Oh, the Places You'll Go with Graphene

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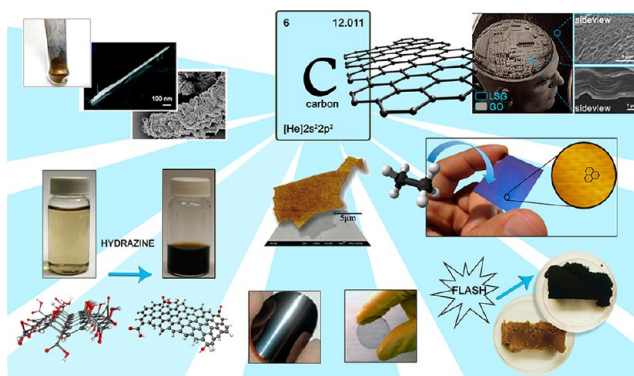
Since the first reported isolation of graphene by peeling graphite with cellophane tape in 2004, there has been a paradigm shift in research. In just nine years, graphene has had a major impact on fields ranging from physics and chemistry to materials science and engineering leading to a host of interdisciplinary advances in nanotechnology. Graphene is attractive because it possesses many extraordinary characteristics that are a direct consequence of its unique atomic structure, as discussed here.

For over a decade, our group has been exploring new routes to synthesize graphene so that this potentially important material can be scaled up for use in practical applications. We have made several significant discoveries starting with the synthesis of few-layer graphene from intercalation/exfoliation reactions that upon sonication produce carbon nanoscrolls. Next, we developed high-throughput methods for producing chemically converted graphene from graphene oxide using either aqueous or anhydrous hydrazine. Recently, we introduced an inexpensive process that uses the laser in an optical drive to deoxygenate graphite oxide layers to create laser scribed graphene.

The impetus of this Account is to discuss both synthetic routes to graphene and their applications. The first part highlights both our top-down and bottom-up routes to graphene, which includes intercalation/exfoliation, chemical reduction with hydrazine and other organic reagents, chemical vapor deposition, and laser scribed graphene. In the later part, we emphasize the significance of these contributions to the field and how each approach has afforded us unique opportunities to explore graphene's properties. This has resulted in new applications such as practical chemical sensors, flash memory storage devices, transparent conductors, distributed ignition, and supercapacitors.

Introduction

Since its isolation,[1] graphene has impacted fields ranging from physics and chemistry to materials science and engineering, leading to a host of interdisciplinary advances in nanotechnology. Graphene is attractive because it possesses many extraordinary characteristics that are a direct consequence of its unique atomic structure. To understand graphene from a chemist's point-of-view, it is helpful to start with a structural perspective. Each carbon atom in graphene's hexagonal lattice has four valence electrons; the first three are used to form covalent sp^2 bonds, while the fourth resides in a p_z orbital that forms π bonds distributed equally along 3 directions, thus leading to a bond order of 1 and 1/3.

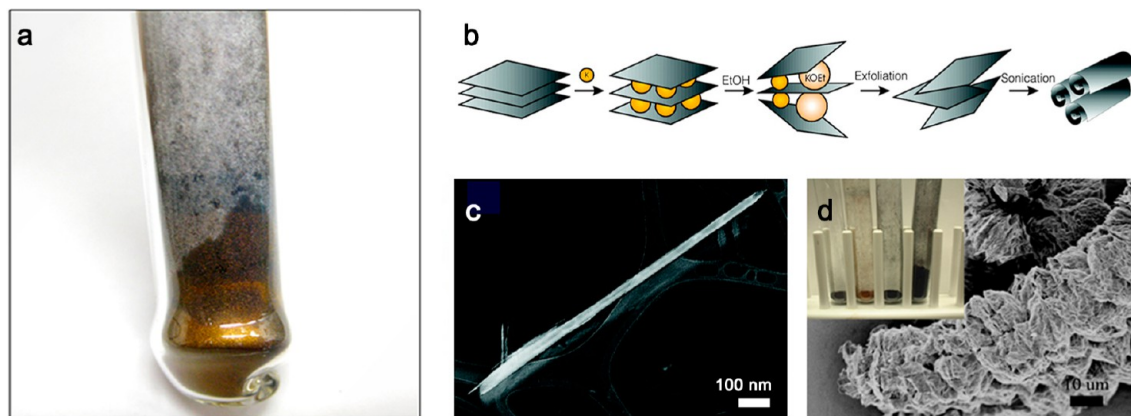This special atomic arrangement allows graphene to have a continuous layer of delocalized electrons and rigid

FIGURE 1. (a) KC$_8$, a first stage graphite intercalation compound that can be converted to graphene-like carbon nano-scrolls via exfoliation as shown (b) schematically and (c) in a TEM image; and (d) microwave-exfoliated graphite. Figures (b, c) reprinted with permission from ref 3 Copyright 2003 AAAS and figure (d) from ref 14 Copyright 2007 Elsevier.
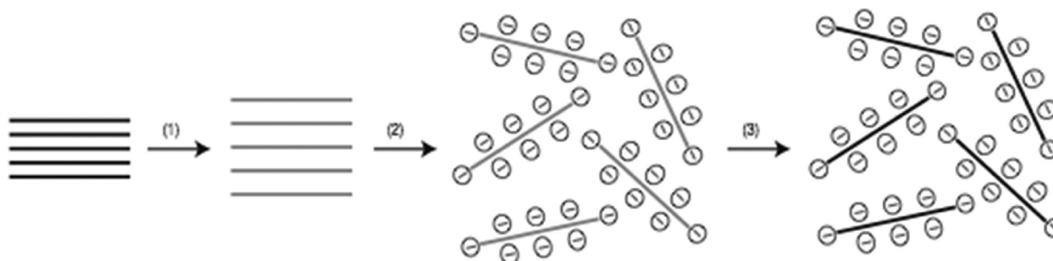

FIGURE 2. Schematic of graphite to chemically converted graphene. (1) Graphite is oxidized into graphite oxide, (2) exfoliated into single sheets of graphene oxide, (3) and then reduced to chemically converted graphene. Reprinted with permission from ref 9. Copyright 2008 Macmillan Publishers Ltd.

covalent bonds, enabling both the rapid movement of injected charge carriers and lattice vibrations, known as phonons, across the plane. The short and rigid covalent bonds that enable graphene to disperse phonons so efficiently also provide it the ability to withstand a great deal of stretching, making it "pound for pound" one of the strongest materials known. Since all carbon atoms are identical, except for the edges, there is no net dipole, rendering graphene nonpolar and hydrophobic.

The extended conjugated network enables graphene to absorb a great deal of light. Smaller conjugated systems are used extensively in dyes and pigments because their delocalized electrons absorb photons of specific wavelengths; as the degree of conjugation increases, longer wavelengths (i.e., lower energies) of the electromagnetic spectrum are more readily absorbed. In general, a strong photon absorbing material generally has a small band gap, thus making it easier for electrons to be promoted to a higher energy level. Since graphene is basically a large aromatic macromolecule without a band gap, it absorbs electromagnetic energy uniformly across the electromagnetic spectrum, from infrared through visible to ultraviolet.[2]
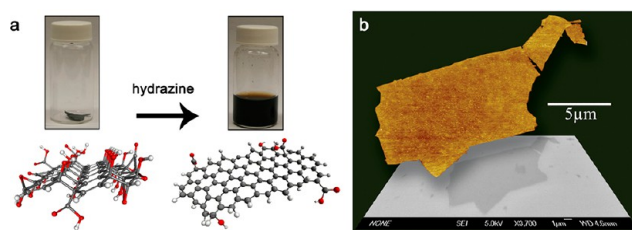

FIGURE 3. High-throughput solution processing of chemically converted graphene. (a) Vacuum filtered films of graphite oxide are reacted with anhydrous hydrazine to form dispersions of CCG. Figure reprinted with permission from ref 11. Copyright 2009 Macmillan Publishers Ltd. (b) The large sheets made it easy to perform multiple characterizations, such as scanning electron (gray) and atomic force (false colored orange) microscopy on the same piece of graphene.

The surface area of nanomaterials is very high, and graphene, with a calculated value of 2630 m^2 g^{-1}, is no exception.[3] In general, high surface area translates into increased reactivity. Since graphene has ample surface area for reactions to take place, it is also of interest in aspects of biology, medicine, and bioengineering because it can be considered to be a biologically compatible electrode and drug delivery material.[4,5] However, careful consideration as

to where graphene is placed, its concentration, and how it is used are of paramount importance.

A distinction should be made between graphene and chemically converted graphene (CCG). The crystalline form of graphene can be obtained through (1) micromechanical cleavage of highly ordered graphite, (2) synthesis via chemical vapor deposition using metal catalysts such as copper, or (3) reduction of silicon carbide at high temperatures.[1,6−8] CCG, on the other hand, is synthesized by a chemical, thermal, and/or photolytic reduction of graphene oxide.[9−13] Chemically converted graphene contains a few residual oxygen species along the basal plane and edges, such as carboxylic acid, hydroxyl, and epoxide groups, which enhance processability, a critical attribute if graphene is to become a useful bulk material.

This Account is divided into two main sections. First, synthetic methods including top-down and bottom-up routes to graphene will be discussed. Since each approach affords unique avenues to study graphene that results in new and different applications—this will be the focus of the second section. With this in mind, we will emphasize the significance of each contribution to the field and then highlight our most recent venture into 3-D graphene architectures, which appears to be of paramount importance in fields requiring high energy density such as supercapacitors.

Synthesis

Top-Down Synthesis. Often scientific discoveries appear to be accidents, but they are only accidental in the sense that, in searching for one thing, one finds something else, often of more interest for a different application. Before graphene was discovered through mechanical exfoliation, there were several attempts to isolate graphene through other top-down approaches. One such method was via intercalation and exfoliation of graphite.[3]

Graphite intercalation compounds (GIC) are composed of ions or molecules inserted between the layers of graphene
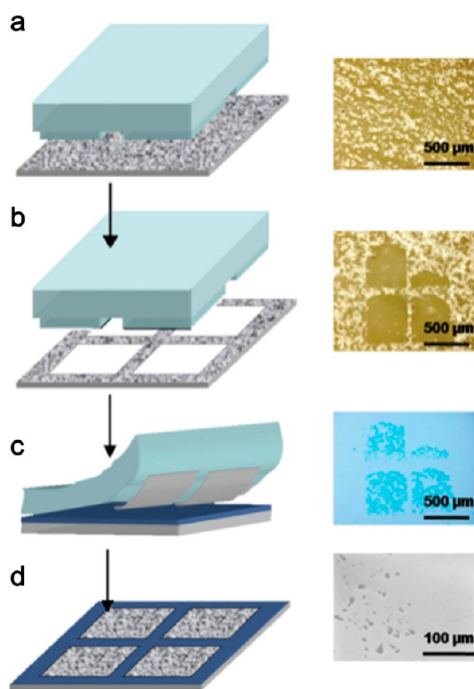

FIGURE 4. Diagram (left) and optical microscope images (right) depict the PDMS transfer process. It begins by (a) depositing materials on a glass substrate and (b) carefully "inking" the pre-patterned PDMS stamp. (c) The inked stamp is contacted to a heated silicon dioxide substrate and peeled away to (d) reveal deposited materials. Figure reprinted with permission from ref 19. Copyright 2009 Wiley-VCH.
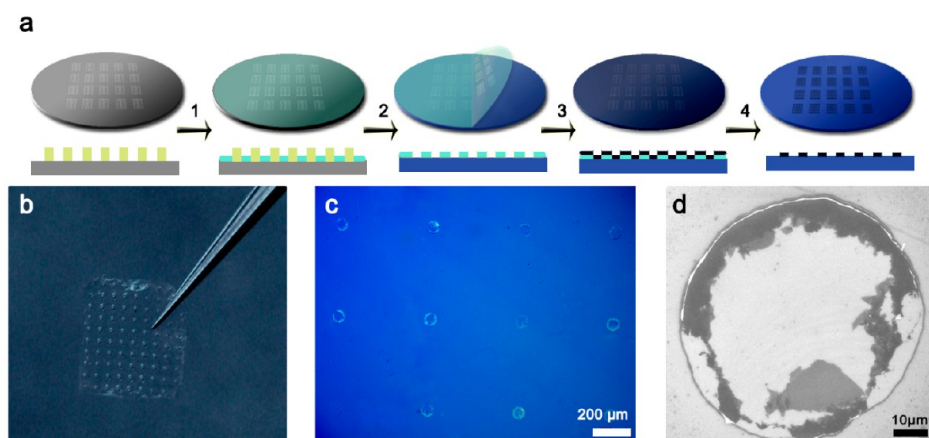

FIGURE 5. (a) Schematic of stenciling chemically converted graphene (CCG). The stenciling process is achieved in four steps: (1) an SU-8 master design is fabricated via photolithography, (2) PDMS is spin-coated over the pattern and cured, before it is removed, and (3) placed onto a target substrate which then gets coated with CCG. (4) The final pattern is revealed after removing the PDMS stencil. Images of (b) a section of a PDMS stencil and (c, d) optical and electron micrographs of pattered CCG. Figure reprinted with permission from ref 20. Copyright 2010 Wiley-VCH.
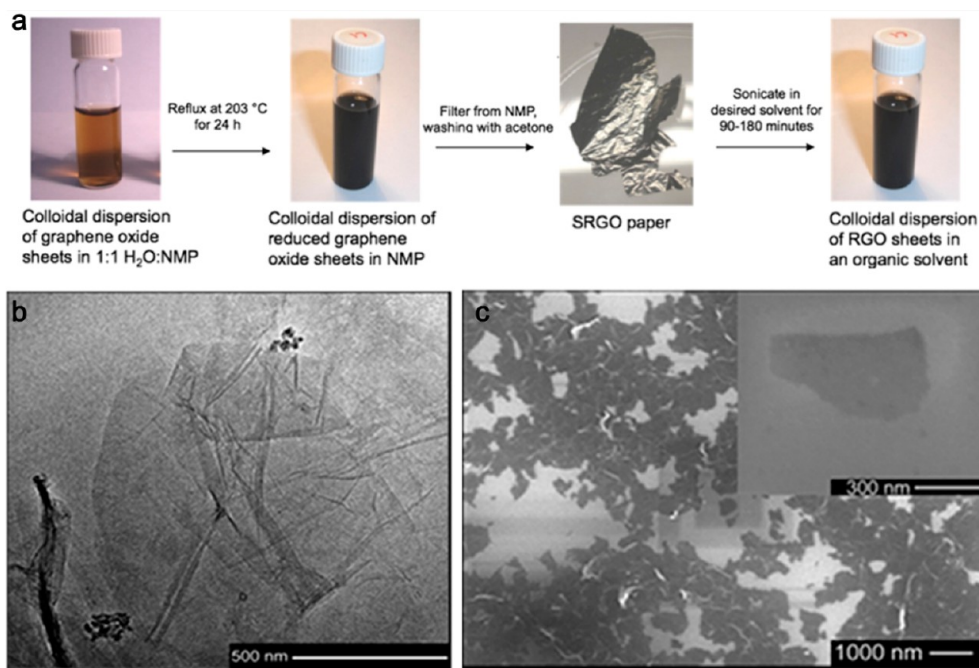
FIGURE 6. CCG produced via solvothermal reduction in N-methyl-pyrrolidinone (NMP). (a) A process showing how graphene oxide can be reduced in NMP, filtered into a paper and dispersed into a variety of organic solvents. (b, c) Scanning electron micrographs show that single sheets can be isolated for study; see inset. Figure reprinted with permission from ref 13. Copyright 2010 American Chemical Society.

that leave graphite's layered structure intact. For example, heating graphite with potassium under vacuum results in a bronze colored first stage intercalation complex with K^+ ions inserted between each layer of carbon (Figure 1a). This alkali metal GIC can be readily exfoliated in aqueous media due to the favorable formation of potassium hydroxide. Upon sonication, few-layer graphene-like nanoscrolls (Figure 1c), analogous to uncapped multiwalled carbon nanotubes, form. Interestingly, microwave radiation can also be used to exfoliate graphite leading to graphitic foams (Figure 1d).[14]

After the first reports on isolating graphene, an important development was the demonstration of solution processed graphene derivatives, especially chemically converted graphene.[9,15] Before this time, the only way to obtain single layer graphene was by peeling away layers of a graphite monolith with cellophane tape or through the reduction of silicon carbide wafers, but neither method appears to be readily scalable or cost-effective. By reducing the well-known precursor, graphene oxide (GO),[16] which is stabilized as individual sheets in aqueous media due to its oxygen-containing functional groups, chemically converted graphene (CCG) can be synthesized.[16]

Hydrated hydrazine was originally used to reduce graphene oxide sheets into CCG.[15] Similar to GO, chemically converted graphene sheets obtained from graphite can readily form stable aqueous colloids through electrostatic
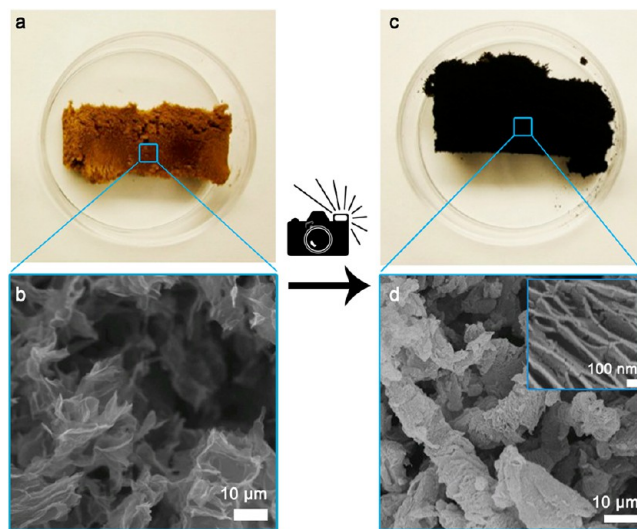

FIGURE 7. (a) Image of a GO foam sample before exposure to a photographic flash. (b) A scanning electron micrograph (SEM) shows the porous nature of the GO foam. (c) After flashing, the GO foam ignites releasing CO_2 and H_2O and leaving behind an exfoliated, deoxygenated graphitic carbon. (d) An SEM image of the material shows exfoliated layers. (Inset) Under high magnification, the layers measure 10−20 nm in thickness. Figure reprinted with permission from ref 21. Copyright 2010 Wiley-VCH.

stabilization as we demonstrated in collaboration with Prof. Dan Li (Monash University) and Prof. Gordon Wallace (University of Wollongong).[9] Figure 2 shows a schematic diagram for the chemical route to CCG dispersions. This discovery

enabled the development of a facile approach to large-scale production of aqueous graphene dispersions without the
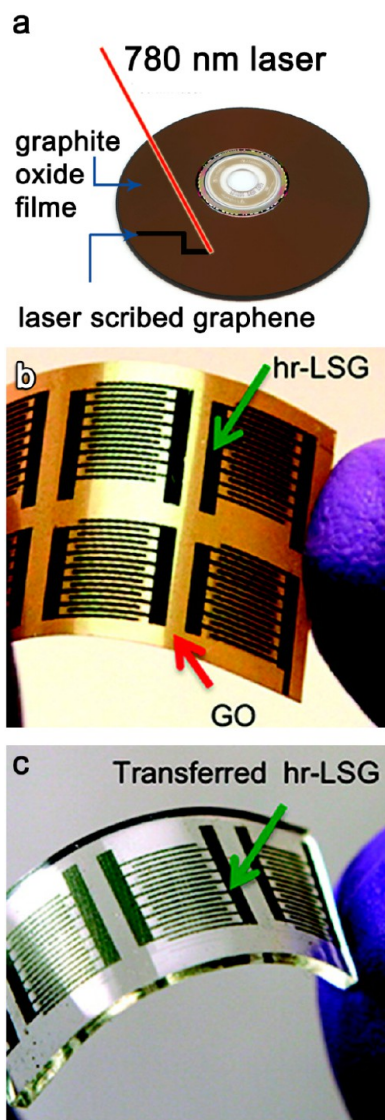

FIGURE 8. (a) Laser-scribed graphene produced via tuning a 780 nm infrared laser and focusing it onto graphite oxide films. The level of reduction is determined by the amount of time the laser focuses on GO films drop-cast and dried on PET-coated compact discs. (b) The PET film can be removed to show regions of reduced and unreduced GO, which are (c) transferred onto other substrates like PDMS. Figure (b,c) reprinted with permission from ref 12. Copyright 2012 American Chemical Society.
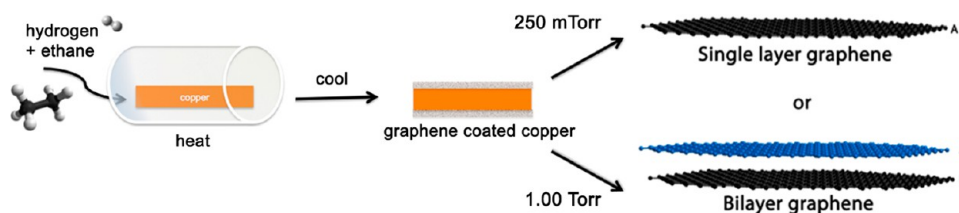
need for polymeric or surfactant stabilizers. Furthermore, the findings made it possible to process graphene materials using a very low-cost solution processing technique that quickly opened avenues for future discoveries, as described later.

Alternative hydrazine-based reduction processes were accomplished with vapors at elevated temperatures as well as the reduction and stabilization in anhydrous hydrazine (Figure 3a).[11,17] Although the electrical properties of these derivatives are still not nearly the quality of pristine graphene, they exhibit comparable electrical characteristics to bilayer graphene produced using the more time-consuming peeling/drawing method.[17] Anhydrous hydrazine also enabled large sheets of CCG to be processed thereby facilitating multiple characterizations, such as scanning electron and atomic force microscopy on the same sample without the need for alignment markers, Figure 3b. Solution processing also enabled carbon nanotubes to be spin-coated with graphene as thin films for use as transparent conducting electrodes.[18]

Solution processing of materials can be accomplished through a variety of techniques such as spin-coating, dip-coating, and doctor blading. In the case of CCG in hydrazine, these methods are limited to the size available in a glovebox. Spin-coating affords the ability to deposit single sheets or overlapping sheets into a film by simply changing the spin speed. Alternatively, the spin-coated materials can be transferred via a stamping technique.[19] Figure 4 shows that chemically converted graphene can be transferred onto a glass substrate and then removed after coming into close proximity with a polydimethylsiloxane (PDMS) stamp. The key to this successful transfer is the low molecular weight polymer at the interface of the PDMS, which helps pull the graphene sheets away from the substrate. After the stamp is "inked", the graphene can be placed onto any desired surface. Alternatively, a stenciling technique enables graphene to be patterned more rapidly with higher resolution, Figure 5.[20] The stenciling process is effective because PDMS is hydrophobic; therefore, wherever PDMS is applied, the hydrazine dispersed graphene will not stick.

FIGURE 9. Synthesis of either single or bilayer graphene using ethane as the feedstock. Changing the system pressure, and thus the concentration of carbon in the reactor, at any given period of time provides selectivity over growth conditions.
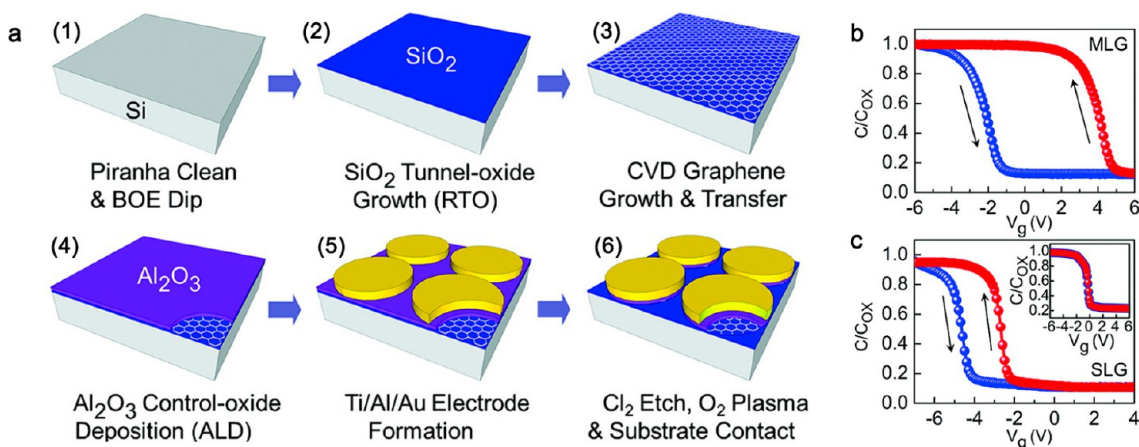
FIGURE 10. Graphene flash memory. (a) Schematic of graphene flash memory fabrication and the figure of merit, the memory window showing that (b) multilayer GFM has a 6 V memory window and (c) single layer GFM has a 2 V memory window using a program/erase voltage of ±7 V. Figure reprinted with permission from ref 23. Copyright 2011 American Chemical Society.
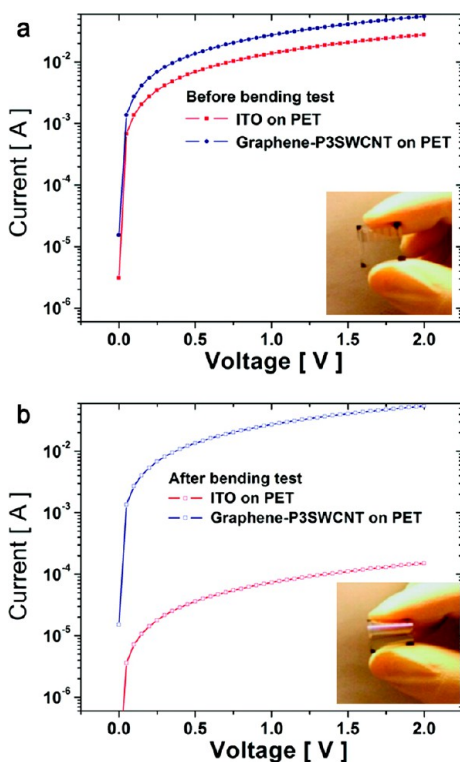

FIGURE 11. Electrical measurements comparing the sheet resistances of a G-CNT film versus an ITO films (a) before and (b) after bending at a 60° angle, 10 times. The ITO resistance increases 3 orders of magnitude, while the resistance of the G-CNT hybrid electrode remains. Figure reprinted with permission from ref 18. Copyright 2009 American Chemical Society.

Since powerful reducing agents, like hydrazine, are generally corrosive and air sensitive, we explored another method to scale up CCG via a simple one-step solvothermal reduction in *N*-methyl-2-pyrrolidinone (NMP).[13] This process utilizes a high boiling point solvent and the fact that GO will

TABLE 1. Optical and Electronic Properties of G-CNT Composite Films before and after Thionyl Chloride Treatment

G-CNT sample	optical transmittance	sheet resistance	peak Raman intensity
untreated	82%	425 Ω/□	1593 cm^{-1}
SOCl$_2$ doped	82%	103 Ω/□	1600 cm^{-1}

begin deoxygenating at 200 °C. In addition, these dispersions can be filtered and dried into papers and redispersed into an array of other polar organic solvents as can be seen in Figure 6.

Using a simple camera flash, we and Prof. Jiaxing Huang's group at Northwestern found that graphene oxide will spontaneously deoxygenate into a conductive form of graphene.[21] This process is enhanced with graphene oxide foams prepared through freeze-drying of bulk GO; see Figure 7. The properties of graphene that make this possible are high light absorption, high surface area, and high thermal conductivity. Thus, the flash of light is converted to heat, leading to ignition and deoxygenation.

This photothermal reduction/deoxygenation process can be fine-tuned using an inexpensive laser available in an optical disk drive, known as a LightScribe.[12] Using the available Lightscribe software, graphene can be readily patterned with micrometer resolution.[12] Figure 8 shows an illustration of graphene oxide deoxygenated with a laser to produce high-fidelity CCG patterns on plastic (PET-polyethylene terephthalate) substrates.

Bottom-Up Synthesis. While there have been many breakthroughs with chemically converted graphene, one shortcoming has been the inability to produce highly crystalline graphene. Chemical vapor deposition (CVD) of graphene
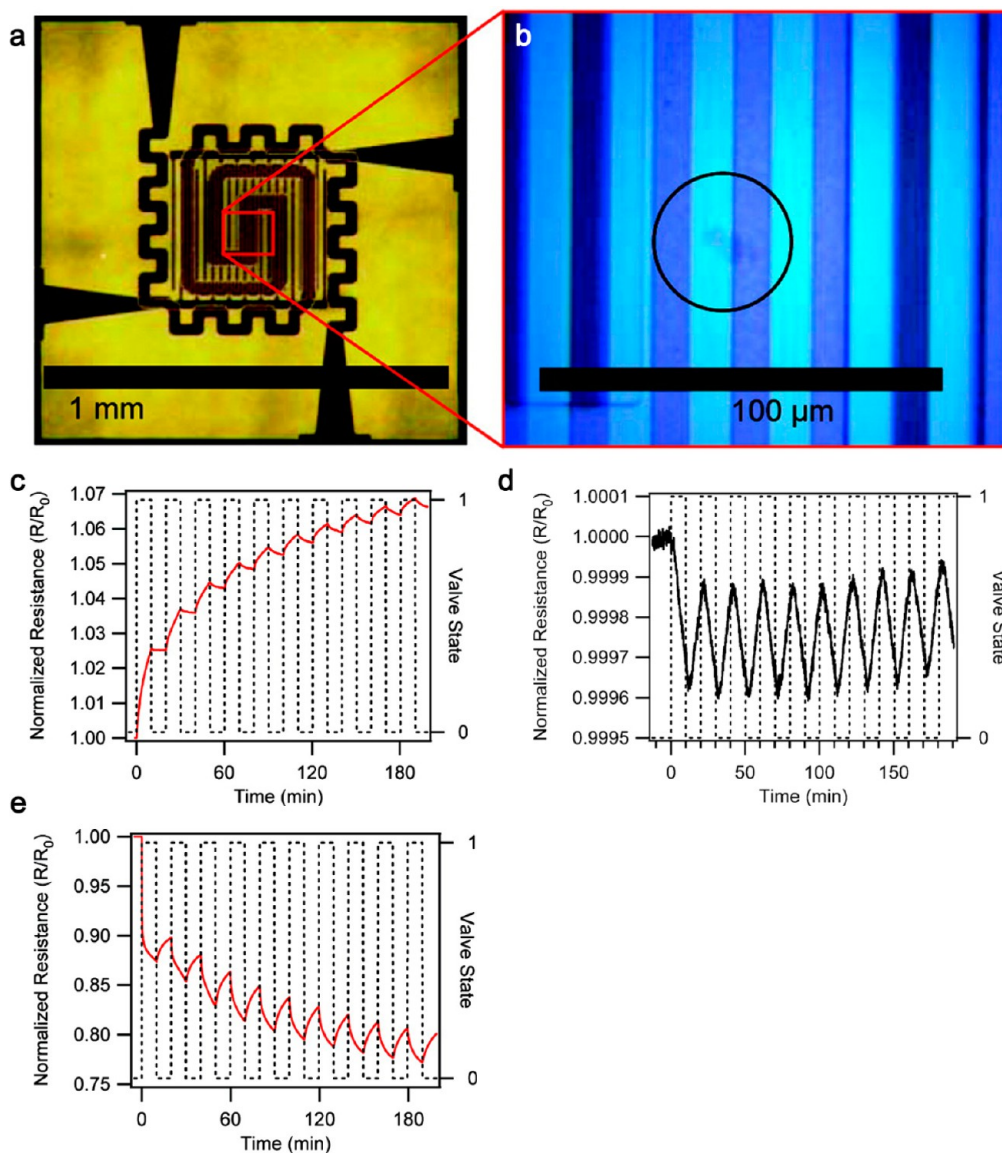
FIGURE 12. Chemical sensor using graphene as an active layer. (a) A simple interdigitated electrode with CCG, (b) on a micro-hotplate, can detect several gases: (c) NH_3, (d) 2,4-dinitrotoluene, and (e) NO. Figure reprinted with permission from ref 27. Copyright 2009 American Chemical Society.

on metallic catalysts from gaseous hydrocarbons, such as methane, ethane, and propane, was used to study the effects of different sized hydrocarbons and to understand their role in the growth of graphene.[8] We found that not only were the graphene domains continuous over various facets of the copper,[22] but single and bilayer graphene could be grown selectively by simply changing the precursor to the more carbon rich precursor ethane and controlling the pressure.[8] Figure 9 shows that ethane as a precursor gas can be used to grow either single or bilayer graphene by simply changing the concentration, that is, the carbon-content, in the reactor for a given period of time.

Applications

Initially, graphene was lauded as a replacement for silicon in electronics, potentially enabling scientists to engineer smaller and faster circuits. While electronic applications may be important, many other applications have emerged and it seems likely that graphene will provide a cornerstone for some new and exciting technologies as described here briefly.

Recent achievements in graphene research have fallen mainly into two categories. First, applications have been developed that rely on the intrinsic in-plane properties of graphene, such as new types of circuitry, robust films, and

photonic absorption. Second, applications requiring conductive thin films have benefited from graphene as a single atomic layer. Growing graphene via chemical vapor deposition provides scientists access to large area and highly crystalline material. With this in mind, in collaboration with Prof. Kang Wang's group, we explored using graphene for information storage, that is, graphene flash memory (GFM), which utilizes graphene's high surface area, high work function, and low dimensionality.[23] Our devices demonstrated that GFM has a 6 V memory window and using a program/erase voltage of ±7 V, long retention time, and low cell-to-cell interference. The figure of merit from our work can be seen in Figure 10. Our results indicate that the device performance of GFM is promising for achieving flash memory at a fraction of the current operating voltage.

An advantage that chemically converted graphene has over other synthetic routes is the enhanced processability afforded by the additional functional groups. For example, in collaboration with Prof. Yang Yang's group, we found that hydrazine-reduced graphene when combined with carbon nanotubes has the potential to be used as a transparent conducting alternative to indium tin oxide (ITO).[18,24,25] Different concentrations of graphene can be applied to a desired substrate by changing the loading concentration of an aqueous dispersion and/or by altering the spin speed. In addition to their transparency, the graphene films are very flexible and retain high conductivity after bending tests, while ITO films fracture and become quite resistive (Figure 11). We have also explored vapor-phase, ionic doping with thionyl chloride to increase the number of p-type charge carriers and reduce the sheet resistance without degrading the optical properties (see Table 1).[26] This doping process is successful because graphene possesses an interesting chemical duality: it can react with either electron donating or electron withdrawing groups and form either covalent or ionic bonds. While covalent bonds interrupt the delocalized sp^2 network, ionic bonds simply interact with it. Thionyl chloride decomposes into chlorine anions, which effectively chlorinate oxygen-containing graphene through a dehydration mechanism.[26] Additionally, some chlorine anions will adsorb onto the basal plane of graphene to enhance the p-type behavior of the graphitic system.

Graphene is very sensitive to its chemical environment such that single molecular adsorption events can be detected under vacuum when either electron withdrawing or donating species lead to a change in the local carrier concentration and effectively p- or n-type dope the graphene.[27] However, since both p- and n-doping of pristine graphene
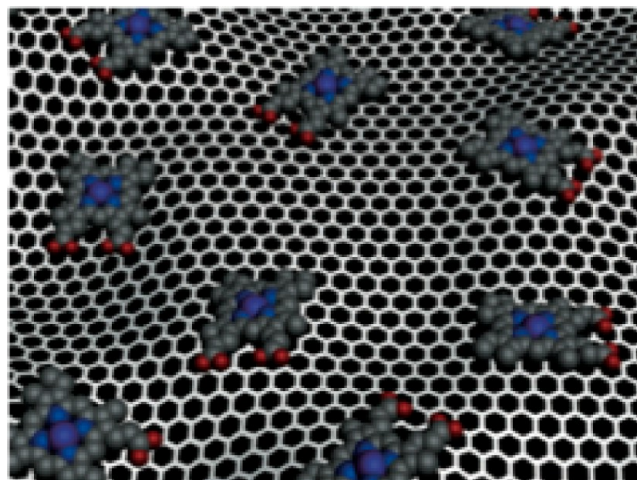

FIGURE 13. Artistic rendering of the formation of hemin—graphene conjugates through $\pi-\pi$ stacking. Figure reprinted with permission from ref 29. Copyright 2012 Wiley-VCH.

increases its conductivity, it is not really an effective and practical chemical sensor.[27] However, coating large sheets of chemically converted graphene on interdigitated electrode arrays can lead to more practical chemical sensors as we demonstrated in collaboration with Dr. Bruce Weiller at Aerospace Corp.[27] Figure 12 shows an optical image of the interdigitated electrode and the sensor response curves. The sensor response is consistent with a charge transfer mechanism between the CCG and the analyte. Since the CCG is partly oxidized, electron withdrawing species such as NO_2 further increase the number of charge carriers and hence the conductivity, while electron donating species such as NH_3 decrease the number of charge carriers and the conductivity. Thus CCG makes detection of molecular species simpler than when using pristine graphite. In fact, species such as 2,4-dinitrotoluene, the volatile component in TNT (trinitrotoluene), can be readily detected at the part per billion level. To monitor the effects of other potential harmful gases, such as carbon monoxide, we deposited CCG sheets onto surface acoustic wave (SAW) transducers made from lithium tantalate ($LiTaO_3$).[28]

Graphene is also of interest in areas of biology, medicine, and bioengineering because it can be considered to be a biologically compatible material. A biocompatible material consists of two elements, biosafety (absence of negative responses) and biofunctionality (ability to perform a designed task). Since graphene meets these two requirements, it can be studied as a scaffold for drug delivery.[5]

Artificial enzymes are synthetic, organic molecules that mimic the activity of their naturally occurring counterparts. One of the major challenges for chemists has been to produce

a synthetic equivalent that has both high substrate selectivity and catalytic activity. Hemin, an iron-containing porphyrin, can behave as the catalytic center for many proteins in a variety of oxidation reactions, similar to the peroxidase enzyme. However, the utilization of hemin has been hampered due to inevitable molecular aggregation in aqueous media, which renders it inactive. In collaboration with Prof. Xiangfeng Duan and Prof. Yue Wang, we recently demonstrated that graphene can act as a large-area molecular scaffold to support the porphyrin structure via $\pi-\pi$ interactions.[29] Figure 13 shows an artistic rendering of a graphene supported hemin structure that exhibits enzymatic activity.

Diffusive thermal transport is a reason why some materials cannot dissipate heat effectively. In an extreme case, graphene oxide (GO) will collect so much heat that it will eventually reach a high enough temperature to reduce itself. Distributive ignition in rockets has been achieved through the use of relatively heavy liquid propellants.[21] We show in Figure 7 the rapid change in GO foams before and after an almost instantaneous and highly exothermic flash reduction process. This demonstrates that graphene oxide foams can

potentially store enough energy for distributed ignition processes and offers a lightweight and effective alternative.[21]

With conventional energy sources peaking, the demand for renewable energy and energy efficient technology is on the rise. Many researchers have explored the potential of graphene and CCG as materials of choice for high energy density applications due to its high-surface area and its intrinsically high conductivity. The graphitic material produced via GIC precursors led to an array of applications. For example, composite reinforcements, gas sensors, and high surface area anodes in electrochemical cells.[14,30] On the other hand, the laser-scribed graphene creates a three-dimensional structure with many active sites from which energy transfer can occur. These new derivatives of graphene have shown remarkably large charge capacitance values, while maintaining high conductivity (Figure 14).[31] The exceptional electrochemical performance of graphene-based supercapacitors can be attributed to reversible charge storage within the available high surface area. Graphene may also find use in improving battery electrodes, especially since carbon is an earth abundant material.
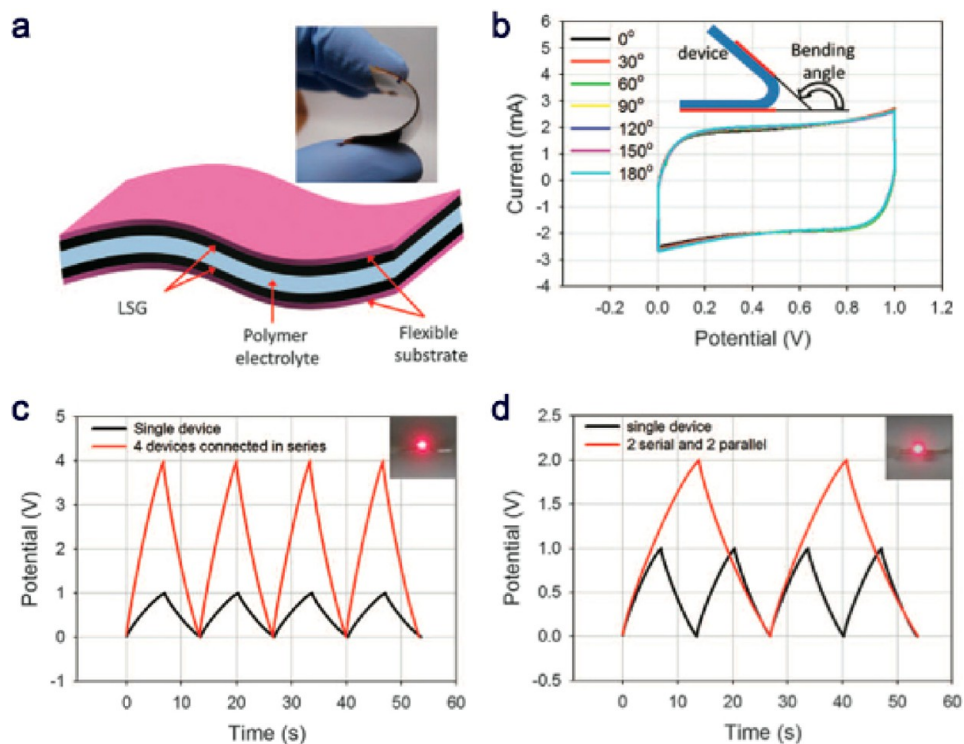

FIGURE 14. Design and fabrication of a flexible, all-solid-state laser scribed graphene electrochemical capacitor. (a) A schematic diagram illustrates that the gelled electrolyte can serve as both the electrolyte and separator, with an inset photograph demonstrating the flexibility and the (b) bending tests show no change in performance, as seen in these CVs collected at a scan rate of 1000 mV/s. (c) Galvanostatic charge/discharge curves for four tandem ECs connected in series, and (d) a combination of series and parallel devices. The inset shows a glowing LED when powered by tandem cells. The serial connection extends the output voltage to 4 V (versus 1 V for a single device), whereas the output voltage and current can both be doubled with the serial-parallel connection. Figure reprinted with permission from ref 31. Copyright 2012 AAAS.

In this Account, we have highlighted several interesting synthetic routes to graphene that we have helped develop including intercalation/exfoliation, chemical reduction with hydrazine and other organic reagents, chemical vapor deposition, and laser scribed graphene. Potential applications include practical chemical sensors, memory storage devices, transparent conductors, distributed ignition, and supercapacitors. While a plethora of properties and potential applications have already been discovered, there is likely new phenomena and applications on the horizon. While graphene research is no longer in its infancy, the effort devoted to its study will likely pay off in the near future.

BIOGRAPHICAL INFORMATION

Jonathan K. Wassei is a graduate student in the Kaner laboratory at UCLA. He received his B.S. in Chemistry from UC Davis, where he studied lightweight clathrates for their thermoelectric behavior. Before joining the Kaner lab, he worked on the development of a retinal prosthesis at Lawrence Livermore National Laboratory.

Richard B. Kaner received a Ph.D. in inorganic chemistry from the University of Pennsylvania in 1984. After carrying out postdoctoral research at UC Berkeley, he joined UCLA in 1987 as an Assistant Professor, earned tenure in 1991, became a Full Professor in 1993 and was given the title Distinguished Professor in 2012. Professor Kaner is a Fellow of the Materials Research Society and the American Association for the Advancement of Science. He has received awards from the Dreyfus, Fulbright, Guggenheim, Packard and Sloan Foundations, as well as the Exxon Fellowship in Solid State Chemistry, the Tolman Medal and the Award for the Chemistry of Materials from the American Chemical Society for his work on refractory materials, including new synthetic routes to ceramics, superhard metals, conducting polymers, and nanostructured carbon.

FOOTNOTES

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