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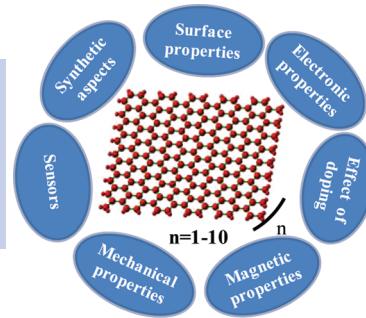
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Some Novel Attributes of Graphene

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ABSTRACT Graphene has generated great sensation due to its amazing properties, and extensive research is being pursued on single- as well as bi- and few-layer graphenes. In this Perspective, we highlight some aspects of graphene synthesis, surface, magnetic, and mechanical properties, as well as effects of doping and indicate a few useful directions for future research.



Graphene, the mother of all graphitic materials, has emerged to become an exciting two-dimensional material with wondrous properties.^{1–4} Some of the significant properties include ballistic electron transport, anomalous integer quantum Hall effect at room temperature and fractional quantum Hall effect at low temperatures, and the ability to sustain very high current densities. Atomic and electronic structures of graphene have been investigated by employing a variety of microscopic, spectroscopic, and other techniques. Direct imaging of individual carbon atoms in single-layer graphene by aberration-corrected transmission electron microscopy has shown the formation and annealing of Stone–Wales defects.⁵ Studies of graphene are not limited to one-atom-thick single-layer graphene alone but also include bi- and few-layer (< 10 layers) graphenes. There have been a few reviews^{1–4} of graphene, and in this Perspective, we shall concern ourselves with the aspects of interest to us, which include synthesis and functionalization, effects of doping by various means, as well as magnetic, mechanical, and a few other properties. Raman spectroscopy has been indispensable in investigating doping effects and related aspects.

Changes in graphene brought about by molecular charge transfer should be explored for applications.

Synthetic Aspects. A large majority of the studies of graphene have been directed toward synthesis (Chart 1). Since micromechanical cleavage of HOPG was first employed to obtain single-layer graphene (SG), various methods including epitaxial growth on an insulator surface such as SiC and chemical vapor deposition (CVD) on surfaces of transition metals such as Ni and Cu have been employed.^{3,6} We find that graphene layers can be grown on

different transition-metal substrates by decomposing a variety of hydrocarbons such as methane, ethylene, acetylene, and benzene with the number of layers varying with the hydrocarbon and reaction parameters. Hydrazine reduction of single-layer graphene oxide seems to be an effective means of obtaining a dispersion of SG in solvents such as DMF. Many of the above methods are, however, not suitable to make large quantities of graphene samples. Bi- and few-layer graphenes can be obtained by different chemical procedures, such as thermal exfoliation of graphite oxide, reduction of graphene oxide with reducing agents such as hydrazine under microwave irradiation, and microwave solvothermal treatment of graphene oxide.^{3,6} The most common method of preparing graphene samples seems to be through the reduction of graphene oxide.

There are a few studies directed toward the formation of carbon nanoscrolls (CNSs) from graphene. Because of the novel scroll topology, properties of CNSs differ from those of SWNTs and MWNTs. CNSs provide interlayer galleries that can be intercalated with donors and acceptors and may be of value in energy storage in supercapacitors or batteries, in addition to exhibiting novel electronic and optical properties as predicted.⁷ The scrolls can be prepared by ultrasonication of potassium intercalated graphite⁸ or by simply dipping the single-layer graphene deposited on a substrate in isopropyl alcohol.⁹ Developing an efficient approach to roll chemically derived graphene to CNSs would be worthwhile. Transformation of graphene oxide to carbon nanotubes and carbon nanoparticles is induced by ultrasconication under acidic conditions.¹⁰ In this one-pot transformation, two-dimensional sheets, susceptible to acid cutting, are decomposed into polyaromatics in concentrated acid in minutes. Polyaromatics are further reconstituted by acid dehydration reactions to form carbon nanoparticles and

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Chart 1

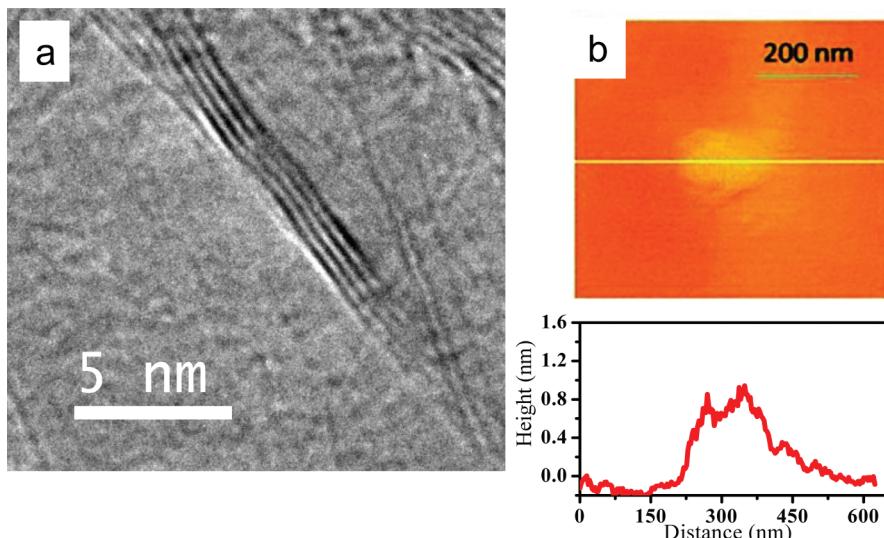
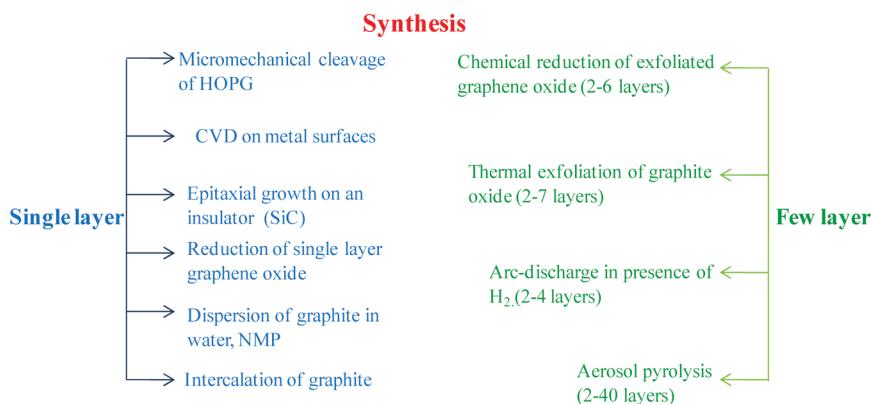


Figure 1. (a) TEM and (b) AFM images of graphene prepared by arc-discharge of graphite in a hydrogen atmosphere (From ref 11).

nanotubes. There is much to be done on such transformation as well as on CNSs.

Properties of nanoscrolls and edge effects on graphene need greater study.

We have explored a new method of preparing graphene containing 2–4 layers on a relatively large scale (Figure 1).¹¹ The procedure involves arc evaporation of graphite electrodes in a hydrogen atmosphere and makes use of the knowledge that the presence of H_2 during an arc-discharge process terminates the dangling carbon bonds with hydrogen and prevents the formation of closed structures. The conditions that are favorable for obtaining graphene are high current (above 100 A), high voltage (> 50 V), and high pressure of hydrogen (above 200 Torr). If the content of hydrogen in the

arc-discharge chamber is decreased, the relative proportion of closed-shell polyhedral particles increases, yielding only polyhedral graphitic particles at low H_2 pressures. An important aspect of the arc-discharge method is its use in doping graphene with boron and nitrogen. Boron- and nitrogen-doped graphene have been obtained by carrying out the discharge in the presence of $H_2 +$ diborane and $H_2 +$ (pyridine or ammonia), respectively.¹² The doping levels of boron and nitrogen are 1–3 and 0.6–1.0 wt %, respectively. Nitrogen doping of graphene is also achieved by electrothermal reaction, in which the doping occurs mostly at the edges.¹³ Despite the progress made in graphene synthesis, there is still need for methods which can yield pure and doped samples with the desired number of layers.

It often becomes necessary to prepare dispersions or solutions of graphene in organic or aqueous media. Different strategies have been employed to functionalize graphene for this purpose (see Chart 2).^{14,15} Covalent functionalization employs amidation with organic amines and interaction of organosilane and organotin reagents.¹⁵ Noncovalent functionalization¹⁵ is achieved by wrapping graphene with

Chart 2

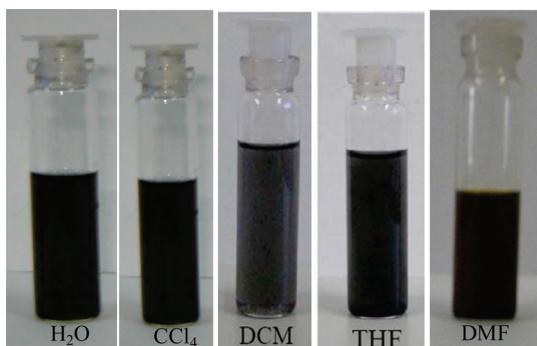
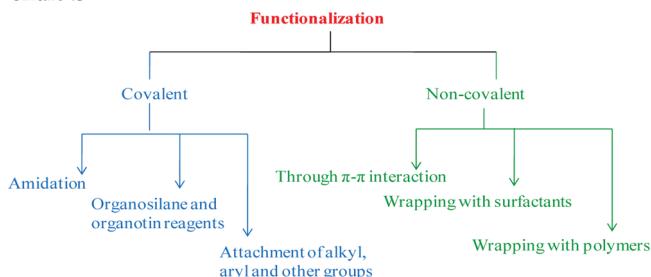


Figure 2. Photographs of the dispersions of functionalized graphene in different solvents.

surfactants such as poly(ethyleneglycol) (PEG), sodiumdodecylsulfate (SDS), polyoxyethylene nonylphenylether (IGP), and cetyltrimethylammoniumbromide (CTAB) or through $\pi-\pi$ interaction with aromatic molecules such as 1-pyrenebutanoic acid succinimidyl ester (I) and the potassium salt of coronene tetracarboxylic acid (II).¹⁶

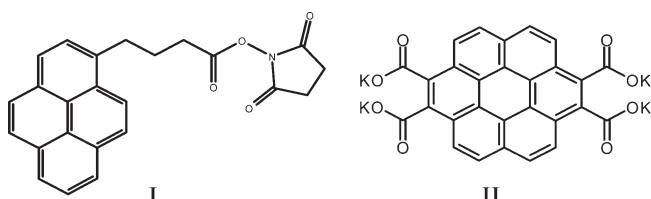


Figure 2 shows photographs of dispersions of few-layer graphenes in different solvents. Interaction of II with a large π network with few-layer graphene is found to selectively solubilize single- and double-layer graphenes through molecular charge-transfer interaction, thereby causing exfoliation.¹⁶

Surface Properties. Single-layer graphene is theoretically predicted to have a large surface area of $2600\text{ m}^2/\text{g}$. Studies have been carried out on the surface properties of few-layer graphene samples prepared by different methods. The BET surface area of these samples was found to be in the range of $270\text{--}1550\text{ m}^2/\text{g}$, some of them approaching the value of single-layer graphene (Figure 3a).¹⁷ We considered that these high-surface-area samples might enable storage of hydrogen. Hydrogen storage reaches 3 wt % at 100 bar and 300 K, and

the uptake varies linearly with the surface area (see inset of Figure 3a). Theoretical calculations show that SG can accommodate up to 7.7 wt % of hydrogen, while bi- and trilayer graphene can have an uptake of $\sim 2.7\%$. The H_2 molecule sits on the graphene surface in end-on and side-on fashion alternatively. CO_2 uptake of few-layer graphenes at 1 atm and 195 K is around 35 wt % (Figure 3b). Theoretical calculations show that SG can have a maximum uptake of 37.9 wt % of CO_2 . The CO_2 molecule sits alternatively in a parallel fashion on the rings.

Decoration of graphene with a variety of nanoparticles is an active aspect of graphene research. There are several reports on the decoration of graphene with metal nanoparticles such as Au, Pt, and Pd and different semiconducting nanoparticles.¹⁸ These composites might find applications in catalysis, optoelectronic devices, and energy conversion devices.

Electronic, Optical, and Related Properties. Electronic properties constitute the most investigated aspect of graphene. Single-layer graphene is a two-dimensional zero band gap semiconductor with a linear electronic dispersion relation of $H = v_F \vec{\sigma} \cdot \vec{P}$ near the K-point of the Brillouin zone, where v_F is the Fermi velocity. The electrons obey the Dirac equation rather than the Schrödinger equation, with zero effective mass. Here, $\vec{\sigma}$ is the Pauli matrix for the pseudospin representing the relative contributions of two sublattices A and B of the graphene to the electron wave function. A challenge is to manipulate the pseudospin,¹⁹ similar to the manipulation of real spin by a magnetic field. Theoretically, it has been argued that strain can manipulate pseudospin. It is expected that strain-engineering of graphene will lead to many interesting physical phenomena.²⁰

Right in the beginning of graphene research in 2004, the two-dimensional nature of the carriers with zero effective mass (i.e., relativistic character) was demonstrated by the quantum Hall plateau in magnetotransport measurements at $G_{xy} = \nu e^2/h$, with filling factor $\nu = 4(n + 1/2)$, where the factor 4 accounts for spin and valley degeneracy.^{21,22} The factor 1/2 in ν arising from the linear electronic dispersion, termed as the anomalous integer quantum Hall effect, can be understood in terms of the single-particle picture, without taking into account strong electron correlations. The latter is essential for observing the fractional quantum Hall effect (FQHE), which had eluded scientists so far due to extrinsic effects of the substrate on which graphene is transferred. FQHE has been observed recently in suspended graphene with $\nu = 1/3$, thereby revealing strong interactions and electron correlations.²³ This offers a challenge to look for other fractional filling factors like 2/5, relevant for observing anion statistics. Furthermore, the case of bilayer graphene, where electrons are massive Dirac Fermions, will be interesting for observing FQHE. The effect of electron correlations and interactions on the electron-transport mechanisms that limit the carrier mobility especially near the Dirac point are yet to be understood. Graphene nanoribbons with interesting morphologies and junctions offer many challenges to explore quantum size effects on transport, edge states, ballistic transport, spin-polarized currents, and nanoelectronic devices. Recent experiments on bilayer graphene demonstrate a gate-controlled

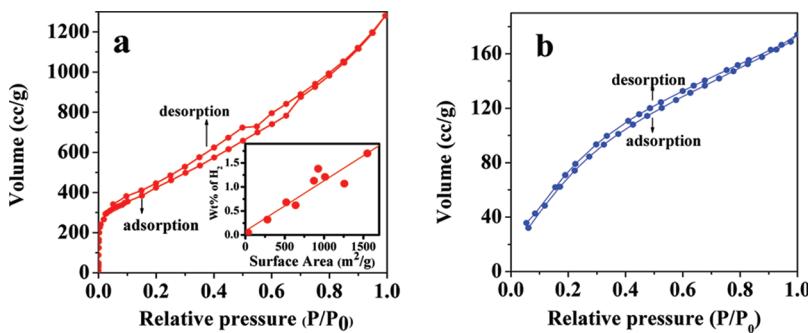


Figure 3. (a) Nitrogen adsorption and desorption isotherms of graphene at 1 atm and 77 K. (b) Adsorption and desorption isotherms of CO₂ at 1 atm and 195 K. The inset in (a) shows the linear relation between the BET surface area and the weight percentage of hydrogen uptake at 1 atm and 77 K. (From ref 17.)

continuously tunable band gap of up to 250 meV.²⁴ Combining the tunable band gap in bilayer graphene and the possibility of formation of a p–n junction along the graphene channel, it is proposed that the back and top gated bilayer can be a novel source of terahertz radiation, a possibility which is worth studying.²⁵

Theoretical predictions suggested extremely high carrier mobility and an ambipolar field effect in graphene. SG prepared by reduction of single-layer graphene oxide does indeed exhibit ambipolar behavior. A single layer of mechanically exfoliated graphene can show a carrier mobility in excess of 200 000 cm²/(V s).²⁶ Graphene sheets prepared from graphite oxide also show well-behaved field effect transistor (FET) properties. It is remarkable that field effect transistor properties are found even in the samples with defects. We have been examining FET devices that have been fabricated with a variety of bi- and few-layer graphenes as well as N- and B-doped samples.

Graphene substrates can suppress fluorescence by $\sim 10^3$ times, and this feature has been used to measure resonance Raman spectra of fluorescent molecules.²⁷ The quenching phenomenon can be utilized to visualize single-layer graphene by fluorescence microscopy.²⁸ Understanding the detailed mechanism of quenching of fluorescence in molecules by graphene needs to be examined. Fluorescent carbon nanoribbons, nanoparticles, and graphene from a graphite electrode have been obtained by making use of ionic liquid-assisted electrochemical exfoliation.²⁹ Oxygen plasma treatment also induces photoluminescence in single-layer graphene.³⁰ Intrinsic fluorescence of graphene oxide could be of use in drug delivery applications and in chemical sensors.

Effects of Doping and Molecular Interaction. Raman spectroscopy has emerged as the most powerful and convenient probe to characterize the graphene samples in terms of the number of layers and their quality.¹ Single-layer graphene shows the well-known G band at around 1580 cm⁻¹ and a band at around 1620 cm⁻¹ (D'). The D band at around 1350 cm⁻¹ is defect-induced and is not found in graphite. The 2D Raman band at ~ 2680 cm⁻¹ differs for single- and few-layer graphenes, which can be understood on the basis of the double resonance Raman process involving different electronic dispersions.³¹ The 2D band can be employed to determine the number of layers in few-layer graphene. By combining

Raman experiments with in situ transport measurements of graphene in field effect transistor geometry,³² it has been shown that the G-mode of monolayer and bilayer graphene blue shifts upon doping with electrons as well as holes, as shown in Figure 4a. On the other hand, the 2D band blue shifts upon hole doping, whereas it red shifts upon doping with electrons. Theoretical calculations based on time-dependent perturbation theory, as opposed to treating the phonons as a static perturbation in the Born–Oppenheimer approximation, along with the effect of doping on the lattice constant of graphene are able to explain quantitatively the experimentally observed phonon shifts of the G band. The comparison between them and experiment however is poor at high doping levels ($> 1 \times 10^{15}/\text{cm}^2$). The disagreement is even poorer for the 2D band, thereby pointing to our inadequate understanding of phonon renormalization in doped graphene. For the case of bilayer graphene,³³ the blue shift of the G band with doping has contributions from phonon-induced interband and intra-band electronic transitions, thereby giving an experimental measure of γ_1 , the overlap integral between A and B atoms in the two layers. Furthermore, the in-plane vibration in bilayer graphene splits into a symmetric Raman-active mode (E_g) and an antisymmetric infrared-active mode (E_u). The doping dependence of these modes has been studied by Raman scattering³⁴ and infrared reflectivity measurements.³⁵ The latter show a drastic enhancement of intensity and a softening of the mode as a function of doping, along with a Fano-like asymmetric line shape due to a strong coupling of the E_u mode to the interband transitions. It would be worthwhile to study the effect of doping on phonons in graphene nanoribbons, in particular, the edge phonons near 1427 (zigzag edge) and 1535 cm⁻¹ (arm-chair edge).³⁶

The electronic structure of carbon nanotubes is known to be sensitive to molecular charge transfer. The same is true of graphene. The G band softens progressively with the increasing concentration of aniline and tetrathiafulvalene (TTF), which are electron donors, while the band stiffens with increasing concentration of nitrobenzene and tetracyanoethylene (TCNE), which are electron-acceptor molecules (Figure 4b).^{37,38} Both electron donors and acceptors broaden the G band. The 2D-band position is also affected by interaction with electron donors and acceptors. The width of the G band increases upon interaction with these molecules.

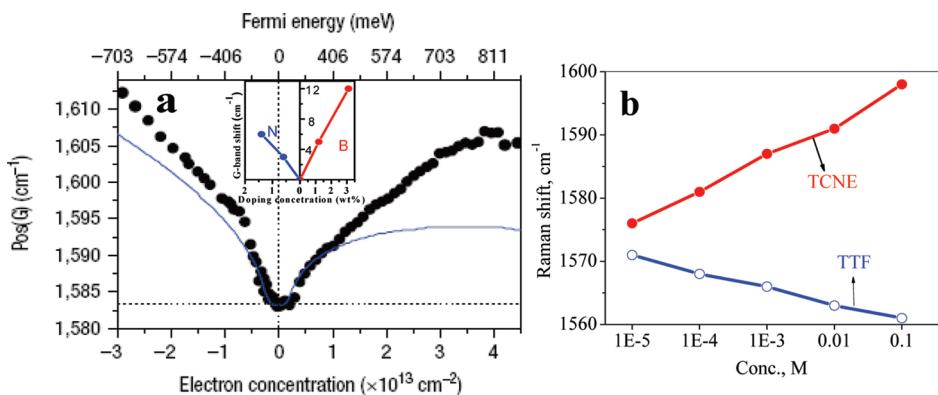


Figure 4. (a) Position of the Raman G band as a function of electron and hole doping (from ref 32). (b) Plot showing the variation in the Raman G band position of graphene upon interacting with varying concentrations of electron-donor (TTF) and electron-acceptor (TCNE) molecules (from ref 38). The inset in (a) shows shifts of the G band caused by nitrogen and boron doping (from ref 12).

The intensity of the 2D band decreases markedly with the concentration of either. The ratio of intensities of the 2D and G bands, $I(2D)/I(G)$, is a sensitive probe to examine the effect of the electron-donor and electron-acceptor molecules on the electronic structure of graphene. The remarkable changes in Raman spectra show how the electronic structure and phonons of graphene are markedly affected by the interaction with electron-donor and -acceptor molecules. Electrical resistivity of graphene varies in opposite directions upon interaction with electron-donors and -acceptor molecules. All of these effects occur due to molecular charge transfer, as evidenced by the observation of charge-transfer bands in the electronic absorption spectra. The magnitude of interaction between the different graphenes and donor/acceptor molecules is dependent on the surface area of the graphene samples. Isothermal titration calorimetry (ITC) interaction energies of graphene with electron-acceptor molecules are higher than those with electron-donor molecules.³⁹ DFT calculations confirm the occurrence of charge-transfer-induced changes in graphene giving rise to midgap molecular levels with tuning of the band gap region near the Dirac point and show how they are different from the effects of electrochemical doping. The shifts in the Raman-active modes of graphene upon molecular doping demonstrate the possible use of Raman spectroscopy to determine the nature and concentration of carriers in graphene with molecular doping.

Raman studies show that the G band stiffens in the case of both boron and nitrogen doping in comparison with the undoped sample (see inset of Figure 4a).¹² This is similar to what happens with electrochemical doping.³² Upon doping, the relative intensity of D increases, whereas 2D band decreases with respect to the G band. DFT calculations also have been carried out to understand the effect of substitutional doping on the structure of graphene as well as its electronic and vibrational properties.

It is interesting to compare the effect of doping induced by gating³² or chemical doping¹² with that caused by molecular charge transfer caused by the adsorption of electron-acceptor molecules like TCNE and electron-donor molecules like TTF³⁸ (see Figure 4). The G band is shifted to higher frequencies

when an electron-acceptor molecule is adsorbed on graphene, while it is shifted to lower frequencies when an electron-donor molecule is adsorbed. This is in contrast to the gate-induced or chemical doping, where the G band increases in frequency for both the electron and hole doping. The difference may partly be due to distortions caused by molecular charge transfer, and this aspect needs further study.

Graphene can be employed as a sensor to detect different gases such as NO_2 , NH_3 , and dinitrotoluene^{3,40} due to its highly sensitive electronic structure. Thick film sensors have been fabricated using few-layer graphene prepared by different methods.⁴¹ Graphene prepared by nanodiamond conversion shows the best sensitivity for NO_2 , although it does not have the highest surface area. It may be because the surface of nanodiamond-converted graphene is less functionalized compared with that obtained by thermal exfoliation of graphite oxide and/or that prepared by arc evaporation of graphite in hydrogen. N-doped graphene shows enhanced sensitivity for NO_2 since the latter is an electron-withdrawing molecule. HG prepared by arc-discharge in a H_2 atmosphere shows the best sensitivity for humidity. Since water is an electron-donor molecule, it appears that HG, which has no oxygen functional groups, shows the best sensing characteristics. It is interesting that the sensing characteristics of EG for aliphatic alcohols depend on the chain length and branching. Water-soluble graphene oxide can be used for the detection of DNA and proteins by quenching of fluorescence by graphene oxide.⁴² Interaction of graphene with DNA nucleobases and nucleosides has also been studied by employing ITC.⁴³ There is much to be done on the use of graphene as a biological sensor and for DNA hybridization.

Magnetic Properties. There has been considerable interest in the magnetism of nanographite particles for some time. Enoki et al.⁴⁴ pointed out that edge states as well as adsorbed or intercalated species play an important role in determining magnetic properties of these nanographite particles. Recently, magnetic properties of graphene samples prepared by exfoliation of graphite oxide, conversion of nanodiamond, arc evaporation of graphite, and partial chemical reduction of graphene oxide have been studied.^{45,46} All of these samples show the divergence between field-cooled (FC) and

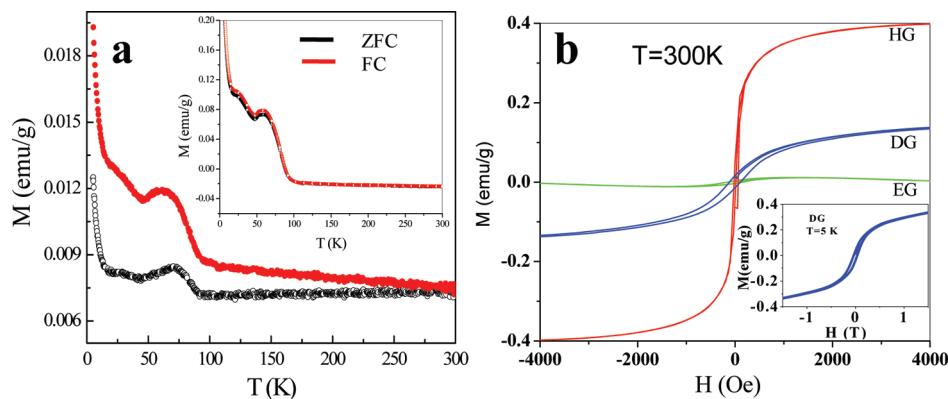


Figure 5. (a) Temperature variation of magnetization of exfoliated graphene at 500 Oe showing the ZFC and FC data. The inset shows the magnetization data at 1 T. (b) Magnetic hysteresis in different samples at 300 K. The inset shows magnetic hysteresis in DG at 5 K. (From ref 45.) (EG: by exfoliation of graphite oxide; DG: by conversion of nanodiamond; HG: by arc evaporation of graphite rod in the presence of H_2 .)

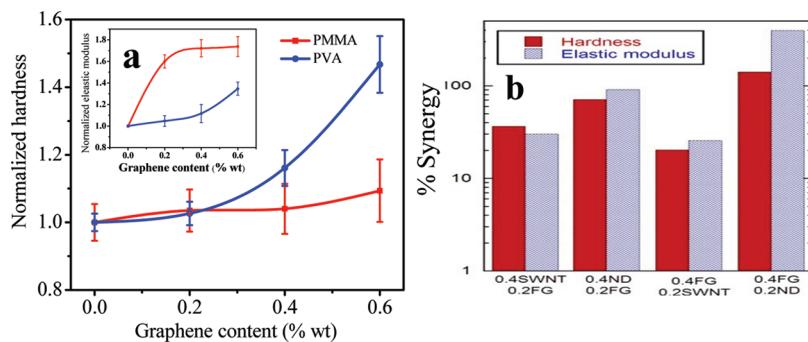


Figure 6. (a) Normalized hardness (H) plotted as a function of graphene content for PVA and PMMA composites. The inset shows the normalized elastic modulus (E) as a function of graphene content for PVA and PMMA (the pristine values of PMMA and PVA are $E_{PMMA} = 2.1$ GPa, $H_{PMMA} = 140$ MPa, $E_{PVA} = 0.65$ GPa, and $H_{PVA} = 38$ MPa) (from ref 47). (b) Percentage synergy in hardness and elastic modulus for composites with two nanocarbons (from ref 48).

zero-field-cooled (ZFC) data at 500 Oe (Figure 5a), and the divergence nearly disappears upon the application of 1 T, as can be seen from the inset of Figure 5a. All of the samples show magnetic hysteresis at room temperature (Figure 5b).⁴⁵ The possible influence of magnetic impurities has been excluded by EPR measurements. The graphene samples show Cuire–Weiss-type behavior with negative Weiss temperature. AC susceptibility data show the absence of spin-glass behavior. Magnetic properties of graphene reveal that dominant ferromagnetic interactions coexist along with antiferromagnetic interactions in all of the samples, somewhat like in frustrated or phase-separated systems. It is not possible to exactly pin down the origin of magnetism in the graphene samples, although defects and edge effects are likely to play a major role. The effect of molecular charge transfer on the magnetic properties of graphene has been examined by adsorption of TTF and TCNE. Adsorption of these molecules drastically decreases the magnetization values of graphene. The concentration-dependent effects of TTF and TCNE provide additional evidence, suggesting that the magnetism in the graphene samples is intrinsic. Although these studies establish the coexistence of antiferromagnetic and ferromagnetic interactions in graphene, there is need for careful studies required to delineate edge effects and layer-dependent aspects.

Mechanical Properties. Polymer composites of carbon nanotubes are well-known to exhibit high mechanical strength. Similar studies on graphene–polymer composites have shown promising mechanical properties. Recently, it has been shown that mechanical properties of polyvinyl alcohol and poly(methyl methacrylate) composites reinforced with small quantities of few-layer graphene (FG) lead to a significant increase in both elastic modulus and hardness (Figure 6a).⁴⁷ It is noteworthy that when graphene is incorporated along with another nanocarbon, such as single-walled carbon nanotubes (SWNT) and nanodiamond (ND) in polymer composites, the stiffness and hardness increase by as much as 400 % compared to those obtained with single nanocarbon reinforcements (Figure 6b).⁴⁸ This synergy is not due to crystallization. Further studies are to be pursued on the tensile strength and other mechanical properties of such composites. It would be of interest to examine properties of polymer composites incorporating two different nanocarbons which are covalently linked.

Controlled synthesis of graphene with the desired number of layers is still a challenge.

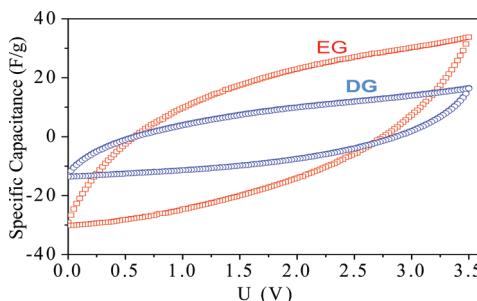


Figure 7. (a) Voltammetry characteristics of a capacitor built from graphene electrodes (5 mg each) at a scan rate of 100 mV/s using an ionic liquid (PYR14TFSI). (From ref 55.)

Graphene Analogues. Soon after fullerenes were discovered, their analogues formed by layered inorganic materials such as MoS₂ were prepared and characterized.⁴⁹ After the discovery of carbon nanotubes, nanotubes of inorganic materials such as MoS₂, BN, and TiO₂ were prepared and characterized.⁵⁰ It has been indicated that it should be possible to prepare analogues of graphene.⁵¹ It has been indeed shown recently that a new material of the composition BCN forms structures similar to few-layer graphene.⁵² This material exhibits a high surface area of around 2900 m²/g and adsorbs 100 wt % of CO₂. It should be indeed possible to develop chemical methods to prepare graphene analogues such as MoS₂, WS₂, and BN with a variable number of layers. Synthesis of these materials with a controlled number of layers would be a challenge.

There are many properties of graphene that may find potential applications. The use of chemically derived graphene as a transparent conductive electrode material has been investigated by many groups.⁴ Electrolyte-gated graphene FET has been employed for detecting pH and protein adsorptions.⁵³ The high Young's modulus, low density, and high surface area of graphene enable it to be a potential candidate for nanoelectrochemical systems (NEMs), and the radio frequency resonators fabricated from graphene films showed high quality factors up to 4000.⁵⁴ Graphene has been shown to be potential candidate as an electrode material. It shows high lithium storage capacity for lithium secondary batteries, and the capacity can be further extended by adding other nanocarbons such as CNTs and C₆₀.³ Studies of graphene as an electrode in supercapacitors have shown high specific capacitance in aqueous H₂SO₄, the value reaching up to 117 F/g.^{55,56} By using ionic liquid, the operating voltage has been extend to 3.5 V instead of 1 V in the case of aqueous H₂SO₄ (Figure 7). Recent imaging of ultralow-contrast objects such as individual hydrogen and carbon adatoms and carbon chains on graphene demonstrates the use of graphene as a membrane for TEM imaging, owing to its highly transparent, crystalline background.⁵⁷ It can also be employed as a impermeable membrane for gases.⁵⁸

Functionalization of graphene with different molecules is a powerful chemical route to tailor its properties. Thus, changes in properties brought about by molecular charge-transfer could be used for certain applications. Functionalization of monolayer graphene by hydrogen, yielding graphane, introduces a

gap in the electronic structure and alters the transport properties significantly.⁵⁹ It will be interesting to use other functional groups to tune the properties of graphene. Studies of graphene subjected to reduction by various chemical methods are being pursued. Properties of graphene nanoribbons obtained by the bottom-up chemical approach and the opening of nanotubes would be of interest, just as large-area films formed by the assembly of graphene sheets. It will be interesting to characterize and study the role of the edge states and defects in graphene synthesized by different routes by advanced microscopy and other tools and the effect of edge states on electronic and magnetic properties. It is important that toxicological effects of graphene be thoroughly examined before using.

Analogues of graphene formed by layered inorganic materials constitute a future direction.

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REFERENCES

- (1) Geim, A. K.; Novoselov, K. S. The Rise of Graphene. *Nat. Mater.* **2007**, *6*, 183–191.
- (2) Geim, A. K. Graphene: Status and Prospects. *Science* **2009**, *324*, 1530–1534.
- (3) Rao, C. N. R.; Sood, A. K.; Subrahmanyam, K. S.; Govindaraj, A. Graphene: The New Two-Dimensional Nanomaterial. *Angew. Chem., Int. Ed* **2009**, *48*, 7752–7777.
- (4) Allen, M. J.; Tung, V. C.; Kaner, R. B., Honeycomb Carbon: A Review of Graphene. *Chem. Rev.* **2009**, DOI: 10.1021/cr900070d.
- (5) Meyer, J. C.; Kisielowski, C.; Erni, R.; Rossell, M. D.; Crommie, M. F.; Zettl, A. Direct Imaging of Lattice Atoms and Topological Defects in Graphene Membranes. *Nano Lett.* **2008**, *8*, 3582–3586.
- (6) Park, S.; Ruoff, R. S. Chemical Methods For the Production of Graphenes. *Nat. Nanotechnol.* **2009**, *4*, 217–224.

- (7) Braga, S. F.; Coluci, V. R.; Legoa, S. B.; Giro, R.; Galvao, D. S.; Baughman, R. H. Structure and Dynamics of Carbon Nanoscrolls. *Nano Lett.* **2004**, *4*, 881–884.
- (8) Vrucilis, L. M.; Mack, J. J.; Kaner, R. B. A Chemical Route to Carbon Nanoscrolls. *Science* **2003**, *299*, 1361.
- (9) Xie, X.; Ju, L.; Feng, X.; Sun, Y.; Zhou, R.; Liu, K.; Fan, S.; Li, Q.; Jiang, K. Controlled Fabrication of High-Quality Carbon Nanoscrolls from Monolayer Graphene. *Nano Lett.* **2009**, *9*, 2565–2570.
- (10) Wang, S.; Tang, L. A. I.; Bao, Q.; Lin, M.; Deng, S.; Goh, B. M.; Loh, K. P. Room-Temperature Synthesis of Soluble Carbon Nanotubes by the Sonication of Graphene Oxide Nanosheets. *J. Am. Chem. Soc.* **2009**, *131*, 16832–16837.
- (11) Subrahmanyam, K. S.; Panchakarla, L. S.; Govindaraj, A.; Rao, C. N. R. Simple Method of Preparing Graphene Flakes by an Arc-Discharge Method. *J. Phys. Chem. C* **2009**, *113*, 4257–4259.
- (12) Panchakarla, L. S.; Subrahmanyam, K. S.; Saha, S. K.; Govindaraj, A.; Krishnamurthy, H. R.; Waghmare, U. V.; Rao, C. N. R. Synthesis, Structure, and Properties of Boron- and Nitrogen-Doped Graphene. *Adv. Mater.* **2009**, *21*, 4726–4730.
- (13) Wang, X.; Li, X.; Zhang, L.; Yoon, Y.; Weber, P. K.; Wang, H.; Guo, J.; Dai, H. N-Doping of Graphene Through Electrothermal Reactions with Ammonia. *Science* **2009**, *324*, 768–771.
- (14) Niyogi, S.; Bekyarova, E.; Itkis, M. E.; McWilliams, J. L.; Hamon, M. A.; Haddon, R. C. Solution Properties of Graphite and Graphene. *J. Am. Chem. Soc.* **2006**, *128*, 7720–7721.
- (15) Subrahmanyam, K. S.; Ghosh, A.; Gomathi, A.; Govindaraj, A.; Rao, C. N. R. Covalent and Noncovalent Functionalization and Solubilization of Graphene. *Nanosci. Nanotechnol. Lett.* **2009**, *1*, 28–31.
- (16) Ghosh, A.; Rao, K. V.; George, S. J.; Rao, C. N. R. Non-Covalent Functionalization, Exfoliation and Solubilization of Graphene in Water Employing a Fluorescent Coronene Carboxylate. *Chem.—Eur. J.* Accepted.
- (17) Ghosh, A.; Subrahmanyam, K. S.; Krishna, K. S.; Datta, S.; Govindaraj, A.; Pati, S. K.; Rao, C. N. R. Uptake of H₂ and CO₂ by Graphene. *J. Phys. Chem. C* **2008**, *112*, 15704–15707.
- (18) Kamat, P. V., Graphene-Based Nanoarchitectures. Anchoring Semiconductor and Metal Nanoparticles on a Two-Dimensional Carbon Support. *J. Phys. Chem. Lett.* **2010**, DOI: 10.1021/jz900265j.
- (19) Guinea, F.; Geim, A. K.; Kaltnelson, M. I.; Novoselov, K. S. Generating Quantizing Pseudomagnetic Fields by Bending Graphene Ribbons. 2009, arXiv:0910.5935v1.
- (20) Bao, W.; Miao, F.; Chen, Z.; Zhang, H.; Jang, W.; Dames, C.; Lau, C. N. Controlled Ripple Texturing of Suspended Graphene and Ultrathin Graphite Membranes. *Nat. Nanotechnol.* **2009**, *4*, 562–566.
- (21) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Katsnelson, M. I.; Grigorieva, I. V.; Dubonos, S. V.; Firsov, A. A. Two-Dimensional Gas of Massless Dirac Fermions in Graphene. *Nature* **2005**, *438*, 197–200.
- (22) Zhang, Y.; Tan, Y.-W.; Stormer, H. L.; Kim, P. Experimental Observation of the Quantum Hall Effect and Berry's Phase in Graphene. *Nature* **2005**, *438*, 201–204.
- (23) Du, X.; Skachko, I.; Duer, F.; Luican, A.; Andrei, E. Y. Fractional Quantum Hall Effect and Insulating Phase of Dirac Electrons in Graphene. *Nature* **2009**, *462*, 192–195.
- (24) Zhang, Y.; Tang, T.-T.; Girit, C.; Hao, Z.; Martin, M. C.; Zettl, A.; Crommie, M. F.; Shen, Y. R.; Wang, F. Direct Observation of a Widely Tunable Bandgap in Bilayer Graphene. *Nature* **2009**, *459*, 820–823.
- (25) Chakraborty, B.; Das, A.; Sood, A. K. The Formation of a p–n Junction in a Polymer Electrolyte Top-Gated Bilayer Graphene Transistor. *Nanotechnology* **2009**, *20*, 365203.
- (26) Bolotin, K. I.; Sikes, K. J.; Jiang, Z.; Klima, M.; Fudenberg, G.; Hone, J.; Kim, P.; Stormer, H. L. Ultrahigh Electron Mobility in Suspended Graphene. *Solid State Commun.* **2008**, *146*, 351–355.
- (27) Xie, L.; Ling, X.; Fang, Y.; Zhang, J.; Liu, Z. Graphene as a Substrate to Suppress Fluorescence in Resonance Raman Spectroscopy. *J. Am. Chem. Soc.* **2009**, *131*, 9890–9891.
- (28) Kim, J.; Cote, L. J.; Kim, F.; Huang, J. Visualizing Graphene Based Sheets by Fluorescence Quenching Microscopy. *J. Am. Chem. Soc.* **2009**, DOI: 10.1021/ja906730d.
- (29) Lu, J.; Yang, J.-x.; Wang, J.; Lim, A.; Wang, S.; Loh, K. P. One-Pot Synthesis of Fluorescent Carbon Nanoribbons, Nanoparticles, and Graphene by the Exfoliation of Graphite in Ionic Liquids. *ACS Nano* **2009**, *3*, 2367–2375.
- (30) Gokus, T.; Nair, R. R.; Bonetti, A.; Bohm, M.; Lombardo, A.; Novoselov, K. S.; Geim, A. K.; Ferrari, A. C.; Hartschuh, A. Making Graphene Luminescent by Oxygen Plasma Treatment. *ACS Nano* **2009**, *3*, 3963–3968.
- (31) Ferrari, A. C.; Meyer, J. C.; Scardaci, V.; Casiraghi, C.; Lazzeri, M.; Mauri, F.; Piscanec, S.; Jiang, D.; Novoselov, K. S.; Roth, S.; Geim, A. K. Raman Spectrum of Graphene and Graphene Layers. *Phys. Rev. Lett.* **2006**, *97*, 187401–4.
- (32) Das, A.; Pisana, S.; Chakraborty, B.; Piscanec, S.; Saha, S. K.; Waghmare, U. V.; Novoselov, K. S.; Krishnamurthy, H. R.; Geim, A. K.; Ferrari, A. C.; Sood, A. K. Monitoring Dopants by Raman Scattering in an Electrochemically Top-Gated Graphene Transistor. *Nat. Nanotechnol.* **2008**, *5*, 210–215.
- (33) Das, A.; Chakraborty, B.; Piscanec, S.; Pisana, S.; Sood, A. K.; Ferrari, A. C. Phonon Renormalization in Doped Bilayer Graphene. *Phys. Rev. B* **2009**, *79*, 155417–7.
- (34) Malard, L. M.; Elias, D. C.; Alves, E. S.; Pimenta, M. A. Observation of Distinct Electron-Phonon Couplings in Gated Bilayer Graphene. *Phys. Rev. Lett.* **2008**, *101*, 257401–4.
- (35) Kuzmenko, A. B.; Benfatto, L.; Cappelluti, E.; Crassee, I.; van der Marel, D.; Blake, P.; Novoselov, K. S.; Geim, A. K. Gate Tunable Infrared Phonon Anomalies in Bilayer Graphene. *Phys. Rev. Lett.* **2009**, *103*, 116804.
- (36) Zhou, J.; Dong, J. Vibrational Property and Raman Spectrum of Carbon Nanoribbon. *Appl. Phys. Lett.* **2007**, *91*, 173108–3.
- (37) Das, B.; Voggu, R.; Rout, C. S.; Rao, C. N. R. Changes in the Electronic Structure and Properties of Graphene Induced by Molecular Charge-Transfer. *Chem. Commun.* **2008**, *41*, 5155–5157.
- (38) Voggu, R.; Das, B.; Rout, C. S.; Rao, C. N. R. Effects of Charge Transfer Interaction of Graphene with Electron Donor and Acceptor Molecules Examined using Raman Spectroscopy and Cognate Techniques. *J. Phys.: Condens. Matter* **2008**, *20*, 472204.
- (39) Varghese, N.; Ghosh, A.; Voggu, R.; Ghosh, S.; Rao, C. N. R. Selectivity in the Interaction of Electron Donor and Acceptor Molecules with Graphene and Single-Walled Carbon Nanotubes. *J. Phys. Chem. C* **2009**, *113*, 16855–16859.
- (40) Schedin, F.; Geim, A. K.; Morozov, S. V.; Hill, E. W.; Blake, P.; Katsnelson, M. I.; Novoselov, K. S. Detection of Individual Gas Molecules Adsorbed on Graphene. *Nat. Mater.* **2007**, *6*, 652–655.
- (41) Ghosh, A.; Late, D. J.; Panchakarla, L. S.; Govindaraj, A.; Rao, C. N. R. NO₂ and Humidity Sensing Characteristics of Few-Layer Graphenes. *J. Exp. Nanosci.* **2009**, *4*, 313–322.
- (42) Chun-Hua, L.; Huang-Hao, Y.; Chun-Ling, Z.; Xi, C.; Guo-Nan, C. A Graphene Platform for Sensing Biomolecules. *Angew. Chem., Int. Ed.* **2009**, *48*, 4785–4787.

- (43) Varghese, N.; Mogera, U.; Govindaraj, A.; Das, A.; Maiti, P. K.; Sood, A. K.; Rao, C. N. R. Binding of DNA Nucleobases and Nucleosides with Graphene. *ChemPhysChem* **2009**, *10*, 206–210.
- (44) Enoki, T.; Kobayashi, Y. Magnetic Nanographite: an Approach to Molecular Magnetism. *J. Mater. Chem.* **2005**, *15*, 3999–4002.
- (45) Matte, H. S. S. R.; Subrahmanyam, K. S.; Rao, C. N. R. Novel Magnetic Properties of Graphene: Presence of Both Ferromagnetic and Antiferromagnetic Features and Other Aspects. *J. Phys. Chem. C* **2009**, *113*, 9982–9985.
- (46) Wang, Y.; Huang, Y.; Song, Y.; Zhang, X.; Ma, Y.; Liang, J.; Chen, Y. Room-Temperature Ferromagnetism of Graphene. *Nano Lett.* **2009**, *9*, 220–224.
- (47) Das, B.; Eswar Prasad, K.; Ramamurty, U.; Rao, C. N. R. Nano-Indentation Studies on Polymer Matrix Composites Reinforced by Few-Layer Graphene. *Nanotechnology* **2009**, *20*, 125705.
- (48) Prasad, K. E.; Das, B.; Maitra, U.; Ramamurty, U.; Rao, C. N. R. Extraordinary Synergy in the Mechanical Properties of Polymer Matrix Composites Reinforced with 2 Nanocarbons. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 13186–13189.
- (49) Tenne, R. Inorganic Nanotubes and Fullerene-Like Materials. *Chem.—Eur. J.* **2002**, *8*, 5296–5304.
- (50) Rao, C. N. R.; Govindaraj, A. Synthesis of Inorganic Nanotubes. *Adv. Mater.* **2009**, *21*, 4208–4233.
- (51) Novoselov, K. S.; Jiang, D.; Schedin, F.; Booth, T. J.; Khotkevich, V. V.; Morozov, S. V.; Geim, A. K. Two-Dimensional Atomic Crystals. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 10451–10453.
- (52) Raidongia, K.; Nag, A.; Hembram, K. P. S. S.; Waghmare, U. V.; Datta, R.; Rao, C. N. R. BCN: A Graphene Analogue with Remarkable Adsorptive Properties. *Chem.—Eur. J.* **2010**, *16*, 149–157.
- (53) Ohno, Y.; Maehashi, K.; Yamashiro, Y.; Matsumoto, K. Electrolyte-Gated Graphene Field-Effect Transistors for Detecting pH and Protein Adsorption. *Nano Lett.* **2009**, *9*, 3318–3322.
- (54) Robinson, J. T.; Zalalutdinov, M.; Baldwin, J. W.; Snow, E. S.; Wei, Z.; Sheehan, P.; Houston, B. H. Wafer-scale Reduced Graphene Oxide Films for Nanomechanical Devices. *Nano Lett.* **2008**, *8*, 3441–3445.
- (55) Vivekchand, S. R. C.; Rout, C. S.; Subrahmanyam, K. S.; Govindaraj, A.; Rao, C. N. R. Graphene-Based Electrochemical Supercapacitors. *J. Chem. Sci.* **2008**, *120*, 9–13.
- (56) Stoller, M. D.; Park, S.; Zhu, Y.; An, J.; Ruoff, R. S. Graphene-Based Ultracapacitors. *Nano Lett.* **2008**, *8*, 3498–3502.
- (57) Meyer, J. C.; Girit, C. O.; Crommie, M. F.; Zettl, A. Imaging and Dynamics of Light Atoms and Molecules on Graphene. *Nature* **2008**, *454*, 319–322.
- (58) Bunch, J. S.; Verbridge, S. S.; Alden, J. S.; van der Zande, A. M.; Parpia, J. M.; Craighead, H. G.; McEuen, P. L. Impermeable Atomic Membranes from Graphene Sheets. *Nano Lett.* **2008**, *8*, 2458–2462.
- (59) Elias, D. C.; Nair, R. R.; Mohiuddin, T. M. G.; Morozov, S. V.; Blake, P.; Halsall, M. P.; Ferrari, A. C.; Boukhvalov, D. W.; Katsnelson, M. I.; Geim, A. K.; Novoselov, K. S. Control of Graphene's Properties by Reversible Hydrogenation: Evidence for Graphane. *Science* **2009**, *325*, 610–613.