

Unique synthesis of graphene-based materials for clean energy and biological sensing applications

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Graphene has unique physical properties, and a variety of proof-of-concept devices based on graphene have been demonstrated. A prerequisite for the application of graphene is its production in a controlled manner because the number of graphene layers and the defects in these layers significantly influence transport properties. In this paper, we briefly review our recent work on the controlled synthesis of graphene and graphene-based composites, the development of methods to characterize graphene layers, and the use of graphene in clean energy applications and for rapid DNA sequencing. For example, we have used Auger electron spectroscopy to characterize the number and structure of graphene layers, produced single-layer graphene over a whole Ni film substrate, synthesized well-dispersed reduced graphene oxide that was uniformly grafted with unique gold nanodots, and fabricated graphene nanoscrolls. We have also explored applications of graphene in organic solar cells and direct, ultrafast DNA sequencing. Finally, we address the challenges that graphene still face in its synthesis and clean energy and biological sensing applications.

graphene, clean energy, chemical and biological sensors, synthesis, chemical vapor deposition, surface segregation, organic solar cells, DNA sequencing

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Graphene is an atomically thin layer of sp^2 hybridized carbon atoms arranged in a honeycomb lattice [1]. It is the fundamental building block for all sp^2 -hybridized carbon allotropes (e.g., graphite, nanotubes and fullerenes). Observation of graphitic monolayers by chemists and surface scientists dates back to the 1960s [2,3]. In 1986, Boehm et al. [4] referred to such a single layer of graphite as graphene. However, exfoliation of graphite into individual graphene sheets remained a curiosity until 2004, when graphene sheets isolated using the simple Scotch tape method were first reported [5,6]. The subsequent discovery of its unusual electronic properties has led to an extraordinary amount of interest amongst researchers across virtually all scientific disciplines [7–10]. Graphene has a large theoretical specific surface area ($2630 \text{ m}^2 \text{ g}^{-1}$) [11], high intrinsic mobility ($200000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [12], high Young's modulus ($\sim 1.0 \text{ TPa}$) [13],

good thermal conductivity ($\sim 5000 \text{ W m}^{-1} \text{ K}^{-1}$) [14] and optical transmittance ($\sim 97.7\%$) [15]. Graphene is thus considered as an attractive candidate for next-generation electronic materials and holds great promise for widespread applications [16–24] including ultrafast optoelectronic devices, chemical and biological sensors, energy generation and storage, and novel composites.

As the first step to investigate its properties and further to realize these practical applications, graphene must be synthesized in a controlled manner, so the controlled synthesis of graphene is of great importance for both fundamental research and practical applications [25]. Recent synthetic efforts have diverged in a number of different directions. For instance, micromechanical cleavage [6], liquid-phase exfoliation [26,27], reduction of graphene oxide [28,29], chemical vapor deposition (CVD) [30–32], carbon segregation [33,34], chemical synthesis [35,36] and deterministic placement [37] have been developed to produce single-layer

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graphene (SLG) or few-layer graphene (FLG). Current efforts in graphene synthesis are mainly focused on the control of area, structural quality, and number of layers [38].

Liquid-phase exfoliation (LPE) involves making dispersions of graphite in various solvents by ultrasonication. LPE can probably be viewed as an alternative to solid-phase micromechanical cleavage that is more facile and gives larger yields. However, it is difficult to control the number of graphene layers using LPE [27,39]. In this micromechanical approach, interaction between solvents such as *N,N*-dimethylformamide (DMF) or *N*-methylpyrrolidone and graphene may lower the energy barrier of exfoliation by providing a better match of surface energies between the two components [27]. Moreover, appropriate organic molecules (both small molecules and polymers) can also be used to help exfoliate graphite into graphene by insertion between graphite layers [40,41].

Reduction of graphene oxide (GO) is the most popular wet chemical approach to produce colloidal suspensions of graphene, which is called reduced graphene oxide (rGO) [42]. GO in aqueous solution, which is generated by oxidation (resulting in oxidation of graphite, i.e., graphite oxide) and subsequent exfoliation of graphite, can be reduced to graphene by reducing agents [43], thermal treatment [44] or electrochemical methods [45], transforming electrically non-conductive GO to conductive graphene. Because of facile solution processing, large yields, and low cost, this wet chemistry approach to graphene is especially attractive in the fields of chemistry and biomaterials. However, the transport properties of the resulting rGO are moderate because of the presence of defects and oxygen groups in the graphene plane.

SLG and FLG can be grown on metal substrates via CVD. When a catalytic metal surface is heated to a suitable temperature, gaseous hydrocarbons decompose into carbon atoms and hydrogen gas (or oxygen gas), and the carbon atoms then form a graphene mono- or multilayer [46]. Although large-area SLG or FLG films have been generated by CVD, and graphene-like carbon materials have been produced by substrate-free CVD, radio-frequency plasma-enhanced CVD, aerosol pyrolysis and solvothermal synthesis, the uniform growth of SLG or graphene with a predefined number of layers is still a major challenge possibly because of the large amount of carbon sources adsorbed by catalytic metals [47].

Carbon segregation has also been used to prepare graphene layers from silicon carbide (SiC) or carbon-doped metal substrates [33,34]. SLG or FLG can be fabricated via sublimation of Si from SiC or catalytic decomposition of hydrocarbons following high temperature annealing. Similar to CVD, this segregation method also faces the challenge of how to achieve high quality graphene layers with accurate thickness control over an entire substrate.

In this article, we briefly review our recent work on the controlled synthesis of graphene and graphene-based composites, the development of methods to characterize graphene

layers, and the use of graphene in clean energy applications and rapid DNA sequencing.

1 Synthesis and characterization of graphene-based materials

1.1 Large-scale synthesis of SLG

In contrast to GO and rGO synthesized by solution-based oxidation and reduction, graphene layers synthesized by dry methods such as CVD and surface segregation have superior electron transport characteristics and features derived from these transport properties [1,9]. The unique electronic, photonic, mechanical, and thermal properties of graphene layers are dependent on the number of layers and crystalline structure of graphene layers as well as their stacking. Although coverage of SLG grown on Cu foil of more than 95% has been achieved [47], this graphene is not epitaxial. The controlled synthesis of graphene with a predefined number of layers over an entire substrate is still a major challenge. Variability in the thickness of graphene layers and grains over the same substrate leads to the fluctuation of electron transport properties [30], and thus prevents us from taking advantage of the distinct properties of monolayer (ML), bilayer (BL), and trilayer (TL) graphene in practical large-scale integrated applications.

Among the substrates used in the synthesis of graphene, Ni(111) surfaces are one of the best templates because of the small lattice mismatch of this surface with that of graphene and highly oriented pyrolytic graphite (HOPG) [48]. This makes Ni(111) one of the most promising catalytic metals for commensurate epitaxial growth of structurally homogeneous graphene. However, the large solubility of carbon in Ni makes it difficult to obtain graphene layers with uniform thickness over the whole substrate. To solve this problem and realize commensurate epitaxial growth of graphene on metal templates, we recently developed a simple method to produce SLG on a Ni film substrate [38] via surface segregation [49–51]. We first deposited a thin film of Ni (~100 nm thick) on a HOPG(0001) surface and then treated the sample under high vacuum. During heating, the polycrystalline Ni film was transformed into a Ni(111) surface, and simultaneously carbon atoms diffused into the Ni template from HOPG. Finally, SLG on top of the Ni template was formed via carbon segregation during cooling. We investigated the homogeneity of the synthesized SLG by various methods including Raman spectroscopy and scanning tunneling microscopy (STM) [52–54]. All of the results suggested that the graphene layer synthesized on the whole Ni film was SLG (Figure 1).

1.2 Auger electron characteristics of graphene layers

As mentioned above, the optical and electronic properties of graphenes rely heavily on the number of graphene layers

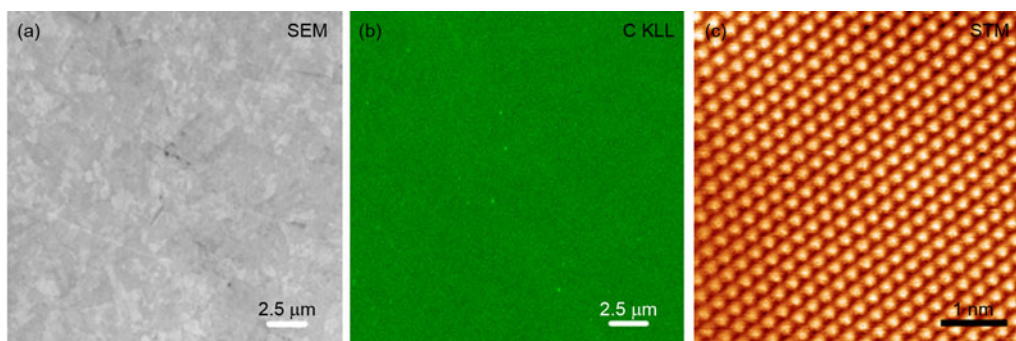


Figure 1 Extended SLG synthesized on a Ni film. (a) Scanning electron microscopy (SEM) image; (b) C KLL Auger electron map corresponding to the image in (a); and (c) typical ultrahigh vacuum STM image of graphene on a Ni film. Reprinted with permission from [38], Copyright 2011, American Chemical Society.

and their stacking, dopants, defects, and coupling with the underlying substrate. It has been pointed out that ML, BL, and TL graphenes show different electronic properties, and the electronic structure rapidly evolves with the number of layers, approaching the three-dimensional limit of graphite at ~ 10 layers [55]. Thus, identification of the number of graphene layers, i.e., determination of the thickness of a graphene sample, is essential for informed research and distinct applications. Raman spectroscopy is a standard technique to identify graphene and count the number of graphene layers based on the features of G and 2D bands, including the intensity and shape of the peaks and the full

width at half-maximum of the 2D peak [56]. However, in most cases, Raman spectroscopy is only suitable for identifying the graphene layers on SiO_2 substrates with a typical thickness of ~ 300 nm [57]. Also, Raman spectroscopy is not a high-resolution technique.

Recently, we established Auger electron spectroscopy (AES) as a method to characterize the number and structure of graphene layers on arbitrary substrates [58]. We found that AES gives distinct spectrum shape, intensity and energy characteristics with an increasing number of graphene layers (Figure 2). Based on a study of standard graphene sheets, we directly calculated electron inelastic mean free

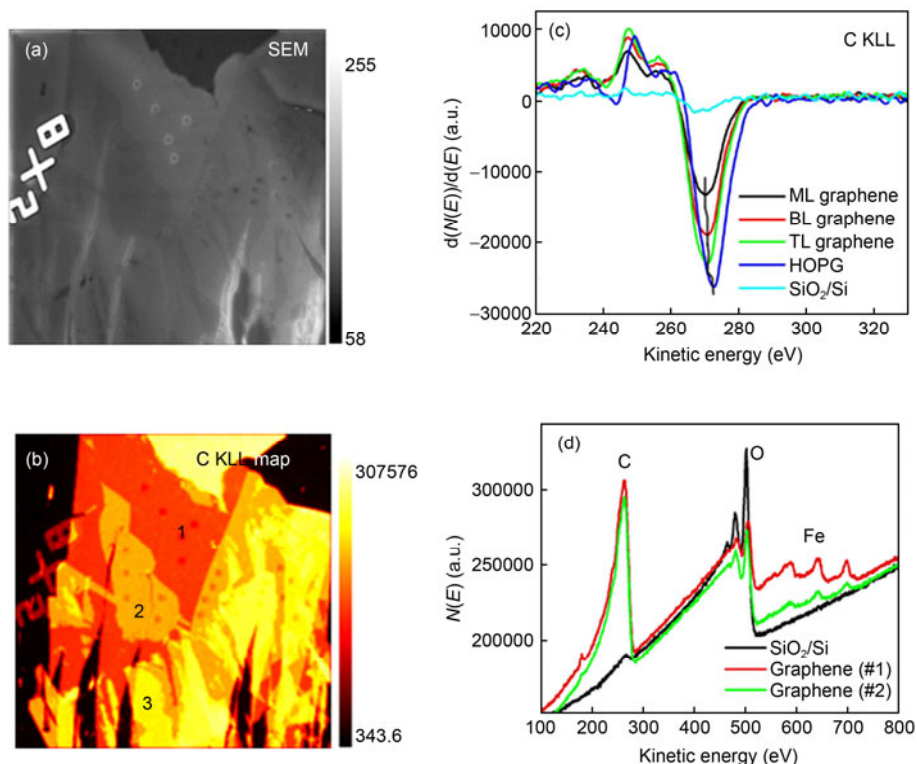


Figure 2 AES characterization of the number and structure of graphene layers. (a) SEM image of a graphene flake on SiO_2 ; (b) C KLL Auger electron map corresponding to (a), showing the different color contrast of different numbers of layers; (c) AES spectra acquired for ML, BL, and TL graphene, and HOPG; (d) AES spectra of a graphene sheet transferred onto SiO_2 . Fe impurity from FeCl_3 etchant used for remove Ni substrate was detected. Reprinted with permission from [58], Copyright 2010, American Chemical Society.

paths (IMFP) for graphene layers. Once we know the IMFP for graphene layers, we can determine the number of graphene layers simply by measuring the peak intensity according to the electron attenuation model. AES can allow up to six layers of ML graphene on any substrate to be accurately measured. Furthermore, AES is a high-resolution technique so it can be used to study the uniformity of graphene layers at the nanoscale, allowing the resolution of defects in graphene layers [59]. Therefore, impurities and dopants in graphene layers can be detected based on Auger electron characteristics.

1.3 Covalent surface modification of GO for graphene-based materials

GO is a major precursor of graphene-based materials. It is easily produced by chemical oxidation and subsequent exfoliation of graphite, which is inexpensive and available in large quantities from natural and synthetic sources [28,29]. Generally, GO is synthesized by one of the three methods developed by Brodie, Staudenmaier, or Hummers [60]. All of these methods involve oxidizing graphite to various levels. In the Brodie method [61], graphite is repeatedly treated with potassium chlorate (KClO_3) and nitric acid (HNO_3). This method was modified by Staudenmaier [62], who used a mixture of sulfuric acid (H_2SO_4) and HNO_3 with KClO_3 . Hummers et al. [63] later developed a less hazardous and more efficient method that involves treatment of graphite with a mixture of sodium nitrate (NaNO_3), potassium permanganate (KMnO_4), and concentrated H_2SO_4 . Xu et al. [64] reported that mildly oxidized GO can be prepared using a modified Hummers' method involving a single chemical exfoliation of graphite with a smaller amount of KMnO_4 . Compared with GO made by Hummers' method, the mildly oxidized GO contains fewer defects and can be used to prepare highly conductive graphene by chemical reduction. GO is a nonstoichiometric compound of carbon, oxygen and hydrogen in variable ratio, which is dependent on the synthesis method and degree of oxidation [65,66]. The chemical structure of GO is often assumed to be a graphene sheet bonded to oxygen-containing functionalities including epoxide and hydroxyl groups on the basal plane and carbonyl and carboxyl groups at the edges [28,65]. These functional groups make GO hydrophilic, which allow it to disperse effectively in some polar solvents such as water, alcohol and DMF [67]. These groups also facilitate the chemical functionalization of GO [68,69].

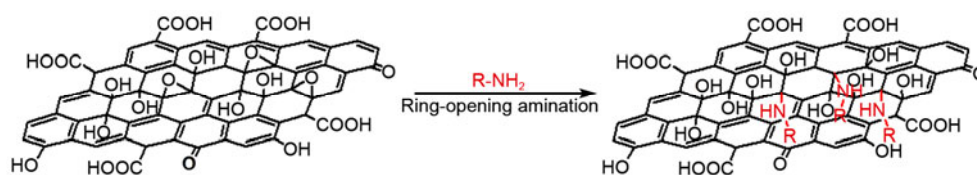


Figure 3 Ring-opening amination of epoxy groups on GO with octadecylamine.

A variety of reactions have been developed for chemical functionalization of GO. Stankovich et al. [70] successfully functionalized GO by treating it with organic isocyanates. Isocyanate treatment results in the functionalization of the carboxyl and hydroxyl groups in GO via formation of amides and carbamate esters, respectively. Such isocyanate-derivatized GOs do not exfoliate in water but readily form stable dispersions in polar aprotic solvents such as DMF, which facilitates the formation of graphene-polymer composites [42]. The coupling reaction between carboxyl groups and nucleophilic species such as amine or hydroxyl moieties can also be used to functionalize GO with activation by thionyl chloride (SOCl_2) or catalysis by carbodiimide to form amides or esters, respectively [71–73].

It has been demonstrated that epoxy groups behave as an electrophilic center in typical organic chemistry. Inspired by this, we synthesized alkyl-functionalized graphene materials by the ring-opening amination of epoxy groups on the basal plane of GO with octadecylamine (Figure 3) [74]. Octadecylamine-functionalized GO (ODA-GO) is hydrophobic and can be dispersed well in many organic solvents as single sheets. We fabricated carbon nanoscrolls (CNSs) using ODA-GO nanosheets as building blocks by compression of Langmuir-Blodgett (LB) films. In this process, a dispersion of ODA-GO in toluene was added dropwise onto a water subphase in a LB trough. After the evaporation of toluene, individual ODA-GO nanosheets floated on the water surface because of their hydrophobic nature. The scattered nanosheets were pushed together into a compact ML by two moving barriers. Further compression caused the scrolling of flexible ODA-GO nanosheets to form CNSs, as shown in Figure 4. The scrolls can be unwound by specific solvents. Activated by thionyl chloride before amine treatment, GO can be grafted with more alkyl chains through both acylation of carboxyl groups and ring-opening amination of epoxy groups [75].

1.4 Graphene-based hybrid nanomaterials

Graphene has been produced efficiently in bulk amounts at low cost using chemical conversion from graphite such as by chemical reduction from GO [30]. Unlike other approaches, chemical synthesis of graphene using graphite, graphite oxide or other graphite derivatives as starting materials is not only scalable but can also produce graphene that is processable and possesses new functions. The unique two-dimensional structure as well as the extraordinary electronic,

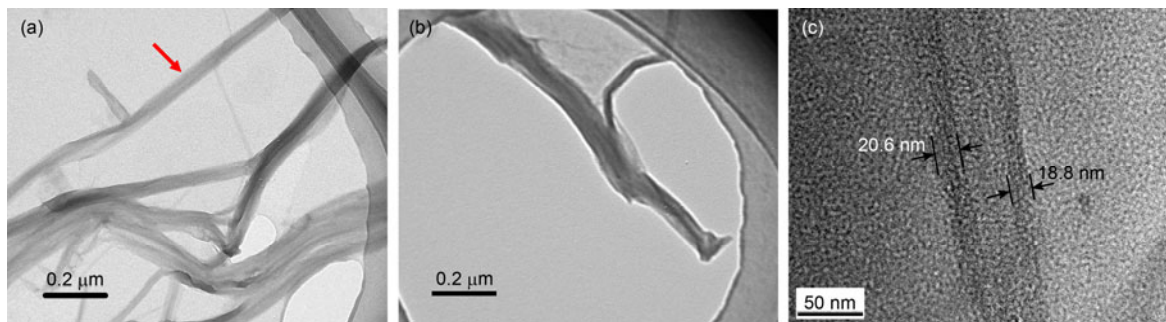


Figure 4 Typical CNS structures produced by compression of LB films. (a) TEM image of CNSs (the red arrow shows a CNS with a well-defined hollow core); (b) a half scrolled CNS without a cap at the end; (c) high-resolution TEM image of a CNS with a tubular structure. Reprinted with permission from [73]. Copyright 2010, Elsevier.

optical, mechanical and chemical properties of graphene provides a robust atomic-scale scaffold for the design of new graphene-based hybrid nanomaterials [76]. For example, when decorated with metal nanoparticles, the intrinsic properties of graphene can be finely tuned to adapt varied applications such as catalysis, energy generation and storage, optoelectronics, and sensors [77]. Most hybrids reported in the literature consist of graphene with noble metal nanoparticles including Au [20], Pt [78,79], Pd [80] and Ag [81]. Fe [82], Cu [83], Sn [84] and Co [85] nanoparticles have also been used to fabricate composites with graphene.

Despite great progress in the synthesis of various metal-graphene composites recently, anchoring metal nanoparticles to GO or rGO surfaces to modulate electronic and other properties, improving the dispersibility of rGO, and controlling the size, uniformity, and density of nanoparticles on the graphene planes remains a major challenge. In contrast to the unique transport properties of graphene, GO is insulating.

Randomly distributed oxygen functionalities on the surface of GO can result in inhomogeneous GO-based composites [86]. Chemical reduction of GO to rGO results in conductivity but also poor dispersibility because of π - π stacking interactions, which make individual rGO sheets almost inaccessible for modification or functionalization [74]. Currently, there are several methods used to prevent aggregation of rGO and graphene composites [87–89].

We recently developed a strategy to synthesize a water-dispersible graphene composite uniformly functionalized with gold nanodots (GNDs) [20]. The basic principle of this strategy is to use ethanethiol-*perylene* tetracarboxylic diimide (ETPTCDI) as an adhesive that, on one hand, uniformly assembles on graphene with its *perylene* π -motif and, on the other hand, bonds to the GNDs through thiol-Au interactions. ETPTCDI causes rGO to disperse well after reduction from GO-ETPTCDI, and serves as a template to orderly decorate graphene with GNDs (Figure 5). This novel *in situ*

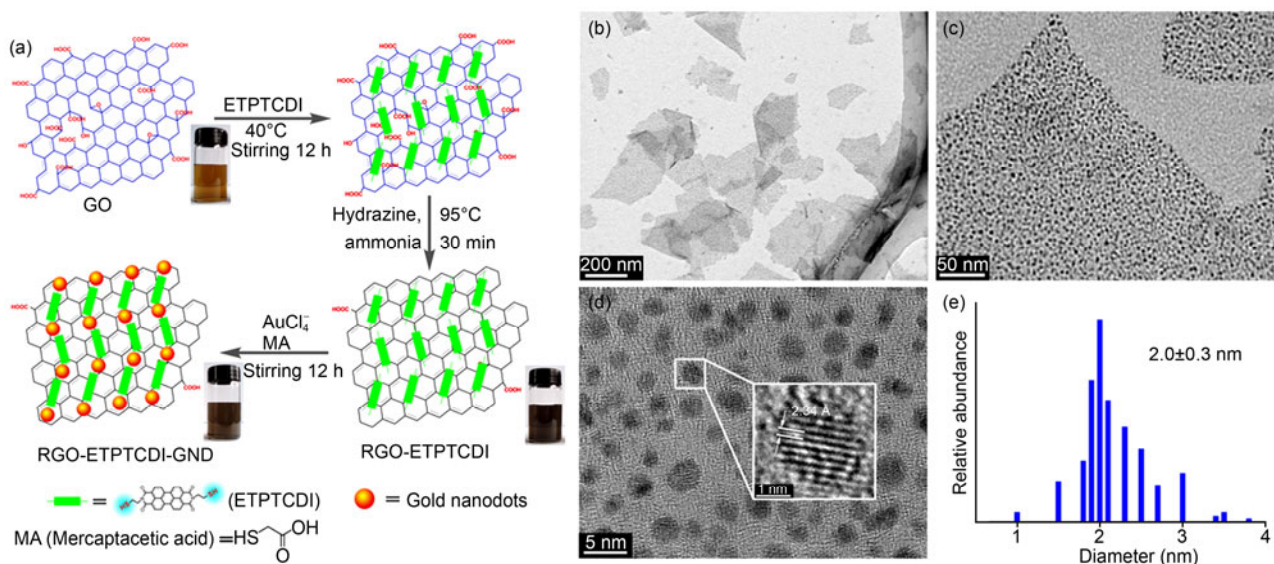


Figure 5 Uniform decoration of GNDs on rGO-ETPTCDI sheets. (a) Synthesis of rGO-ETPTCDI-GND; (b)–(d) TEM images of rGO-ETPTCDI-GND; (e) particle size distribution of Au GNDs on rGO-ETPTCDI-GND sheets estimated by measuring the size of more than 400 GNDs, expressed as mean \pm standard error. Reprinted with permission from [20]. Copyright 2011, Royal Society of Chemistry.

method enables us to produce dispersible, reliable, and processable rGO-ETPTCDI-GND sheets with improved electrocatalytic activity and varying size and density of GNDs.

We demonstrated that to attain dispersible graphene-based hybrids, aggregation of nanoparticle-crosslinked rGO must be prevented. Nanoparticles themselves generally tend to aggregate, so the nanoparticles could attach to more than one rGO sheet and thus form nanoparticle-crosslinked rGO aggregates. RGO sheets need to be well-dispersed to allow further functionalization. These two principles need to be considered to synthesize high quality graphene hybrid materials and explore further potential applications.

2 Use of graphene-based materials in clean energy applications and as biosensors

2.1 Organic photovoltaic devices

Because of unique properties such as tunable electronic properties, optical transparency, robustness and flexibility, graphene-based materials have been widely explored for use in polymer solar cells (PSCs). It has been reported that graphene-based materials and composites can be used as transparent electrodes [90,91] and electron acceptors in PSCs [92–95].

We used GO as an interfacial layer (IFL) to modify the bulk-heterojunction (BHJ)/metal anode contact in inverted poly[3-hexylthiophene] (P3HT):[6,6]phenyl C₆₁ butyric acid methyl ester (PCBM) PSCs [17]. GO was deposited onto the active layer simply by spin-coating a butyl alcohol solution of GO. The device containing GO exhibited a remarkable improvement in power conversion efficiency compared to the device lacking an interfacial layer, indicating that GO can effectively modify the BHJ/metal anode interface to facilitate hole collection. In addition, the device performance with a ~2–3 nm thick GO layer is even better than that of a control device containing poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) as the IFL. Further increase in the thickness of the GO layer will result in the decrease of the device performance with higher series resistance, which can be attributed to the high electrical resistance of GO.

To further understand the mechanism of GO as an IFL on the anode in PSCs, we investigated the chemical composition of GO by various techniques such as X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, and pH titration analysis [18]. GO is acidic in nature because of the presence of chemical species such as carboxylic acid, phenolic and enolic hydroxyl groups, which can lead to proton dissociation. The proton density of GO used in this research was calculated to be one exchangeable proton per 8.7 carbon rings. We measured the electrical conductivity of the P3HT thin film before and after GO deposition by fabricating organic field-effect transistor (OFET)

devices (Figure 6(a)). It was found that the electrical conductivity of the P3HT thin film increased by six orders of magnitude and exhibited metallic-like characteristics when GO was deposited on its surface. The dramatic increase in conductivity of the P3HT thin film was attributed to protonic doping of the surface of P3HT by the GO layer, which was confirmed by the observation of new charge transfer absorption peaks in the NIR region of the UV-Vis-NIR spectrum. Compared to small molecule dopants (e.g., FeCl₃, I₂, HCl and NOPF₄) [96–98], the unique 2D structure of GO prevents it from penetrating into the bulk of conjugated polymers, making it an ideal material for surface doping. This finding provides a new strategy to improve the electrical contact of metal/conjugated polymer interfaces in organic electronic devices such as PSCs, organic light-emitting diodes, and OFETs. The surface doping effect was demonstrated in inverted P3HT:PCBM PSCs using metals (Au, Ag, Al) with different work functions (WFs) as the top anode, as shown in Figure 6(b). When a thin layer of GO is incorporated between the anode and active layer, the devices show improved performance with a open circuit voltage of ~0.62 V, independent of the WFs of the different metals. This can be attributed to the formation of an Ohmic contact between the active layer and top metal electrode caused by the surface doping of P3HT by GO [99].

2.2 Graphene for rapid DNA sequencing

Biosensing has the potential to improve the quality of human life. Because of their large surface area and excellent transport properties, biological applications of graphene, GO and rGO have attracted significant interest based on research experience in carbon nanotubes and various nanowires. Graphene-based materials have been used in electrochemical, impedance, and fluorescence biosensors, as well as biomolecular labels and transducers in OFETs.

The most ambitious biological application of graphene is for rapid, inexpensive electronic DNA sequencing. Affordable and rapid genome sequencing is widely regarded as the

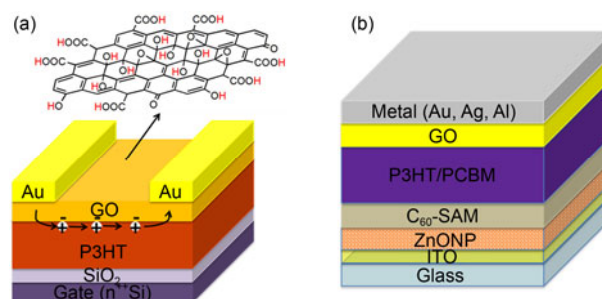


Figure 6 (a) Schematic diagrams of the cross-section of an OFET containing P3HT and GO (P3HT/GO); (b) device configuration of inverted PSCs containing GO as a hole-selective IFL and different metals as the top electrode. Reprinted with permission from [18], Copyright 2011, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

next great frontier for science and will eventually revolutionize personalized and predictive medicine and custom medical treatment, enabling doctors to determine genetic susceptibility to a host of diseases and tailor therapies to an individual's genome. We proposed in 2009 that using graphene can solve the bottle-neck issue of how to achieve single-base resolution of electronic DNA sequencing (Figure 7) [100]. Our proposal was based on the following facts: the base-specific electronic signatures of the four DNA bases [101,102], and the 0.335 nm thickness of conducting graphene is equivalent to or less than the separation between neighboring DNA bases in a stretched single-stranded DNA chain. We further proposed to integrate the graphene sensing element with nanofluidics because it could be easy to control the movement of DNA chains and the interaction between graphene and DNA bases in a nanochannel [103]. Later numerical simulation revealed that graphene-based nanopores or nanochannels may rapidly read out sequences of individual DNA molecules with 100% accuracy [104–106]. It has been shown experimentally that graphene nanopores can be used as subnanometer electrodes [107–109]. All of the studies to date show that graphene is promising for direct, rapid and inexpensive DNA sequencing. This is a new and rapidly expanding field, and the development of such technology would surely lead to the “\$1000 genome” and allow personalized medicine to be realized.

3 Perspective

Herein, we have highlighted our recent efforts to fabricate graphene-based materials and explore their application in organic photovoltaic devices and rapid electronic DNA sequencing. Because of their unique two-dimensional structure and excellent electronic, optical and mechanic properties, graphene-based materials show tremendous potential in various applications. In energy conversion, one promising

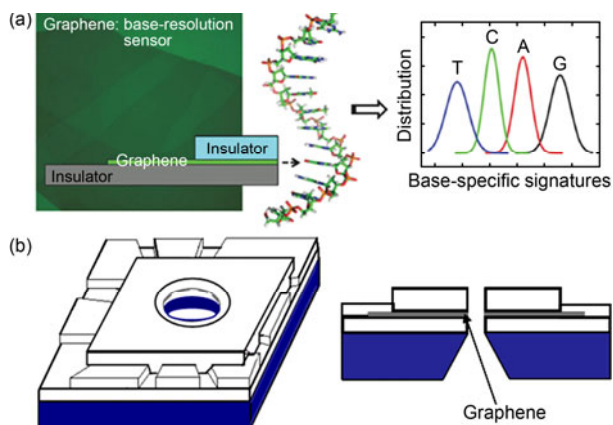


Figure 7 Graphene for DNA sequencing. (a) Basic principle of using graphene for electronic DNA sequencing with single-base resolution. Reprinted with permission from [100], Copyright 2009, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim; (b) a graphene-based nanopore.

application is exploiting graphene as a transparent conducting electrode for solar cells and displays. Compared to traditional transparent indium tin oxide films, advantages in cost, resources, and mechanical flexibility make graphene especially useful in the emerging field of flexible organic electronic devices. However, the sheet resistance of graphene electrodes synthesized by CVD remains higher than that of ITO, which is mainly caused by structural defects in the graphene films. Doping graphene can increase carrier concentration; however, the stability of dopants needs to be improved. The development of low-cost and solution-processable graphene-based IFLs for PSCs also has attracted great attention. Incorporation of semiconductor or metal nanoparticles into graphene-based materials can provide greater versatility in energy harvesting and conversion, and selective catalytic and sensing applications. The use of graphene-based materials to form lightweight, strong, and electrically tunable composites will also emerge in many applications. One challenge facing graphene used as an active material in PSCs is the absence of a band gap in pristine graphene.

Since researchers completed sequencing the first human genome in 2003 at a cost of about \$3 billion, the cost of DNA sequencing has been dropping steadily by using second generation sequencing platforms. Sequencing the human genome could improve our understanding of the biological functions encoded in it and the biological basis of inherited diseases and cancer. The ultimate goal is for sequencing to become so simple and inexpensive that it can be routinely employed as a general-purpose tool throughout biomedicine. To fulfill this potential, the cost of whole-genome sequencing will need to decrease to a few hundred US dollars. With new approaches under development, these goals may be feasible within the next decade. Graphene-based nanopore technology is one possible method for single-molecule DNA sequencing at low cost and with high throughput. Despite the theoretical possibility of accurately sequencing DNA by graphene nanopores and the demonstration of DNA translocation through graphene nanopores, there are various fundamental questions about sequencing with graphene nanopores that remain. For example, the detection mechanism of the local electrical field [104,105], whether high ionic strength prevent detection of charged DNA molecules [106], how to make graphene pores with a size of ~2 nm [104], and whether single-nucleotide resolution is possible in the presence of thermodynamic fluctuation all require further study. Without doubt, this exciting yet preliminary work will certainly be the precursor for many future studies on the use of graphene for DNA sequencing.

To move forward, controlled fabrication of graphene-based materials and the fine tuning of their properties should be further explored and exploited to meet the needs of emerging applications. Chemical exfoliation of graphite, yielding GO, provides a practical route towards low-cost

bulk production of solution-processable graphene-based materials. Despite the random distribution of functional groups on the GO surface, the presence of such groups provides an excellent platform to tune the electronic and optical properties of graphene-based materials. In particular, the intrinsic fluorescence of GO in the visible and NIR range opens up exciting and previously unforeseen optical applications for graphene-based materials. CVD and surface segregation are two of the most promising methods to produce graphene over large areas. Besides difficulty in controlling the number and structural quality of graphene layers on a whole substrate, a challenge for graphene produced by CVD and surface segregation is reliable and scalable transfer of the fabricated graphene from the synthesized substrate to a target platform for practical applications in ultrafast optoelectronic devices, energy generation and storage, and chemical and biological sensors [110].

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