ACCOUNTS
of chemical research

Focusing on Energy and Optoelectronic Applications: A Journey for Graphene and Graphene Oxide at Large Scale

XIANGJIAN WAN, YI HUANG, AND YONGSHENG CHEN*
Key Laboratory of Functional Polymer Materials and the Centre of Nanoscale Science and Technology, Institute of Polymer Chemistry, College of Chemistry, Nankai University, Tianjin, 300071, China

RECEIVED ON SEPTEMBER 2, 2011

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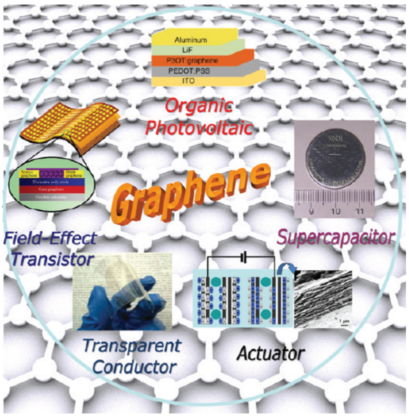

Carbon is the only element that has stable allotropes in the 0th through the 3rd dimension, all of which have many outstanding properties. Graphene is the basic building block of other important carbon allotropes. Studies of graphene became much more active after the Geim group isolated "free" and "perfect" graphene sheets and demonstrated the unprecedented electronic properties of graphene in 2004. So far, no other individual material combines so many important properties, including high mobility, Hall effect, transparency, mechanical strength, and thermal conductivity.

In this Account, we briefly review our studies of bulk scale graphene and graphene oxide (GO), including their synthesis and applications focused on energy and optoelectronics. Researchers use many methods to produce graphene materials: bottom-up and top-down methods and scalable methods such as chemical vapor deposition (CVD) and chemical exfoliation. Each fabrication method has both advantages and limitations. CVD could represent the most important production method for electronic applications. The chemical exfoliation method offers the advantages of easy scale up and easy solution processing but also produces graphene oxide (GO), which leads to defects and the introduction of heavy functional groups. However, most of these additional functional groups and defects can be removed by chemical reduction or thermal annealing. Because solution processing is required for many film and device applications, including transparent electrodes for touch screens, light-emitting devices (LED), field-effect transistors (FET), and photovoltaic devices (OPV), flexible electronics, and composite applications, the use of GO is important for the production of graphene.

Because graphene has an intrinsic zero band gap, this issue needs to be tackled for its FET applications. The studies for transparent electrode related applications have made great progress, but researchers need to improve sheet resistance while maintaining reasonable transparency. Proposals for solving these issues include doping or controlling the sheet size and defects, and theory indicates that graphene can match the overall performance of indium tin oxide (ITO). We have significantly improved the specific capacitance in graphene supercapacitor devices, though our results do not yet approach theoretical values. For composite applications, the key issue is to prevent the restacking of graphene sheets, which we achieved by adding blocking molecules.

The continued success of graphene studies will require further development in two areas: (1) the large scale and controlled synthesis of graphene, producing different structures and quantities that are needed for a variety of applications and (2) on table applications, such as transparent electrodes and energy storage devices. Overall, graphene has demonstrated performance that equals or surpasses that of other new carbon allotropes. These features, combined with its easier access and better processing ability, offer the potential basis for truly revolutionary applications and as a future fundamental technological material beyond the silicon age.

1. Introduction

Graphene, the latest member of carbon allotropes, is actually the basic building block of other important carbon allotropes, including 3D graphite, 1D carbon nanotubes (CNTs), and 0D fullerene (C_{60}) (Figure 1). This is why it has long been an interest of many earlier theoretical studies.[1] Earlier experimental works related to it are mostly about graphite intercalation compounds and *graphite oxide*.[1]

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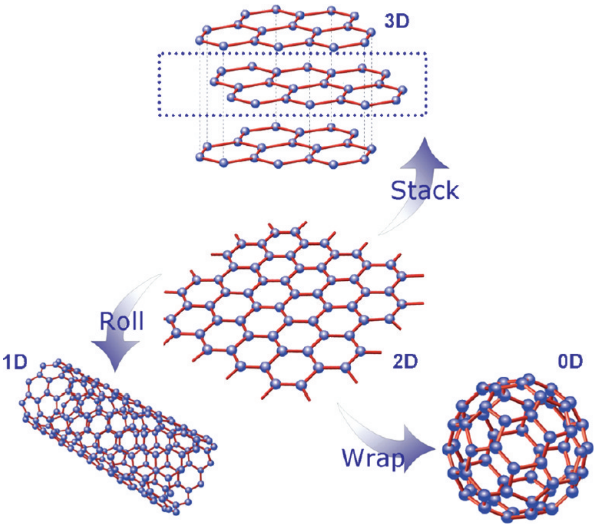

FIGURE 1. Graphene is the basic building block for other carbon allotropes.

Extensive studies of graphene began in 2004, after Geim and co-workers isolated "free" and "perfect" graphene and demonstrated its unprecedented electronic properties.[2] This led to an explosion of interest, partially because of many grand discoveries and results about its high mobility, Hall effect, Dirac electronic structure, transparency, mechanical strength, thermal conductivity, etc.,[2] which all together make this material truly an unprecedented one. So far, there is no any other case where many important properties, in most cases among the best, can be combined in one individual material. Thus, it is natural that many important and revolutionary applications are proposed.[2,3] There have been numerous reviews published about graphene in almost every aspect in the past few years.[2−6] In this Account, we briefly review our effort on graphene and graphene oxide (GO) at bulk scale, from their synthesis to application studies focusing on energy and optoelectronic applications.

2. Synthesis of Bulk Graphene and Graphene Oxide

The methods of preparation for graphene can be divided into two categories, top-down and bottom-up ones. The top-down methods include (1) mechanical exfoliation developed by Geim's team[2] and (2) chemical oxidation/exfoliation.[3] The bottom-up methods include (1) epitaxial growth on SiC and other substrates,[7] (2) CVD,[3,8] and (3) arc discharging[9] methods. Each of these methods has some advantages and limitations. The mechanical exfoliation and epitaxial methods can give close to "perfect" graphene, which is essential for the fundamental studies of graphene, but have a limit for scale up. In contrast, chemical exfoliation methods, giving the product of GO, have the advantage of large scale.

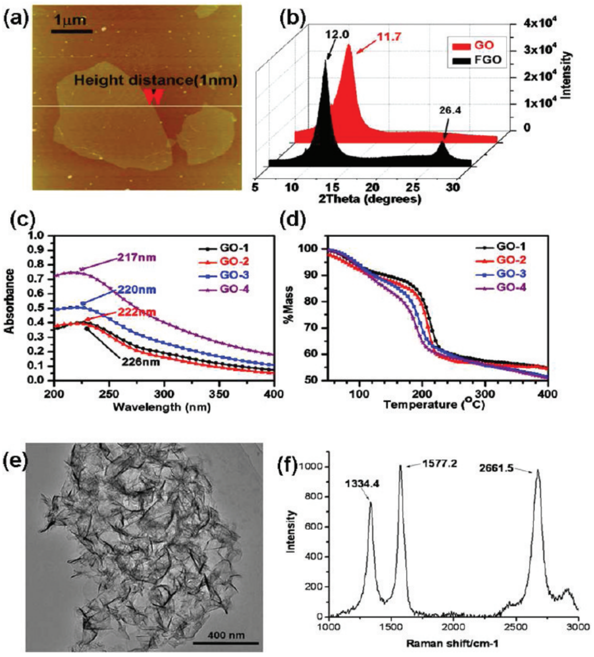

FIGURE 2. (a) A typical AFM image of GO, (b) XRD patterns of GO and FGO, (c, d) UV−vis and TGA curves of different GO with different sizes, (e) SEM image of FLG, and (f) typical Raman of FLG.

Our work started with the synthesis of GO at bulk scale. This method can be traced back a long time,[1] though it mostly then gave *graphite oxide*. Different oxidizing agents have been used, and the most popular one is $KMnO_4$ for Hummer's method.[3,10] With some modification, we are able to prepare GO at the scale of hundreds of grams.[10] This method is very robust and gives all monolayer graphene product verified by AFM and XRD (Figure 2a,b). The size of the graphene sheets is generally in the range of hundreds of nanometers to tens of micrometers depending on the reaction conditions, with the thickness of individual sheets in the range of 0.7−1.2 nm confirmed with AFM (Figure 2a). In its XRD, a broad peak corresponding to a layer distance of >0.7 nm is observed (Figure 2b), and the peak corresponding to the layer distance of 0.34 nm in graphite is diminished completely.

By changing the reaction time and oxidizing agents, we could control the size of graphene sheets from hundreds of square nanometers to hundreds of square micrometers.[11] Obviously, these different GO products come with different degrees of functionalization and disruption of the π systems, which is reflected in their UV−vis and TGA (Figure 2c,d). The number of graphene layers could also be controlled. For

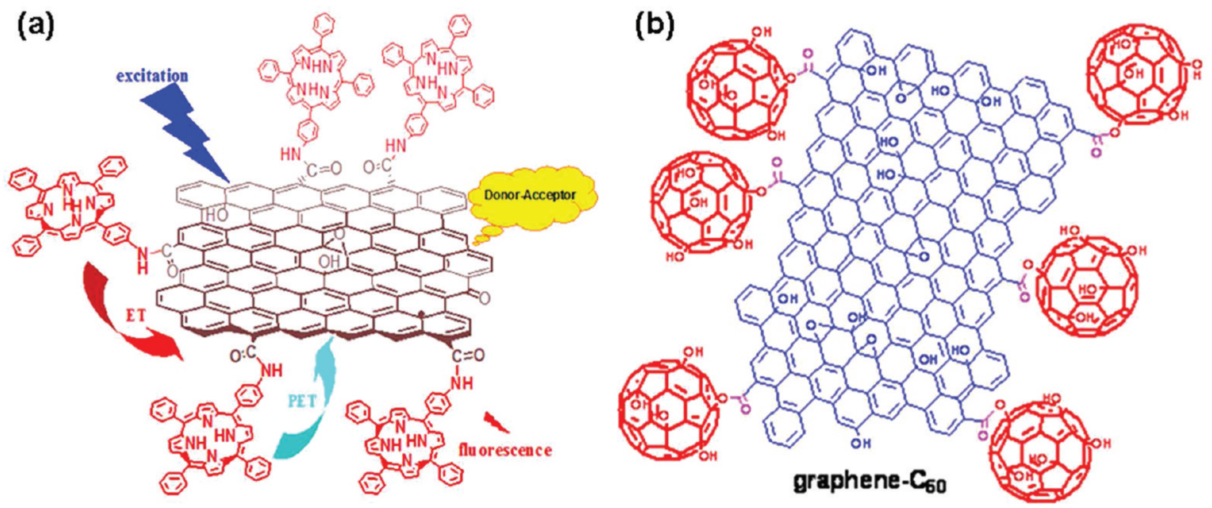

FIGURE 3. Structure representations of (a) TPP−NHCO−SPFGraphene and (b) graphene−C_{60} hybrids.

example, with a reduced amount of $KMnO_4$, the number of the layers is controlled mainly in the range of 3−4, and a few-layered graphene oxide (FGO) product is obtained.[12] Compared with GO, FGO is much less functionalized and the π system is less disrupted. In its XRD (Figure 2b), there are two diffraction peaks at $2\theta = 12.0$ ($d = 0.74$ nm) and 26.4 ($d = 0.34$ nm), different from the single peak around 12 for GO. Similar results have also been reported by Cheng's group.[13]

The graphene materials from chemical methods inevitably come with some defects and functional groups. To tackle this problem, we have developed an arc discharging method.[14] In a typical run with 25% CO_2 in the buffer gas, tens of grams of few-layered graphene (FLG) are generated in minutes (Figure 2e). FLG mostly has 4−5 layers, with size in the range of hundreds of nanometers. Different from GO, its Raman spectrum (Figure 2f) shows a clear 2D peak around 2660 nm for high-quality graphene. It has much fewer functional groups or defects compared with GO/FGO, confirmed by TGA with only a 1.2% weight loss up to 300 °C. Note that the graphene from this method can be dispersed well in organic solvents with mild sonication. This is because of the limited functional groups introduced by CO_2. Similar methods using H_2, NH_3, and even air have been reported by other groups.[9,15]

For any serious applications of graphene, it must be prepared at large scale. So the advantage of easy scale up of the methods using chemical exfoliation[10,11] and arc discharging[14] make them important.

3. Modifying Graphene Edge with Functionalized Molecules for Optical Limiting Applications

The functional groups, including OH and COOH, on GO sheets really work well as a handle for the functionalization of graphene to tune its properties.[3−6] With this strategy, various molecules have been attached to graphene sheets, rendering graphene/graphene oxide more versatile precursors for a wide range of applications.

Porphyrins are a class of conjugated molecules with many interesting optoelectronic properties. Using COOH group on GO and via amide bonding, we prepared a nanohybrid material of graphene with porphyrin, named TPP−NHCO−SPFGraphene (Figure 3a).[16] Fluorescence studies show that there is an efficient energy or electron transfer upon photoexcitation between the porphyrin and graphene structures. This makes it show a superior optical limiting effect, better than the benchmark optical-limiting material C_{60}. Other conjugated molecules, such as C_{60} (Figure 3b) and oligothiophene, have also been used to modify graphene sheets using a similar strategy, which all show similar outstanding optical limiting performance.[17,18]

4. Flexible Transparent Electrodes from GO Solutions

The current market standard for transparent electrode (TE) applications is ITO, which has increasing concerns of limited resources, cost, brittleness, chemical stability, and so on. Graphene has a transparency of 97.7% per monolayer.[2] This unique optical behavior, combined with its remarkably high electron mobility, high chemical stability, superior mechanical strength, and flexibility,[19] make it a top candidate for TE applications.[2,3,8,20]

4.1. Transparent and Flexible Graphene Electrodes from GO. Using GO as the precursor for graphene-based devices has the advantage of using a simple solution process. But GO itself is an insulator due to the heavy disruption

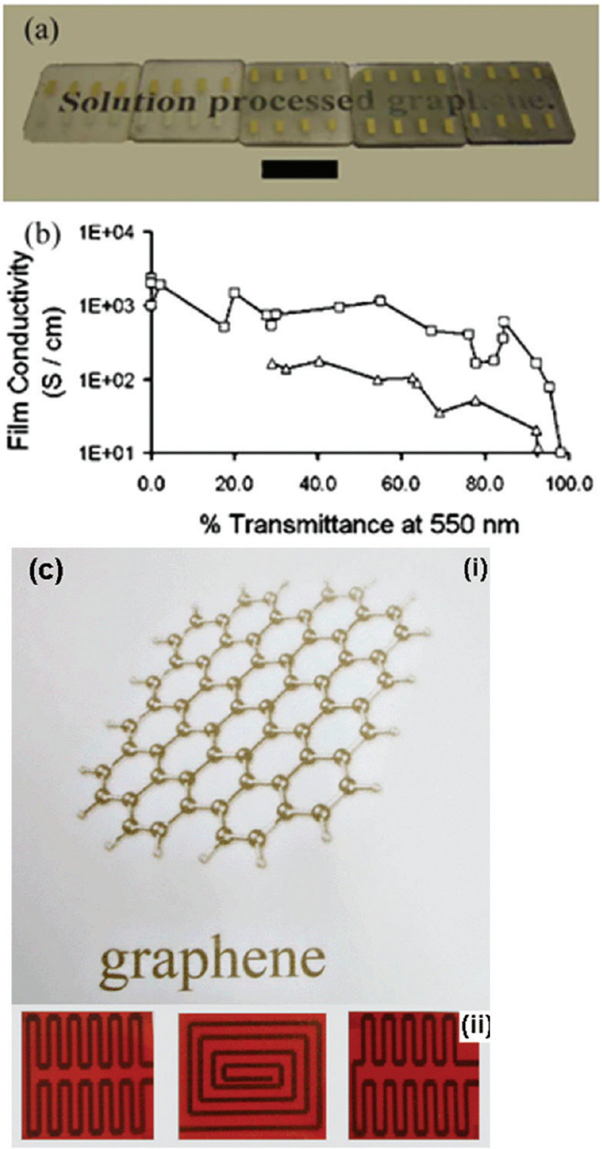

FIGURE 4. (a) Photograph of reduced GO films with increasing thickness, the black scale bar is 1 cm; (b) Film conductivity vs % transmittance for films prepared from GO; (c) Different patterns printed on various substrates from GO or FGO inks.

of its π system. Fortunately, there are many convenient ways to overcome this problem. The two most used methods are (1) chemical reduction and (2) thermal annealing. With these processes, most of the functional groups and defects can be removed, and the graphene intrinsic structure and excellent conductivity could be mostly restored.

The general process for making graphene transparent conducting film electrodes from GO involves the preparation of GO films followed by reduction. The first step can use many different methods such as spin-coating,[10,21,22] vacuum filtration,[23] and so on. Regarding the chemical reduction, many regents have been used.[3] Among them, NH_2NH_2 is most used, which can also be combined with thermal annealing. In our initial report, a simple NH_2NH_2 vapor reduction of GO film prepared by spin coating could bring the film conductivity to the order of 10^{-2} to 10^1 S/cm with 80% transparency.[10] To be used for transparent electrodes, more important parameters are the sheet resistance and transparency. As a reference, ITO has a transparency of >90% at a wavelength of 550 nm with sheet resistances of 10–30 Ω/sq. The combination of NH_2NH_2 reduction with annealing can improve the conductivity $>10^2$ S/cm. (Figure 4a,b) For films with thickness of 3–10 nm, sheet resistance can be improved to 10^2–10^3 Ω/sq with a >80% transparency.[10] Various modifications have been reported after our initial work.[3,4] By replacement of GO with FGO and under similar reduction and annealing processes, the conductivity of the films can be improved about 1 order of magnitude.[12] For the chemical reduction, the method using HI reported by Cheng's groups is particularly worth noting,[24] where GO films were reduced in hydroiodic acid and have a conductivity of 3×10^2 S/cm and a sheet resistance of ~1.6 kΩ/sq with 85% transparency, much better than that by other reducing methods. More importantly, this method maintains the good integrity and flexibility of the original GO films. With FLG produced by arc discharging,[14] the film prepared by spin-coating the dispersion of FLG in DMF without any annealing gave a sheet resistance of ~670 kΩ/sq with transmittance of ~65% at 550 nm, much better than that from GO or FGO under the same conditions.[12]

The graphene electrodes could also be prepared using simple and cost-effective inkjet printing technology because of the easy dispersion of GO.[22] For example, conductivities of ~500 and 874 S/m have been achieved for GO and FGO films on polyimide substrate. The conductivity and mechanical flexibility of the printed graphene electrodes remain literally unchanged after many times of bending tests. Based on these results, various high-quality patterns, and even complete flexible circuits, have been printed on paper and plastic substrates directly (Figure 4c). The conductivity of the films prepared from GO solutions could be also improved significantly by doping or using hybrid materials. For example, immersing reduced GO (rGO) films in thionyl chloride or gold chloride leads to improvement of film conductivity by a factor of 3–5.[25] We have reported a transparent and flexible hybrid film of graphene/PEDOT, which was prepared through in situ polymerization in presence of rGO and shows a conductivity up to 20 S/m with a transparency of 96% without any treatment.[26]

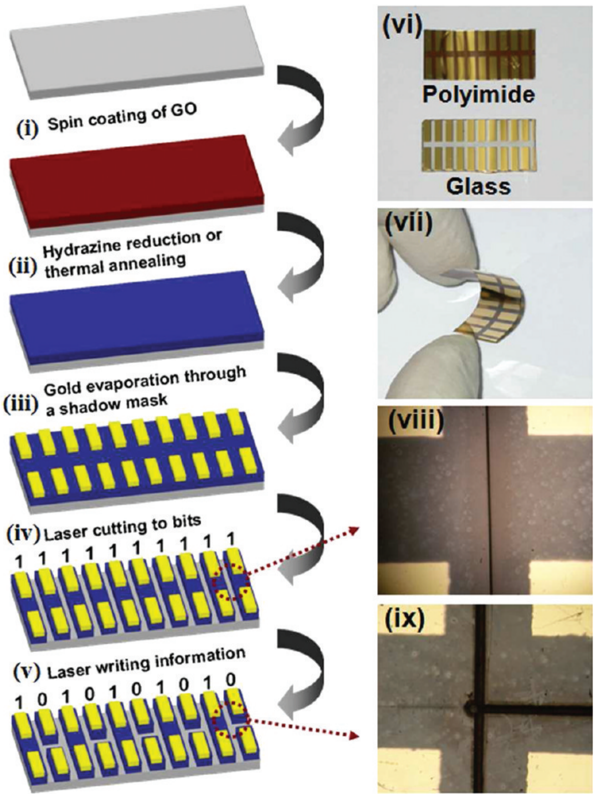

FIGURE 5. (i–v) Schematic illustrations and photographs of the fabrication of a graphene-based memory card with 10 bits; (vi) Optical image for graphene films on PI and glass substrates patterned with gold electrodes; (vii) Device on the PI substrate; (viii, ix) Optical microscope images of the laser-cutting channels for the memory card on a PI substrate.

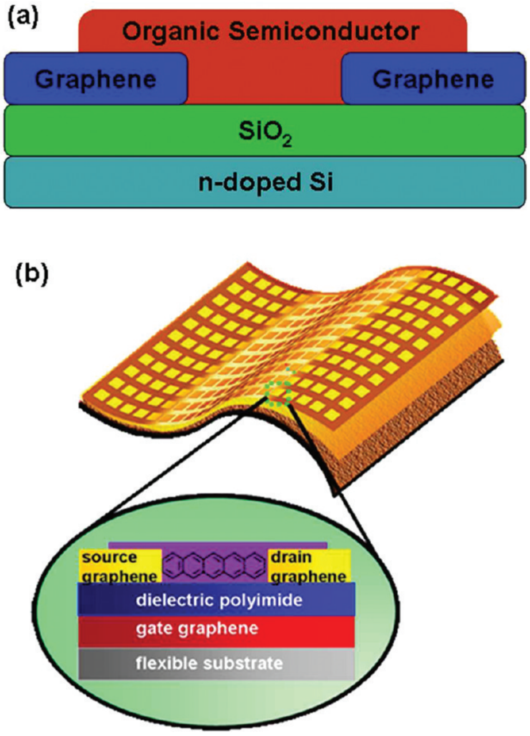

FIGURE 6. A schematic illustration for (a) FETs with graphene as source/gate electrodes and (b) flexible bottom-contact FETs with graphene for all source/drain/gate electrodes.

Low-cost and flexible all-carbon devices or integrated circuits (ICs) have been sought for many years. Many of graphene's excellent properties particularly the tunable electronic and flexible properties make this long time dream closer to a reality. As a proof-of-concept, we have prepared a flexible 10-bit all carbon memory.[27] Following spin coating of a GO solution on a flexible polyimide substrate, the obtained GO film was reduced and annealed, and then a computer-controlled laser cutting was processed to generate the microarchitecture for the memory card. (Figure 5), The data density reaches 500 000 bits per square centimeter even with our very limited processing capability, and much higher data density is expected if using industry level processing techniques. The possible immediate applications for this include connecting electrical wires in ICs, identification cards, radio frequency tags, e-tickets and -books, and so on.

4.2. Graphene Electrodes for FET from GO. There are tremendous works using graphene as the channel (active) material for field-effect transistors (FETs).[3,4,28] Most of them came with low ON/OFF ratios (<10) due to the zero-band gap of graphene. Currently, metals like Au are widely used for the source/drain electrodes in the fabrication of FETs on SiO_2/Si substrates. This makes it rather difficult to have fully solution-processed and flexible devices. Using graphene as the electrodes in FETs might prove to be better for practical applications, particularly for flexible ones. With solution processed GO, flexible FET devices have been fabricated, where graphene works as the source/drain electrodes as shown in Figure 6a.[29] Importantly, the devices with graphene electrodes have lower contact resistances compared with gold electrodes. For all three organic semiconductors tested, currents, mobilities, and ON/OFF ratios are higher for the graphene electrode devices. These results suggest that graphene would be an enticing electrode material for organic electronic devices.

We have carried this further by replacing all the electrodes including the gate one in FETs. Thus, using a solution process from GO, we have fabricated all-graphene-electrode FETs and inverter circuits on flexible substrate PI as illustrated in Figure 6b.[21] The all-graphene-electrode FETs with pentacene as the channel material showed good performance with an average hole mobility of $\sim 0.020\ cm^2/(V \cdot s)$ and ON/OFF ratio of $\sim 10^6$, comparable to or slightly better than the FETs using conventional structure. Better graphene/

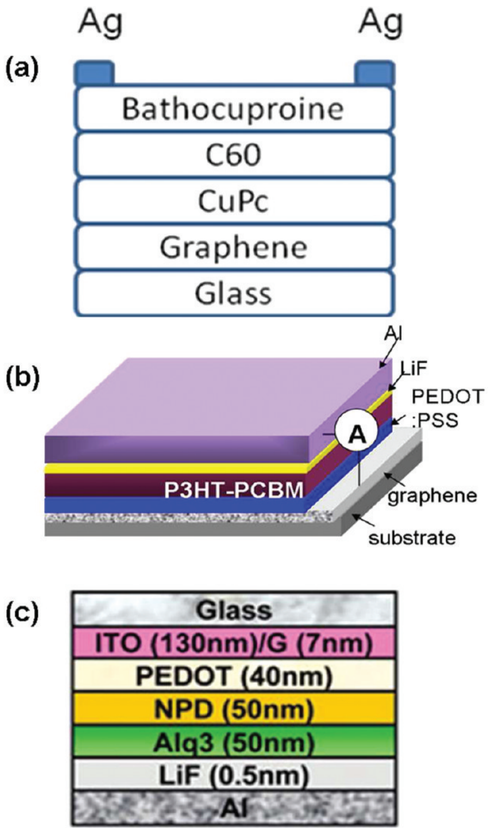

FIGURE 7. (a) Bilayer and (b) bulk heterojunction OPV devices; (c) the structure of LEDs with ITO or graphene (G) as transparent electrode.

pentacene interface contact resistance was also observed for these FETs. Importantly, these devices show excellent mechanical flexibility. This direction was further pushed by a later report from Zhang,[30] where all the source/drain/gate and channel materials are prepared from GO using solution processes.

4.3. Graphene for Transparent Electrodes in Organic Photovoltaic (OPV) and Light-Emitting Diode (LED) Devices. Obviously, based on the excellent transparency and conductivity of graphene, its applications for optoelectronics draw the most intensive attention from the very beginning.[31]

Using solution processing of GO, our collaboration team at Stanford has fabricated a bilayer OPV device (Figure 7a), where the graphene layer works as the transparent electrode.[32] The thickness of graphene films is between 4 and 7 nm, and the corresponding values of the transmittance and sheet resistance are 85%−95% and 100−500 kΩ/sq, respectively. The short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF), and power conversion efficiency (PCE) are 2.1 mA/cm^2, 0.48 V, 0.34, and 0.4%, respectively, for the cell on graphene, and 2.8 mA/cm^2, 0.47 V, 0.54, and 0.84%, respectively, for the cell on ITO. The lower efficiency of the cell on graphene is believed to be due to the high sheet resistance of the graphene film. A similar OPV device, but using CVD graphene with smaller sheet resistance as the transparent electrode gave an improved PCE of 1.27%.[33]

We also fabricated an OPV with bulk heterojunction (BHJ) structure (Figure 7b) with 0.13% PCE.[34] The low PCE for graphene-based devices could have several reasons, including the high sheet resistance of graphene electrode and the hydrophobicity on its surface. Similar results have been reported by Chhowalla with a PCE of 0.13% using a Cl doped graphene electrode.[25] A recent report of OPV with P3HT and PCBM as the active BHJ layer but using a two-step reduction of GO as the transparent electrode showed a much improved power conversion efficiency of 1.01% due to the improved sheet resistance.[35] A similar approach has been applied to fabricate OLEDs using small molecules, where the anode is either graphene or ITO for side by side comparison (Figure 7c).[36] The thickness of the graphene films used is 7 nm, with corresponding sheet resistance and transmission of 800 Ω/sq and 82%, respectively. The OLED turn-on voltages are 4.5 and 3.8 V, and the device reaches a luminance of 300 cd/m^2 at 11.7 and 9.9 V, for graphene and ITO anodes, respectively. The graphene-based OLED performance matches that of the ITO control device despite the higher sheet resistance and different work function of the graphene anode.

5. Graphene for Green Energy Applications

Green energy technologies have been an urgent and important area due to the approaching energy crisis. This includes two parts: energy conversion and storage. Among several possible alternatives for fossil energy, eventually solar energy is probably the only one that can meet the multifold-demand for the long-term human needs. Currently, commercialized solar energy technology is based on Si material. Due to its low cost, light weight, solution processability, and high mechanical flexibility, OPV devices are being pursued as the next generation technology for solar energy conversion. One of the main issues for the OPV is its most used electron acceptor PCBM. This has led to studies of other carbon allotropes, including CNTs as the acceptors. However, some unfavorable factors, such as their insolubility, impurities, and bundling structure, have greatly hindered device performance. Many of graphene's excellent properties indicate that it could be a competitive alternative as the electron-accepting material. Indeed, OPV devices

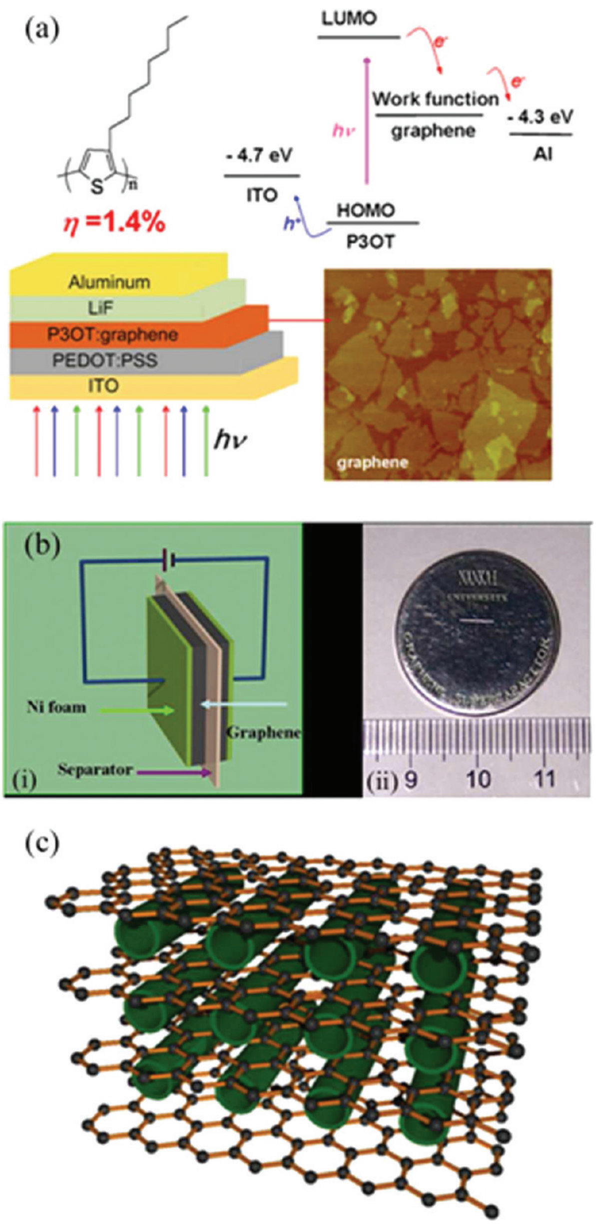

FIGURE 8. (a) The schema of an OPV using graphene as the electron-acceptor material; (b) the schema and a picture of a supercapacitor using graphene as the active material; (c) the model of the 3-D hybrid graphene/CNT material.

(Figure 8a) using an organic functionalized graphene material as the electron acceptor and P3OT as the donor gave a considerable PCE of 1.4%.[37] The power efficiency of 1.4% is moderate compared with the best OPV result so far, but it is comparable with most of the best OPV devices using materials other than fullerenes as electron-accepting materials. After our initial report, similar results were reported by Wang et al.[38] A very recent progress is from Dai's group, where a C_{60}-grafted graphene material was used as the electron acceptor in P3HT based BHJ solar cells with a 1.22% PCE.[39]

For energy storage, the supercapacitor (SC) has been pursued as a promising technology platform, due to its instant charging/recharging capability, long lifetime, and high safety, almost free of maintenance. Currently, the lower energy density (3–5 W·h/kg) of SC compared with that (30–40 W·h/kg for a lead acid battery) of batteries is limiting their wider applications. The key requirements for SC active materials are high specific surface area and conductivity with good electrochemical stability. These requirements almost perfectly match the properties of graphene,[40] which has a theoretical specific capacitance of 550 F/g. We prepared several graphene materials and then used them to fabricate SC devices following the industry standard as shown in Figure 8b.[41] The best result came with 205 F/g for specific capacity, and 10 kW/kg and 28.5 W·h/kg for power and energy density, respectively. Long cycle life of these supercapacitors was observed, and the specific capacitance still remains at ~90% after 1200 cycles of testing. A wide range of performance has been reported by many groups later using different graphene materials.[40] One of the latest works used KOH activated GO material,[42] which achieved a high BET (3100 m^2/g) and 166 F/g specific capacitance in organic media.

The most important issue for SC using graphene, currently mostly started from GO, is to prevent graphene sheets from restacking during the reduction process of GO. To tackle this problem, one of the approaches is to add some spacer to block the restacking. Using this strategy, we made a CNT/graphene hybrid material with an in situ hydrothermal process, and generated a 3D hierarchical structure of graphene and CNT (Figure 8c).[43] Indeed, with this strategy, the restacking of graphene sheets can be almost completely blocked, and a high effective specific capacitance of 318 F/g for graphene was achieved.

6. Actuators Using Graphene-Based Composite Materials

To make any composite material, the first issue is to disperse the filler in matrix homogeneously. This makes GO an excellent precursor for graphene composite applications as GO or its modified materials are rather soluble.[3,6]

Obviously, dispersing graphene sheets at the individual molecule level would be ideal, and a solution process is the most common and probably easiest way. To avoid the restacking of graphene sheets, either functionalization of graphene or adding spacers between the graphene sheets can be used.[3,5] An excellent, also the earliest, example for this is from Ruoff's group,[3] where GO was first functionalized

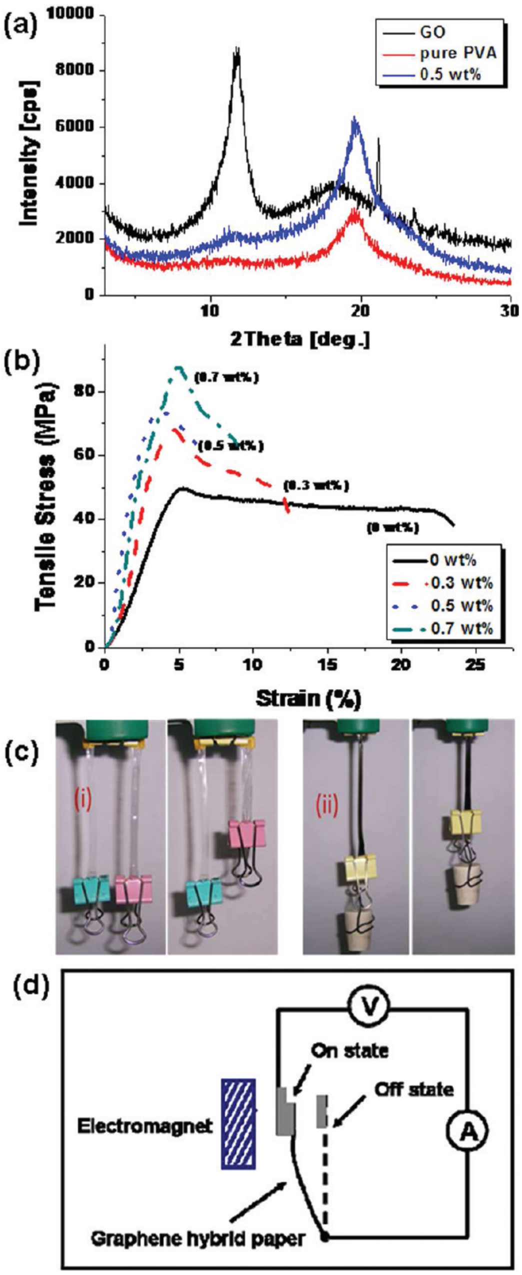

FIGURE 9. (a) XRD for PVA, GO, and the PVA/GO composite; (b) tensile stress of the composites with different loadings of GO; (c) optical images of IR actuation for graphene-based nanocomposites, (i) comparison of shape recovery before (left) and after (right) IR remote actuation, (ii) the 1 wt % sulfonated-graphene/TPU film contracted and lifted a 21.6 g weight 3.1 cm with 0.211 N of force on exposure to IR; (d) the simple circuit using graphene/Fe_3O_4 hybrid paper as a magnetic-controlled switch.

with phenyl isocyanate using its abundant COOH and OH groups to make it soluble in organic solvents such as DMF. The mixed solution of GO and polymer was then treated with dimethylhydrazine to reduce GO. During the reduction step, the intrinsic restacking of graphene sheets was blocked by the polymer molecules.

It would be better to use GO directly without further modification. So, we chose one of the most used polymers, poly(vinyl alcohol) (PVA), as the matrix to make graphene composites, since PVA can be processed in water too. Indeed, in graphene/PVA nanocomposite, made from a simple solution process with water as solvent, graphene sheets were distributed homogeneously at the molecular level, as confirmed by XRD data (Figure 9a).[44] Furthermore, very efficient load transfer was found between graphene and PVA matrix. For example, a 76% increase in tensile strength and a 62% improvement of Young's modulus were achieved by addition of only 0.7 wt % GO (Figure 9b). The efficient load transfer across the graphene–PVA interface is due to both the molecule-level dispersion and strong H-bonding between the OH on PVA and OH/COOH groups on GO.

The fundamental reason to use composite materials is to have multiple or balanced functions from different components, which in the case of using each component independently is unachievable. This is the case when we used the thermal shape or actuation material thermoplastic polyurethane (TPU) as the matrix for actuation composite materials with graphene.[45] TPU possesses the ability to store and efficiently recover large strains by application of thermal stimuli because of its two-phase structure: a thermally reversible phase responsible for fixing a transient shape and a frozen phase responsible for recovering the original shape. This property makes it one of the most widely used polymeric thermal-induced actuator materials. Unfortunately, TPU, an essentially infrared (IR) transparent material, does not show light-induced actuation. This is where graphene comes in to play.[45] When the composite material of TPU/graphene was exposed to light, a remarkable and repeatable IR-triggered actuation was observed at rather low graphene loadings with energy densities up to 0.40 J/g (Figure 9c). Significant improvement in mechanical properties is also achieved for this nanocomposite. Collectively, the results even over perform many commercial elastomer actuators. When exposed to light, graphene sheets in the composites first efficiently absorb and transform light into thermal energy and then serve as the nanoscale heaters and "energy transfer" units through their homogeneous network to heat the TPU matrix uniformly. This causes TPU to change its crystallites and remotely trigger the shape recovery or actuation.

Magnetic conducting materials, particularly with good flexibility, are highly demanded for many applications. The most widely used magnetic material, Fe_3O_4, however, cannot be processed into a flexible standalone film, limiting its applications. Thus, using a solution process, a hybrid material of Fe_3O_4 with graphene was fabricated, and flexible standalone papers were produced through vacuum filtering.[23] This hybrid material shows both good conducting and superparamagnetic properties in addition to improved mechanical strength and high flexibility. The magnetization for the hybrid papers was saturated at a low magnetic field of about $H = 1300$ Oe with saturation magnetization $M_s = 7.29$ emu/g for 7.54% loading of Fe_3O_4. The conductivity of these graphene hybrid papers reaches the order of 10^3 S/m. These combined properties make this material an excellent choice for multiple-channel controlling/actuating functions with a long lifetime. Based on this, a proof-of-concept magnetic fast switch/actuation was demonstrated with excellent performance, as shown in Figure 9d. In this Fe_3O_4/graphene composite material, the interlayer spacing between the graphene layers has been increased due to the intercalation of Fe_3O_4 nanoparticles, and this lead a better access for the external ions to graphene's large surface area. This is demonstrated by its much better electrochemical actuation compared with the pristine graphene material under same conditions.[46]

7. Conclusions and Perspectives

Based on our brief journey for graphene and graphene oxide, it can be concluded that graphene is indeed a very diversified and fascinating material in many aspects. The continuing main driving force for this area eventually depends on the delivery of its many proposed applications. This probably lies in the development of two aspects: (1) the large scale and controlled synthesis of graphene, where for different applications different structures (layer number, size, defect, edge group, etc.) and quantities are needed; (2) truly on-table applications, a couple of which in the nearest term could be the transparent electrode and devices for energy storage.

For the synthesis, CVD growth and graphite exfoliation for GO deserve more attention for their scalability, but domain or sheet size and defect controls are the key. For transparent electrode applications, the electrode made of graphene is still about 1 order of magnitude higher in sheet resistance than ITO, and CVD could be the most successful method for improving this. Having said that, graphene films are chemically stable, robust, and flexible and can even be folded, offering certain advantages over ITO. These shall offer graphene a competitive opportunity for applications in touch screens and bendable applications. Also, it is important to note that theoretical results have indicated that graphene can achieve the same sheet resistance as ITO with a similar or even higher transmittance.[31] For supercapacitor and battery applications, the key is to capitalize graphene's entire surface area and conductivity at bulk state. This means that graphene has to be either modified or used with other material to prevent restacking.

The current fantasy for carbon is the third modern wave after that for C_{60} and CNTs. So far, all these tremendous efforts for carbon have brought us few real and significant applications. Will this time graphene bring us more and revolutionary ones? With a wider and historical view, the big question is: will carbon be the next technological element "beyond the Si age"? It looks like graphene has some advantages over other carbon allotropes, but only time and continuing research will make the final say!

The authors gratefully acknowledge financial support from the MoST (Grants 2012CB933401, and 2011DFB50300) and the NSFC (Grant 50933003).

BIOGRAPHICAL INFORMATION

Dr. Xiangjian Wan received his Ph.D. in 2006 at Nankai University. He joined Prof. Yonsheng Chen's group at Nankai University in 2006.

Dr. Yi Huang received his Ph.D. at Sichuan University in 2001 and joined Yongsheng Chen's group in 2004.

Prof. Yongsheng Chen received Ph.D. in Chemistry at the University of Victoria in 1997. From 2003, he has been a Chair Professor at Nankai University. His main research interests focus on carbon-based nanomaterials.

FOOTNOTES

*Corresponding author. E-mail address: yschen99@nankai.edu.cn.

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