Alkaline metals have strong ionic bonding characteristics, so they are able to donate electrons. This assists the discharge of their lone-paired electrons in the graphene conduction band and rises the intensely charge carrier amount in graphene

[26]. Alkaline metals become excellent applicants for n-type dopants because of the development of this firm ionic bond and substantial charge transportation [27].

**2.1.2. Substitutional Doping.** Substitutional doping of graphene is attained by the substitution or replacement of carbon atoms in the graphene lattice by a foreign atom. Substitutional doping has got specific consideration because of its capability of charge infusion in the graphene electronic structure. This type of doping involves the replacement of carbon atom with another atom near the locations of single or multiple openings. Generally heteroatoms (nitrogen, boron, phosphorous, sulfur, etc.) and metal atoms (gold, platinum, etc.) are used for this doping. These gap defects in lattice are formed by directing a beam of electron using scanning transmission electron microscopy (STEM) or by bombardment of ions [28].

The unpaired electrons of a pristine graphene are powerfully attached and passivated in the delocalized  $\pi$  structure of graphene, making it chemically not reactive, which obstructs its reactivity and absorption capability [21]. The insertion of heteroatoms can give graphene extremely rich active sites. The electroneutrality in graphene could be broken by addition of heteroatom that has a dissimilar electronegativity compared to the carbon atom. This might create instable charged zones in it [29], which could function as active sites. These sites could also be existent as structural defects that may rise from the strain in the lattice imparted from the atomic size differences with the dopants [30]. Generally, the roots of these sites enrich the chemical properties in graphene for better interaction and simultaneously introduce a bandgap that introduce semiconducting properties into graphene; it can thus be utilized in so many applications. Substitutional doping of graphene with heteroatoms has been achieved by several approaches including direct synthesis, solid-phase synthesis, and liquid-phase synthesis. Among all these approaches the most widely used ones are discussed in this section.

The direct synthesis method includes CVD and segregation-growth approach. The chemical vapor deposition is a suitable way for doping different heteroatoms while the graphene films are produced by catalytic growth mechanism. This method involves particularly direct incorporation of heteroatoms into the graphitic carbon lattices [31]. In this process a metal catalyst is used as the substrate. A gaseous

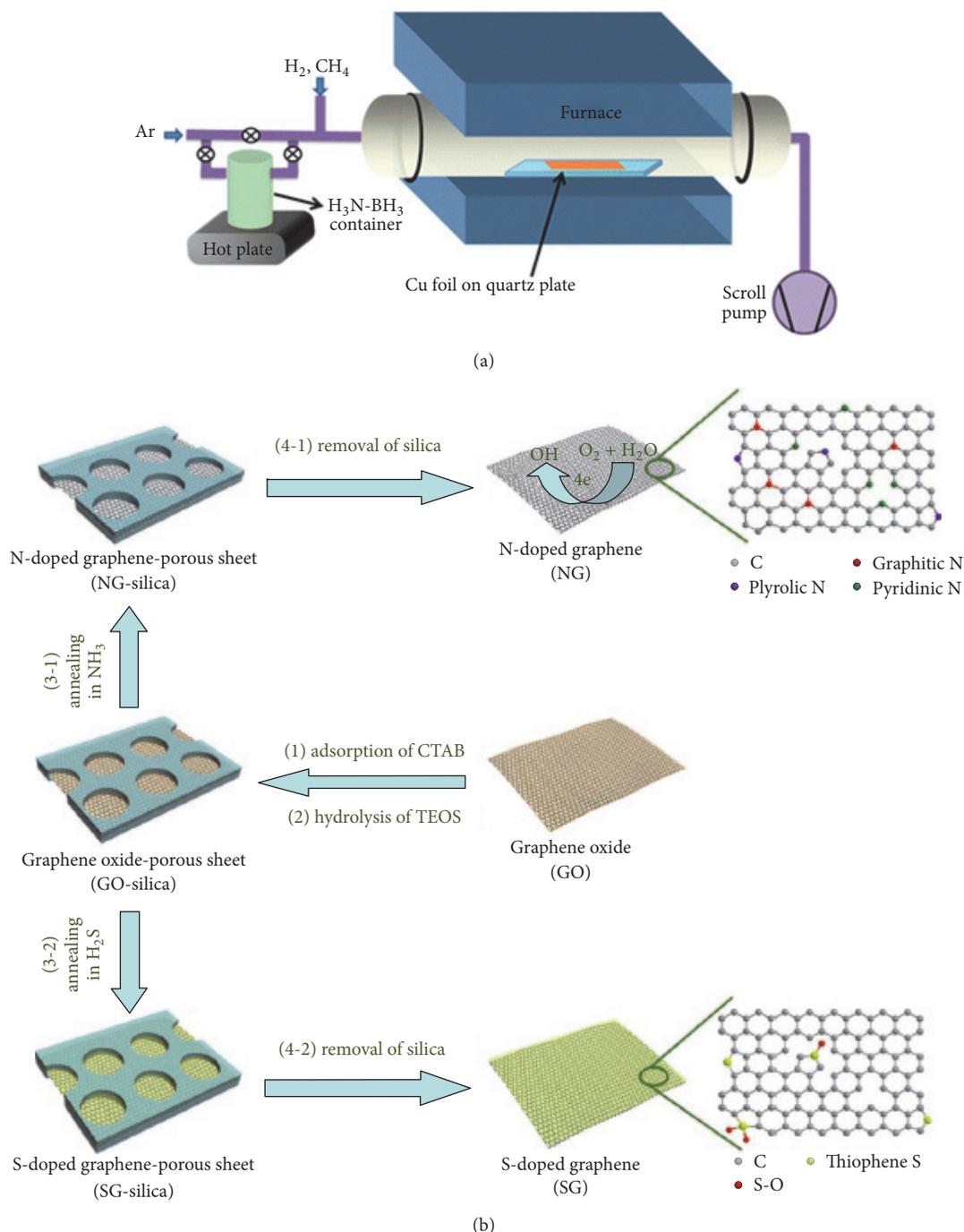


FIGURE 3: Preparation methods of heteroatom-doped graphene. (a) CVD doping experimental setup (reprinted from [31]; copyright 2013, American Chemical Society). (b) N- or S-doping on porous silica confined GO sheets by thermal annealing (reprinted from [50]; copyright 2012, John Wiley and Sons).

source of carbon is then mixed with another solid, liquid, or gas containing heteroatom at high temperature in the furnace together (Figure 3(a)). On the surface of the catalyst, these precursors tend to dissociate and then try to recombine by precipitation into the heteroatom-graphene [32–35]. CVD method has been extensively employed for the formation of nitrogen-doped graphene. Most literature studies predict

this type of substitutional doping of nitrogen may transform graphene into an n-type semiconductor, complemented by significant modification of electronic transport and charge mobility [36–38]. Doping of nitrogen in graphene results in a transition from metal to semiconductor, which has a bandgap varying till 5 eV, thus increasing probable applications of graphene in mostly electronic and optoelectronic

side [39]. The CVD approach enables the growth and doping simultaneously and thus allows controllable doping. This is a complex process which needs high operating temperature. Waste gases and hazardous materials are sometimes also produced in this process. This method involves high cost and usually yield is low [35, 40–45]. The segregation-growth approach is one more significant approach to synthesize doped graphene through direct synthesis. This method allows the selective doping of graphene through the incorporation of heteroatoms into specific areas of the graphene surface [46]. In a recent study Zhang et al. produced nitrogen-doped graphene through this segregation-growth method [47]. In their study they squeezed C-containing Ni layers and the N-containing B layers through thermal annealing. This process formed uniform N-doped graphene which exhibited a substantial bandgap of 0.16 eV. This method provides the option of controlling the concentration and position of dopants. The resultant doped graphene has application in FET [47].

The solid-phase synthesis involves reactions at high temperature including thermal annealing and arc-discharge method [48]. The thermal annealing of GO or reduced GO is effective in attaining doping with heteroatom when suitable precursors are present. Thermal annealing is the method of producing heteroatom-doped graphene using high temperature. For instance, nitrogen-doped graphene has been obtained by Wu et al. by annealing reduced GO in  $\text{NH}_3$  and argon atmosphere at  $600^\circ\text{C}$  [49]. Porous silica was used by Yang et al. to confine GO sheets for N- or S-doping for avoiding aggregation and ensuring free gas transport during the annealing process. S-doping was found to be less effective compared to N-doping, and it forms thiophene-like structure at the defect sites (Figure 3(b)) [50]. Thermal annealing method gives wide choices of dopant precursors (gases, liquids, or solids). It provides controllable doping. Although high temperature is required in this process it is still helpful to recover  $sp^2$  carbon network [51–59]. The arc-discharge approach is one more significant approach to synthesize doped graphene [60]. This method produces heteroatom reactive radicals for the doping. Arc-discharge method may obtain doped graphene by evaporating the carbon source at high temperature. Nitrogen-doped graphene is widely produced by the arc-discharge method. Rao et al. successfully synthesized nitrogen-doped graphene by application of this technique in the presence of  $\text{NH}_3$  or vapor of pyridine [61, 62]. Li et al. have produced multilayered nitrogen-doped graphene sheets by this method where  $\text{NH}_3$ , used as buffer gas, acts as N precursor [63]. Arc-discharge approach has also been applied to prepare boron-doped graphene. For example, Panchakarla et al. have prepared bilayer graphene with boron doping by arc-discharge method in the presence of  $\text{H}_2$  and  $\text{B}_2\text{H}_6$  where a boron-filled graphite electrode was used [62]. This method gives mass production. However it requires high voltage or current. The main limitation is low doping level. This method is generally applied for multilayer graphene [62–64].

The liquid-phase synthesis involves hydrothermal and solvothermal treatment [48]. The solvothermal synthesis was first applied for the production of gram-scale graphene [65]. Currently, the gram-scale production of nitrogen-doped

graphene is attained through using the method at nearly  $300^\circ\text{C}$ . Nitrogen-doped graphene with varying content of nitrogen was achieved by mixing lithium nitride with tetrachloromethane or cyanuric chloride with lithium nitride and tetrachloromethane [66]. Another solvothermal synthesis of nitrogen-doped graphene was developed by Deng et al. under mild condition reaction of the tetrachloromethane and lithium nitride [66]. Sulfur doped graphene can also be prepared by solvothermal method. Liu et al. achieved sulfur doped graphene with pure thiophene S-bonding by a rapid microwave-assisted solvothermal method using graphene oxide and benzyl disulfide. This experiment attained a sulfur doping level nearly at 2.3 percentage in 6 minutes. Doped graphene prepared by this method develops superior electrochemical properties [67].

**2.2. Controlled Reduction of Graphene Oxide.** Controlled reduction of graphene oxide (GO) is a possible way to attain substantial bandgap opening in the graphene structure among several other approaches [68]. This offers tunable optoelectrical properties into the structure of graphene. Modified graphene with this tuned bandgap properties could be employed in many fields including electronic and optical devices [69], sensors [70], catalysts [71], and supercapacitors [72].

Graphene oxides are generally electrically insulating because of the existence of substantial  $sp^3$  hybridized carbon atoms bonded with oxygen. The alteration of  $sp^2$  and  $sp^3$  carbon segments present in graphene oxide are beneficial for the manipulation of its bandgap therefore controlling the transformation of graphene oxide from an insulator to a semiconductor [73]. Reduction of graphene oxide creates numerous defects in the lattice of graphene, which further may affect the resultant transportation properties. The energy gap in GO might be tuned through regulating the reduction extent. The bandgap engineering probability within the GO is of attention due to its application in several sectors including electronic and photonic devices. GO can go through controlled reduction for obtaining the semiconducting properties in its structure [74, 75]. Various reduction methods have been proposed for this purpose. The chemical and thermal reduction routes are mostly implied ones among all reduction approaches.

**2.2.1. Chemical Reduction.** Chemical reduction is advised as very simple and reasonable solution-processing approach that is able to be performed at low temperature and may imply wide-ranging reductants [70, 76]. Controlled chemical reduction of GO leads to substantial bandgap opening in the structure. GO experiences the transition from insulator to semiconductor and then to semimetal with large-scale reduction. The variation in the transportation gap moves from insulating to semiconducting range and advances to zero with extensive reduction [73]. Therefore proper control in the reduction process is important for tuning the semiconducting properties in GO.

A recent study demonstrated the evidence of controlled removal of chemical functional groups from the surface of GO by the chemical reduction of GO [77]. This study has used

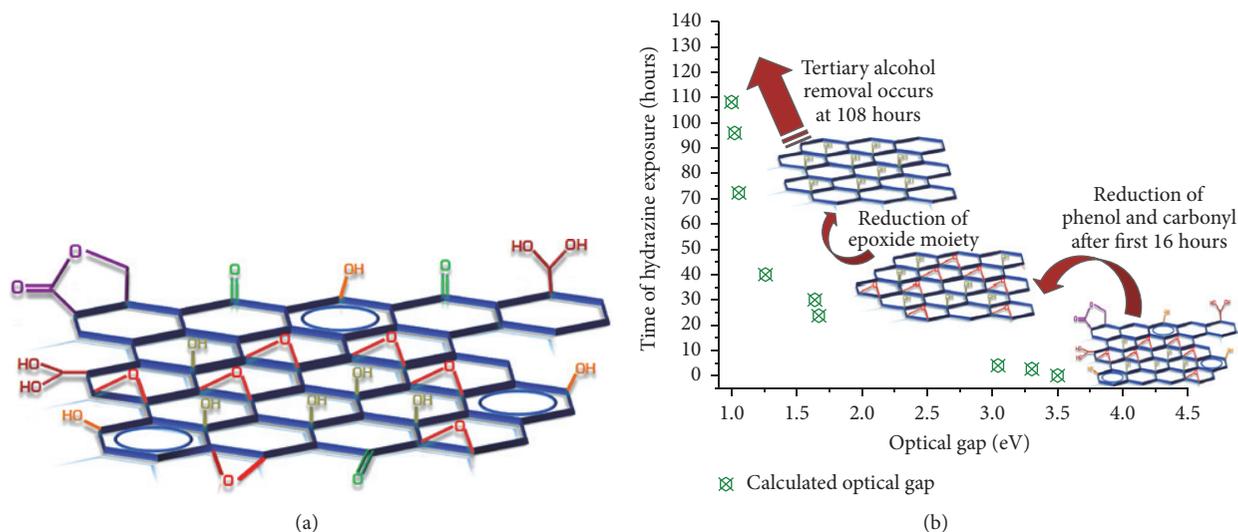


FIGURE 4: Controlled chemical reduction of GO. (a) Structural model of GO with the carbonyl (green), phenols (orange), tertiary alcohols (gray), and epoxide (red) functional groups (reprinted from [78]; copyright 2009, Nature Publishing Group). (b) Change in optical bandgap on disclosure to hydrazine vapors (reprinted from [77]; copyright 2012, American Chemical Society).

hydrazine vapors as a reducing agent for stepwise removing the functionalities (Figure 4(a)) in GO at room temperature.

The data from this study showed that carbonyl groups are the most reactive to hydrazine vapors and they were the first that were reduced at eight hours. Next reduced groups were the phenolic group that were reduced after sixteen hours. Then the epoxy groups are reduced at 21.5 hours. The tertiary alcohols take the longest to be reduced and are reduced after 108 hours of exposure. The optical-gap variation during the reduction process with hydrazine vapor is summarized in Figure 4(b). The initial insulating properties of GO ( $\sim 3.5$  eV at 0 hours) are indicated in the figure. In the first 4 hours, a noteworthy reduction has been observed in the optical energy gap ( $\sim 3.0$  eV at 4 hours).

The optical energy gap value close to semiconductor characteristics ( $\sim 1.6$  eV at 30 hours) resulted from the consequential elimination of the phenolic and epoxy groups. The radical decrease in bandgap decelerates after this point, nearly after forty-five hours. This provides a qualitative knowledge about the challenges related to the elimination of the tertiary alcohol. After completely removing the functional groups, the bandgap decreases to nearly 1 eV at 108 hours [77].

This study provides the information of the bandgap control at different stages of reduction, which creates the potentials for alternating chemical configuration of graphene and GO, and regulating their electric and optical properties aimed at their use in a wide range of applications [79, 80].

**2.2.2. Thermal Reduction.** Thermal reduction is usually attained by heating GO in the presence of inert atmosphere at high temperature [81–83]. Appropriate control in the reduction process is important for tuning the semiconducting properties in GO, as extensive reduction may result in zero bandgap in the structure.

The gradual transition of GO from electric insulator to semiconductor and further to semimetal like graphene

with thermal reduction was reported in a study by Jung et al. The results suggested a close correlation among the electrical properties and the chemical structure of GO [84]. Another study by Eda et al. extended the works of Jung et al. which provided a whole scenario of transportation in GO at different extents of reduction. In particular, they reported the dependence of the transportation properties in GO on temperature as a function of the reduction treatments. At low temperature, a transportation gap was observed for moderately reduced GO. The energy gap was found to be dependent on the degree of the reduction process. The transport gap seems to be ranging from 10 to 50 meV and advances towards zero with large-scale reduction treatment. Proper regulation in the thermal reduction process is able to generate bandgap in GO and induce semiconducting properties in it [73].

Thermal reduction of GO-based composites is a popular method to fabricate 3D graphene networks [85]. This method needs the construction of a GO-based composite and then reduction of the GO for the production of the 3D graphene networks. A challenge in making 3D networks via thermal reduction frequently results in collapse of the pore structure without a support, which must be subsequently removed. However, it is hard to remove the support material completely and the residual would influence the thermal and electrical properties of reduced graphene oxide. Zhang et al. recently implied a method using NC as support materials (Figure 5). NC is an energetic material fill and GO forms a composite material with NC with easy dispersion. NC is easily decomposed during the thermal degradation of the composite and thus provides an efficient technique for reducing GO without any support [85].

**2.3. Functionalization of Graphene.** The functionalization of graphene via chemical methods suggests an alternate method to govern its electronic characteristics. In the process of functionalization of graphene,  $sp^2$  network is converted into

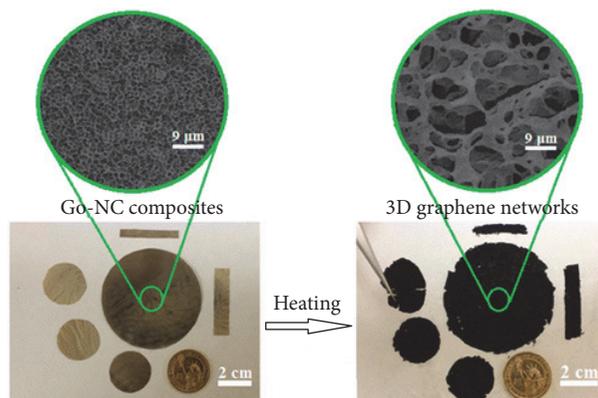


FIGURE 5: Synthesis of 3D graphene network by thermal reduction (reprinted from [85]; copyright 2014, American Chemical Society).

$sp^3$  structure with the transformation of metal characteristics in graphene towards insulating. The metallic properties of graphene are able to be altered to semiconducting by apposite surface functionalization [86, 87]. Furthermore, the large surface exposure can be attained via attachment with other functional groups on graphene or graphene derivatives [88]. By functionalization, graphene surfaces or edges become rich in functional groups, which helps the tuning in molecular level [89]. Graphene could be functionalized by covalent, noncovalent, and also some further approaches that come across the precise necessities of diverse types of applications. Functional group is able to widen the characteristics of graphene by the development of graphene donor-acceptor complex, which gives tunability in electrical conductivity and photovoltaic and optical characteristics [90]. Functionalization of the sheet of pure graphene is very challenging and sometimes almost impossible because of the poor solubility. The GO sheet having reactive groups (carboxylic acid as well as hydroxyl and epoxy groups on its edge and basal plane, resp.) is one of the utmost common starting materials for graphene functionalization.

**2.3.1. Covalent Functionalization.** Covalent interaction involves covalent bond formation either at the basal planes or at the edges of graphene. Graphene derivatives that are covalently attached are formed through attachment of molecular groups or atoms to  $sp^2$  carbons. This conversion upholds the graphene two-dimensional lattice. However there are significant alterations to the characteristics of graphene because of the loss of the  $\pi$ -electron cloud existing in the structure of graphene (above and below). Functionalization of graphene can be achieved through the reaction with unsaturated  $\pi$ -bonds present in graphene, the oxygen atoms on GO, and organic functional moieties [91, 92]. These reactions transform  $sp^2$  carbon atoms to  $sp^3$  hybridization, generating nonconducting and semiconducting areas in the layers of graphene [93]. Literature shows that most of the study focuses on the covalent-linkage among the oxygen moieties in GO as well as other functional groups [90, 94, 95].

Covalent functionalization of graphene with organic compounds has been used to utilize semiconducting application of graphene. In a recent study, Yu et al. have explored

a new class of charge transport materials in PSCs [96]. They have chemically grafted  $\text{CH}_2\text{OH}$ -terminated region regular poly(3-hexylthiophene) (P3HT) onto carboxylic groups of GO via esterification reaction (Figure 6(a)). A bilayer photovoltaic device established on this functionalized compound showed two hundred percent increment in the power conversion efficiency compared to the P3HT/ $\text{C}_{60}$  counterpart.

The significant improvement in the performance of this device is attributed to the strong electronic interaction and good matching in the bandgap among the P3HT and graphene to increase charge transportation. The energy level diagram is shown in Figure 6(b) for the G-P3HT/ $\text{C}_{60}$  device. This experiment demonstrates that derivatives of graphene could be utilized as effective hole transporting material in the active layer of PSCs [96]. Recently, Zhang et al. have also exploited the functionalization of graphite oxide with fullerene via the covalent fisher esterification reaction. This covalent bonding 2D graphene with 0D fullerene is anticipated to bring together some novel characteristics into the structure of graphene and display enormous prospective in solar cells, hydrogen storage, and sensors applications [97].

**2.3.2. Noncovalent Functionalization.** For the modification of graphene sheets, noncovalent functionalization reactions are also frequently utilized. With respect to the covalent modification, these noncovalent approaches do not interrupt the novel  $sp^2$  structure of graphene, which furthestmost retains the high electrical conductivity. The noncovalent interactions between graphene and other functional groups generally involve  $\pi$ - $\pi$  stacking [98, 99], hydrogen bonding [100–102], van der Waals interaction [101, 103], and electrostatic forces [85, 100, 104]. Among these methods,  $\pi$ - $\pi$  stacking and electrostatic interaction are most commonly used for the semiconducting applications [105, 106]. Recently, Zhang et al. have noncovalently functionalized graphene with semiconducting fullerene via  $\pi$ - $\pi$  interaction and integrated this compound into the epoxy composites [107] and conjugated polymer [108] to enhance the thermoelectric performance of the polymer materials. Zhang et al. have also successfully demonstrated the successful enhancement of the thermoelectric properties of  $\text{rGO}_x/\text{F-C}_{60y}$  nano hybrids prepared by a noncovalent lithiation method [109] (Figure 7).

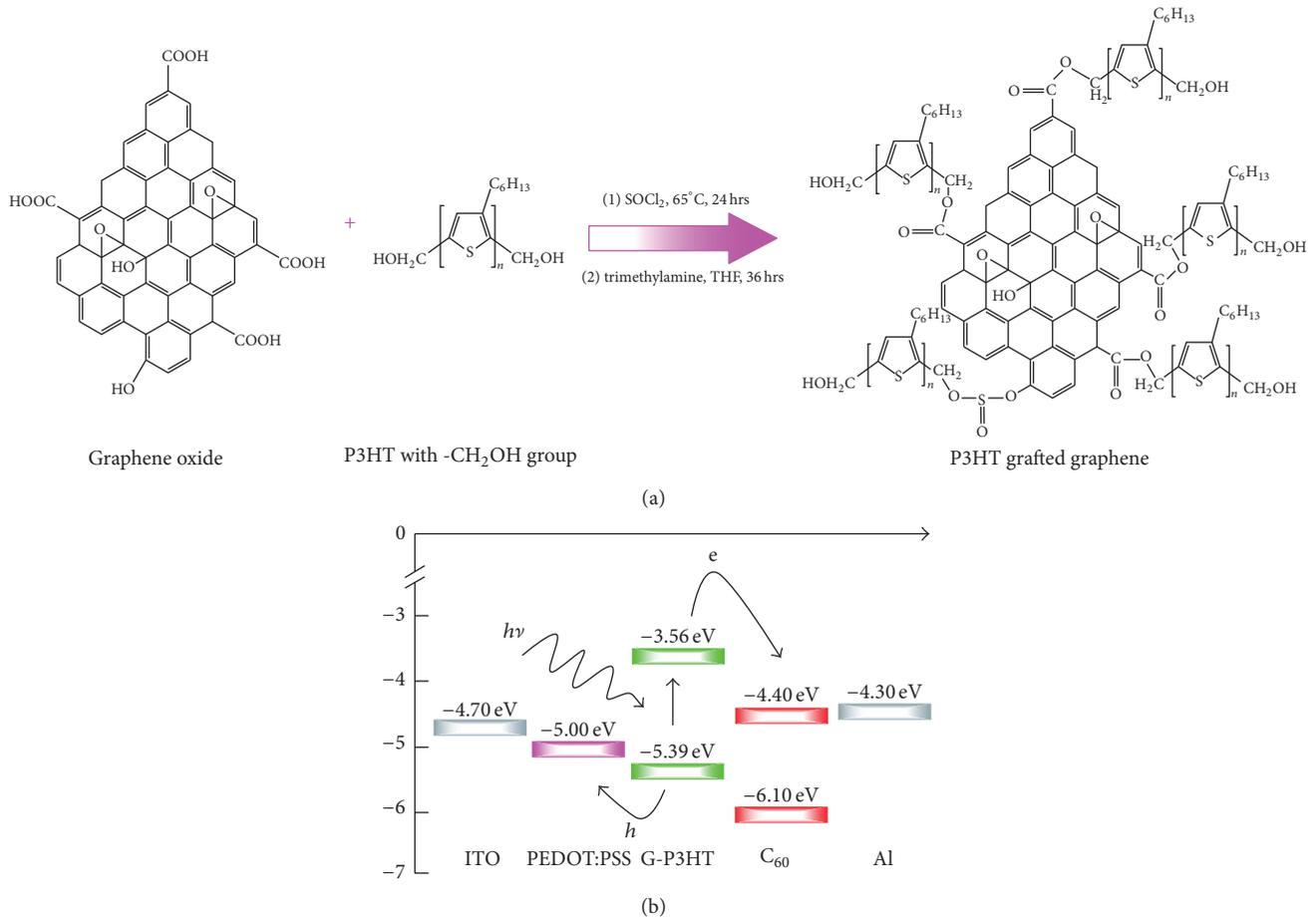


FIGURE 6: (a) A representation of the synthesis process for chemical grafting on graphene with  $CH_2OH$ -terminated P3HT chains (reprinted from [96]; copyright 2010, American Chemical Society). (b) Energy level diagram of a photovoltaic device (reprinted from [96]; copyright 2010, American Chemical Society).

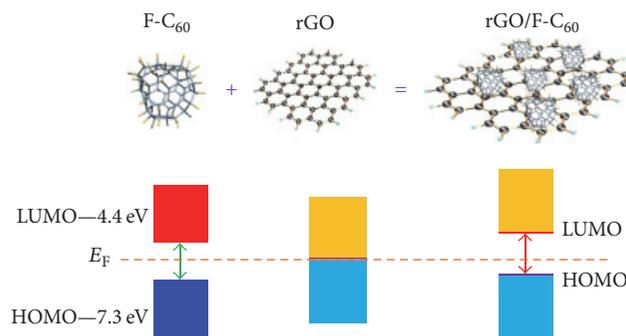


FIGURE 7: Band structure modulation of rGO through F- $C_{60}$  (reprinted from [109]; copyright 2015, Elsevier).

This interaction with semiconducting nanoparticles increases the bandgap of graphene to 2.9 eV and demonstrates p-type characteristics.

Noncovalent functionalization can be implied to graphene by using different types of organic modifiers. Table 1 shows different noncovalent modification of GO using different modifying agents with the changes in electrical conductivity.

### 3. Application of Semiconducting Graphene

**3.1. Fuel Cell.** Fuel cells directly convert chemical energy into electrical energy to provide a green solution to the environment. This process involves high energy conversion by oxidizing at the anode ( $H_2$  gas) and reducing at cathode ( $O_2$  gas) [118]. The electrical power is provided by the electron

TABLE 1: Electrical Conductivity of noncovalent functionalized GO with different modifying agents.

Modifying agent	Conductivity ( $S\ m^{-1}$ )	Reference
SPANI	30	[110]
PMMA	$2.47 \times 10^{-5}$	[111]
PVA	$9 \times 10^{-3}$	[112]
PE	10	[113]
PET	2.11	[114]
PBA	200	[115]
Amine terminated polymer	1500	[116]
PIL	3600	[117]

current that comes from the anode while proton reduces oxygen and generates water at the cathode [118]. The oxygen reduction reaction (ORR) is a slow reaction (rate-limiting step) on the cathode that can be fast in the presence of a considerable quantity of catalyst. Pt is the mostly used catalyst for this process; however its high price is a limitation to commercialize the application of the fuel cells.

In recent research proposals carbon based materials are being considered to replace platinum based electrodes in the fuel cells as reasonable catalysts with exceptional performance. This accompanies the progress of carbon based electrocatalysts for ORR [119, 120]. Literature study revealed that pristine graphene is not effective in facilitating electron transfer and thus catalytic activities towards ORR are absent in it [121]. Structural modification in graphene (such as doping, functionalization) could cause electron modulation to convert it into efficient electrocatalyst for oxygen reduction reaction (ORR) through achieving required electronic structures for catalytic activity [32].

Doping of graphene with heteroatoms may increase the catalytic activity of graphene in oxygen reduction reaction process. The doping-induced ORR improvement mechanism is still not entirely figured out. Multiple steps and numerous intermediates are assumed to be involved with the ORR method depending on the surface chemistry of the catalyst. Considering a general 4-electron pathway, first the oxygen is adsorbed on the catalyst surface and then reduced into hydroxyl group. The oxygen adsorption and cleavage in oxygen-oxygen bond are promoted by heteroatom dopants (including N-, B-, S-, P-, and Se-doped graphene) due to the charge-polarization of the bond between heteroatom and carbon [122, 123] and/or increase in spin density [124, 125]. Heteroatom doping in graphene could also increase the selectivity, stability, and electrochemical window along with the improved catalytic activity for ORR. Consequently graphene materials doped with heteroatoms have possibility of being applied in fuel cells to replace the currently used Pt catalysts. For instance, codoping of graphene with N and S exhibits exceptional activity towards the oxygen reduction reaction, compared to regular platinum based catalysts. This heteroatom-doped material could be a promising cathodic ORR electrocatalyst for fuel cells due to its simple production method, reasonable price, and high performance [126] (Figure 8(a)).

The electrocatalytic activities of graphene in oxygen reduction reaction have also been observed through noncovalent functionalization along with doping which involves intermolecular charge-transfer in the process and causes little or no change to the graphene structure. For instance, a very simple method to chemically functionalize heteroatom-doped graphene sheets with small organic-molecules for their implication as electrocatalysts for the ORR was presented by Ulsan National Institute of Science and Technology (UNIST) research team (Figure 8(b)). They confirmed that, by the variation in the amount and arrangements of the N-dopant, the electrochemical performance can be enhanced. Furthermore, this method was extended to the doping graphene with other heteroatoms, such as B- and S-doped graphene. Greater stability was seen from the N-doped graphene nanosheets in contrast with regular Pt/C catalysts.

To understand the complete mechanism of this catalytic activity and the enhanced lifetime of the fuel cells, additional study is needed. Further research in this developing arena may be proved to be advantageous for fuel cell technology with metal-free graphene-based ORR catalysts.

**3.2. Solar Cell.** Doped and functionalized graphene with semiconducting properties has remarkable implication in solar cell [127]. Atomic doping may bestow graphene with n-type or p-type semiconducting performance. Consequently, these resultant doped compounds could be implied for p-n junction solar cells. Doping enhances the catalytic activity as well as work function in graphene [128–130]. In a recent study a boron-doped graphene has been used as a p-type electrode in solar cells through interfacing boron-doped graphene with n-type Si (Figure 9(a)) [128]. Immense development in the solar cell performance has been experienced due to the improved electrical conductivity in the cell.

Functionalized graphene-based materials are also used for application in solar cells. For instance, polymer solar cells (PSCs) apply a hole-extraction layer among the electrode and the active layer to facilitate the charge collection by electrode [131]. The major role of these layers is to minimize the energy barrier for the extraction of charge carrier. These graphene layers develop very selective interaction for the holes and block the electrons near the electrode. Therefore, the graphene layers modify the morphology of the active layer. Functionalization of graphene/GO in a controlled way has been observed to be advantageous for the charge extraction and active layers in polymeric solar cells [96, 132]. For instance, in a recent study chemically grafted poly(3-hexylthiophene) (P3HT) onto GO has been observed to give 200% rise of the power conversion efficiency (PCE) compared to the counterpart P3HT/ $C_{60}$  [96]. This improvement in the performance of the device is attributed to the firm electronic interaction and great coordination in bandgap among the graphene and P3HT to increase charge transport [96]. Another study using a covalently attached  $C_{60}$  onto graphene in the active layers of a P3HT-based polymer solar cell as electron acceptor resulted in 2.5-fold rise in the PCE [96, 133] (Figures 9(b) and 9(c)). Consequently,  $C_{60}$ -grafted graphene has been acted as an excellent electron accepting or transporting materials in polymer solar cells

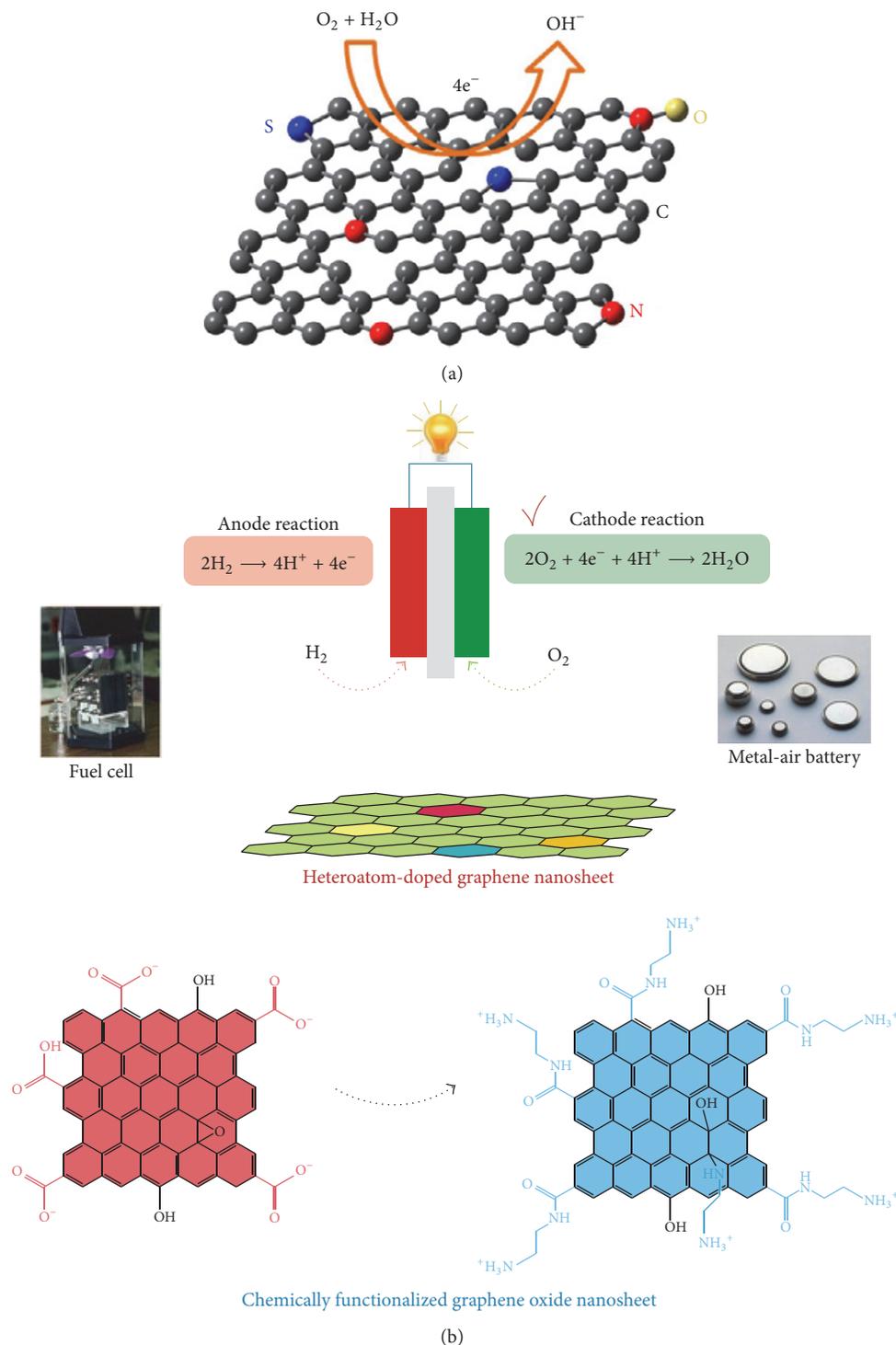


FIGURE 8: (a) Electrocatalytic activity in fuel cell with heteroatom-doped graphene (reprinted from [126]; copyright 2016, John Wiley and Sons). (b) Application of semiconducting graphene in fuel cell (credit: UNIST).

and many other optoelectronic devices. These efforts point out that functionalized semiconducting graphene is able to be operated in the active layer of PSCs as effective hole transportation materials.

**3.3. Thermoelectric Devices.** Thermoelectric devices directly convert the temperature gradient into electric potential difference. These devices are mainly used for heating or cooling purposes. They have vast applications in many industries

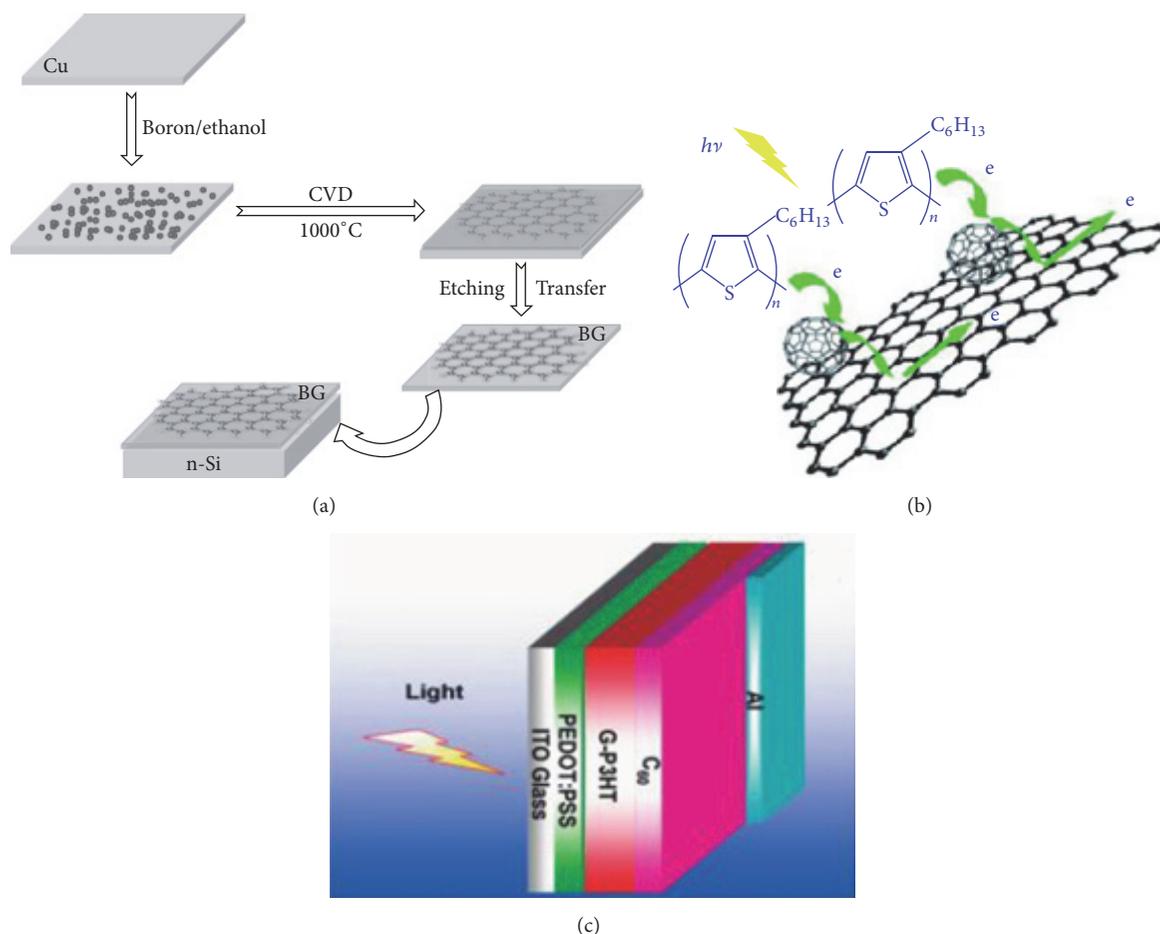


FIGURE 9: (a) Schematic representation of the preparation of boron-doped graphene and solar cell assembly (reprinted from [128]; copyright 2012, John Wiley and Sons). (b) C<sub>60</sub>-grafted graphene for electron transport in a P3HT-based PSC (C<sub>60</sub>-G) (reprinted from [134]; copyright 2010, American Chemical Society). (c) Diagram of a polymeric solar cell including the C<sub>60</sub>-G:P3HT composite as the active layer (reprinted from [96]; copyright 2010, American Chemical Society).

including automotive and power generation [135]. The thermoelectric effect is seen in many thermoelectric materials (TE) [136]. Among them organic TE have received considerable attention as a result of their abundance, environment friendliness, and characteristic of being easily processable, but the prospective of these materials is considerably limited due to the insufficient thermoelectric properties. In a recent study, Zhang et al. have enhanced the thermoelectric performance by integrating noncovalently functionalized graphene with fullerene by  $\pi$ - $\pi$  stacking into a conjugated polymer, PEDOT:PSS (Figure 10). Proper controlling of the fullerene-graphene ratio in this nanohybrid can result in a synergistic effect which may enhance the overall thermoelectric properties [108].

**3.4. Supercapacitors.** Energy storage has also dominant importance in addition to the energy conversion devices (including fuel cells, solar cells) mentioned before. Supercapacitors and batteries have drawn significant attention as energy storage devices due to their long lifecycle and high power density. Supercapacitors are the lower energy storage

devices which possess greater energy delivery capability [137, 138]. These devices require high power delivery capability, high energy storage capacity, and long cycle of life for their applications in large scale. Recently graphene has been used in supercapacitors because of its greater electric double-layer capacitance (EDLC) [139–141]. Although the applicability of graphene-based materials in supercapacitors has encountered some significant challenges, pristine graphene is chemically inert and does not offer any electrochemical capacitance (pseudocapacitance). Therefore, functionalized or doped graphene materials are proved to be favorable for the application in supercapacitors due to their greater EDLC and presence of pseudocapacitance [142].

Some substantial quantity of deviations in the structure of graphene could be introduced by doping for the use of graphene in supercapacitors. Literature reveals that heteroatom-doped graphene (B-, N-, and P-doped graphene) offers increased stability, improved conductivity, and better chemical reactivity compared to pristine graphene. These materials are more advantageous to be used in supercapacitors as they enhance electrochemical activity, lower charge-transfer resistance, and improve conductivity compared to

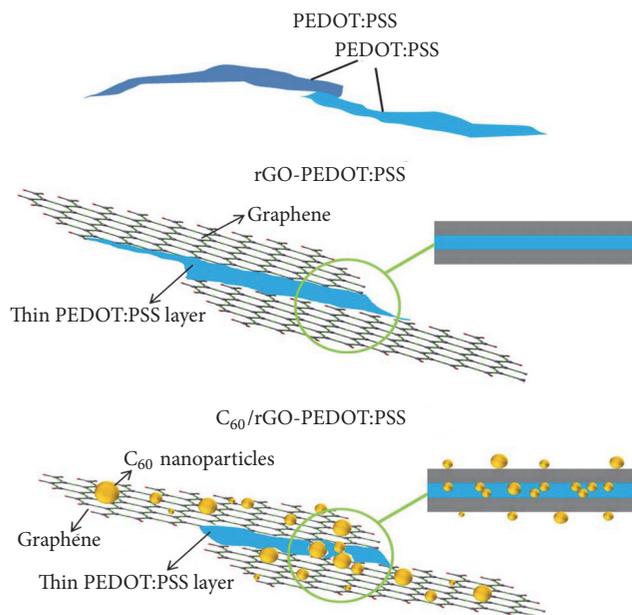


FIGURE 10: Graphic representation of transportation of the carrier in an orderly polymer film, reduced GO polymer, and a polymer composite filled with  $C_{60}$ /rGO nanohybrids (reprinted from [108]; copyright 2013, Nature Publishing Group).

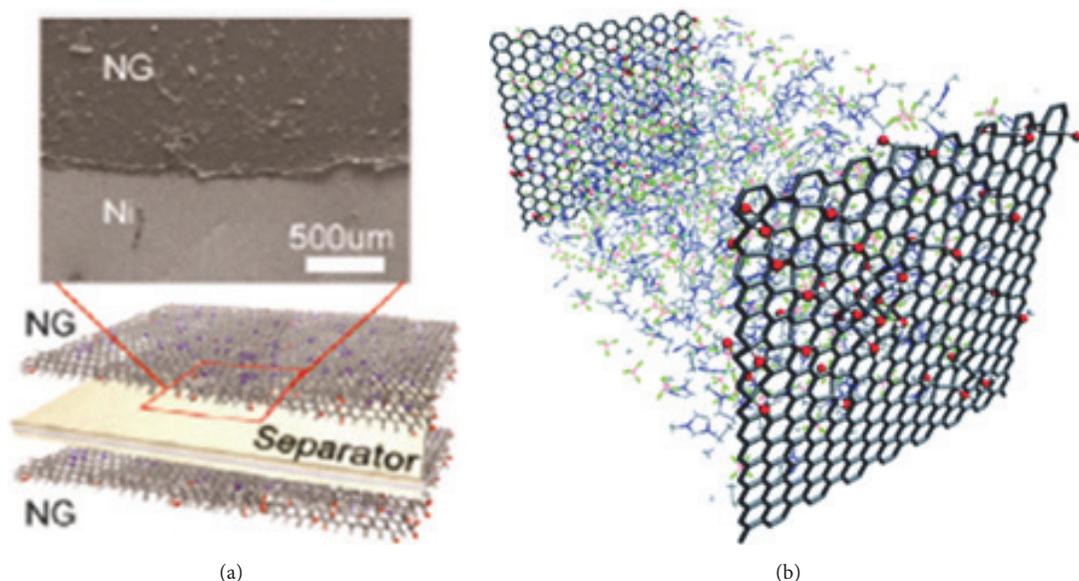


FIGURE 11: (a) Schematic representation of an assembled structure of a supercapacitor, with the SEM image in the top-view (reprinted from [147]; copyright 2011, American Chemical Society). (b) Illustration of a supercapacitor model which consists of GO electrodes (ten percent oxidation) with pure  $EMI^+ BF_4^-$  (reprinted from [149]; copyright 2013, American Chemical Society).

pure graphene [143–146]. Study demonstrates that supercapacitor based on graphene doped with nitrogen showed fourfold greater capacitance compared to its counterpart based on pure graphene [147] (Figure 11(a)). These materials may expedite electron transfer, lower the charge-transfer resistance of the electrode, and thus improve the capacitance [147, 148].

Influence of codoping of graphene with two or more atoms is also observed in different studies. For example, another experiment showed that an electrode based on B

and N codoped graphene resulted in capacitance way higher compared to counterpart electrodes of pristine graphene or only boron-doped graphene or only nitrogen-doped graphene. This might be due the synergetic effects among the two codopants. When these electrodes are implied in supercapacitors they seemed to attain increased energy and power density [143].

Controlled oxidized graphene is also used in semiconducting applications. Recently, Deyoung et al. revealed the dependency of capacitance on the oxidation extent [149]

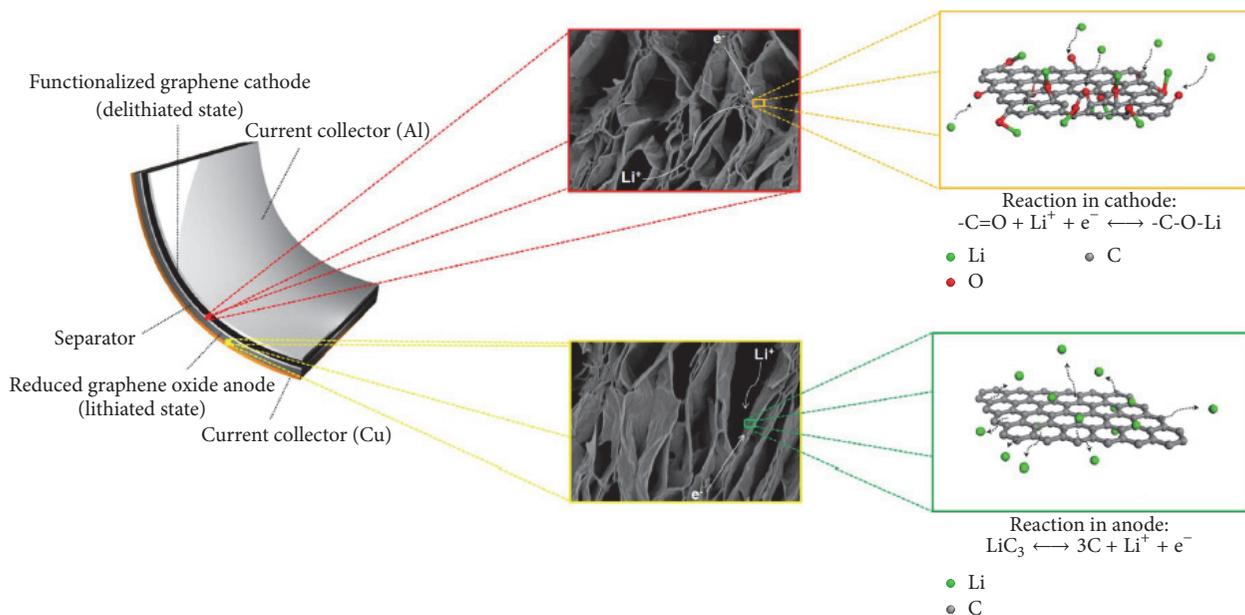


FIGURE 12: Application of functionalized graphene in Li-ion battery (reprint permission from [158]; copyright 2014, Nature publishing Group).

(Figure 11(b)), since oxidation modifies the ion accessibility towards electrode surface. This method demonstrates excessive potential to catalyze electrode optimizations, even though there are restrictions in the parameters measured for the calculations.

**3.5. Lithium-Ion Batteries.** Lithium-ion batteries are regarded as energy storage devices with high energy storage capacity and poor energy delivery capability [138]. In a lithium-ion battery during charging, ions move to the anode from cathode and go in the reverse direction during discharging. Pure graphene materials possess low binding energy towards lithium-ion and high energy barrier for the penetration of ions through the graphene sheet. Therefore, they are not appropriate for lithium-ion storage [150–152]. Modified graphene and carbon materials are often used in lithium-ion batteries [153]. The presence of defects in graphene material allows lithium-ion penetration and prevents clustering of lithium as firm contact exists among the lithium and defect sites [151]. However the number of defect sites should be controlled to avoid some difficulties [154].

Heteroatom doping has been proved to maintain optimal balance between storage of lithium and diffusion for electrodes [155]. Theoretical and experimental study showed that lithium atom is a potent electron donor. Therefore the storage capacity is increased in case of doping of graphene with an electron-deficient atom (such as boron) [156]. This restricts lithium diffusion (delithiation) though increasing binding energy among lithium and boron-doped graphene. So overall these materials enhance the battery capacity [156]. Nitrogen-doped graphene shows reduced storage capacity but more efficient delithiation which may be due to the decreased binding energy and the electrostatic repulsion between lithium and nitrogen. Therefore, these materials increase

the charge/discharge rate performance [150, 156, 157]. Functionalized graphene and chemically modified graphene electrodes are also used in Li-ion batteries for better performance. These modified graphene electrodes provide better paths for electrons and ions conduction in batteries, therefore introducing greater capacity as well as improved rate capability.

Lithium-ions and electrons are reserved at comparatively higher potential in the functional groups on the surface of graphene in the functionalized graphene cathode, while in the reduced GO anode. Lithium-ions and electrons are reserved at comparatively lower potential on the graphene surface. An all-graphene-battery was prepared by Kim et al. through joining a reduced GO anode with a functionalized graphene cathode in lithiated state (Figure 12). This battery showed improved electrochemical properties. The specific capacity was almost  $170 \text{ mAhg}^{-1}$  depending on the cathode mass, which matched approximately hundred percent implementation of this cathode [158].

## 4. Conclusion and Perspective

As discussed in this review, the high surface area, exceptional mechanical characteristics, and reasonable price of graphene materials make them promising material for application in several energy storage and conversion devices. Although the use of pristine graphene in these electronic application experiences so many challenges due to the high conductivity and zero bandgap properties of graphene, different methods have been developed to overcome these limitations and introduce a tunable bandgap in graphene to convert it into semiconducting material. Primarily three major approaches such as doping, controlled reduction, and functionalization of graphene are discussed in this article. The enormous prospects of these semiconducting graphene materials for

energy conversion and storage applications have also been explored in this paper. Appropriate surface modification through doping, reduction, or functionalization may imply their use in fuel cell, solar cell, thermoelectric devices, supercapacitors, and batteries.

Despite the tremendous progress made in the field of semiconducting graphene materials, still many difficulties are associated with their synthesis procedure. In case of surface transfer doping of graphene, the materials do not possess long-term stability. This is due to the fact that the adsorbed species may desorb from graphene surface and react with reactive molecules. The substitutional doped graphene (with metal or heteroatoms) may have more stability in this case, as the atoms are attached to the carbon linkage of graphene. Although the substitutional doped graphene still experiences some critical challenges in the large-scale production, doping controllability, and mechanisms. The large-scale production has been impeded by the requirement of harsh condition and high temperature. A green synthesis method and controlled synthesis of doped graphene are highly desirable. Due to the constant progression of novel materials and innovative applications, the mechanisms for reactions are still complicated in many electrochemical systems. Additional investigations in this interesting field of doped graphene materials will make contribution to the green energy systems. The controlled reduction provides a way for mass production of semiconducting graphene. The major challenge of this method is associated with the effective removal of oxygen-containing groups and proper control over reduction process, which is highly significant to appropriately tune the electrical conductivity into the graphene structure. Moreover, as this process introduces many defects to graphene, further improvements are desired to produce semiconducting graphene of high-quality. The application of semiconducting graphene materials into energy storage devices also experiences some major challenges. Though, doped or functionalized graphene materials are proved to be favorable for the application in supercapacitors due to the presence of pseudocapacitance and greater EDLC, however, the mechanical stability of these compounds is not so high. The use of semiconducting graphene materials in lithium-ion batteries is also discussed in this manuscript, although a material with high specific surface area as graphene may cause some major difficulties, including high irreversible capacity and SEI formation in the battery electrodes. In spite of the difficulties, semiconducting graphene has been considered as an attractive candidate for energy applications. Our expectation is that this review will inspire more exciting applications of this growing family of semiconducting graphene materials.

## Competing Interests

The authors declare that they have no competing interests.

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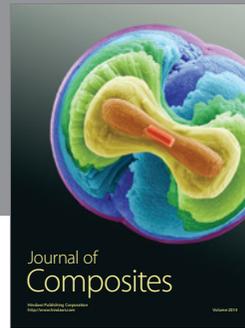
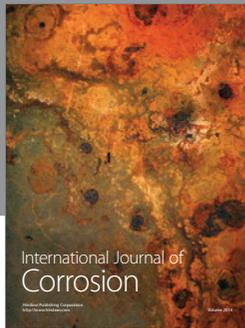
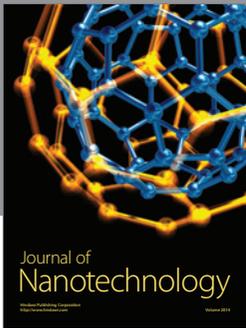
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