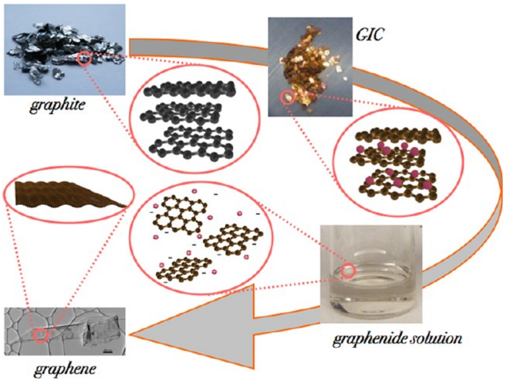
ACCOUNTS
of chemical research

Deconstructing Graphite: Graphenide Solutions

ALAIN PÉNICAUD* AND CARLOS DRUMMOND
CNRS, Centre de Recherche Paul Pascal (CRPP), UPR 8641, F-33600 Pessac, France, and Université de Bordeaux, CRPP, UPR 8641, F-33600 Pessac, France

RECEIVED ON MAY 9, 2012

CONSPECTUS



Growing interest in graphene over past few years has prompted researchers to find new routes for producing this material other than mechanical exfoliation or growth from silicon carbide. Chemical vapor deposition on metallic substrates now allows researchers to produce continuous graphene films over large areas. In parallel, researchers will need liquid, large scale, formulations of graphene to produce functional graphene materials that take advantage of graphene's mechanical, electrical, and barrier properties.

In this Account, we describe methods for creating graphene solutions from graphite. Graphite provides a cheap source of carbon, but graphite is insoluble. With extensive sonication, it can be dispersed in organic solvents or water with adequate additives. Nevertheless, this process usually creates cracks and defects in the graphite. On the other hand, graphite intercalation compounds (GICs) provide a means to dissolve rather than disperse graphite. GICS can be obtained through the reaction of alkali metals with graphite. These compounds are a source of graphenide salts and also serve as an excellent electronic model of graphene due to the decoupling between graphene layers. The graphenide macroions, negatively charged graphene sheets, form supple two-dimensional polyelectrolytes that spontaneously dissolve in some organic solvents. The entropic gain from the dissolution of counterions and the increased degrees of freedom of graphene in solution drives this process. Notably, we can obtain graphenide solutions in easily processable solvents with low boiling points such as tetrahydrofuran or cyclopentylmethylether. We performed a statistical analysis of high resolution transmission electronic micrographs of graphene sheets deposited on grids from GICs solution to show that the dissolved material has been fully exfoliated. The thickness distribution peaks with single layers and includes a few double- or triple-layer objects. Light scattering analysis of the solutions shows the presence of two-dimensional objects. The typical size of the dissolved flakes can be determined by either static or dynamic light scattering (DLS) using models available in the literature for disk-shape objects. A mean lateral size of ca. 1 μm is typically observed. We also used DLS to monitor the reaggregation that occurs as these sensitive solutions are exposed to air.

The graphenide solutions reported in this Account can be used to deposit random arrays of graphene flakes and large single flakes of a lateral size of tens of micrometers onto different substrates. Using the graphenide solutions described in this Account, we foresee the large-scale production of graphene-based printings, coatings, and composites.

Introduction

In order to gain insight into somewhat intricate philosophical concepts, the 20th century philosopher Jacques Derrida proposed *deconstruction* as a way to unravel the fundamental conceptual units behind them.[1] In much the same way, by thinning down a chunk of graphite close to a single constitutive layer, that is, graphene, it has been posssible to unravel the fundamental properties of this paradigmatic two-dimensionnal material.[2] Since then, there has been a great deal of effort to obtain graphene in large quantities. Several reviews have covered graphene obtention in the past few years.[3−7] From a materials perspective, the review by Dujardin et al. is particularly relevant.[8]

Conceptually, the most straightforward route is to obtain graphene from graphite. This is what is done in the repeated peeling process known as mechanical exfoliation.[2] In much the same way, one should be able to use chemistry to peel down a piece of graphite. However, chemical processes aim at obtaining not a few graphene flakes from a macroscopic graphite sample but *deconstructing* that sample into *all* its

Published on the Web 10/25/2012 www.pubs.acs.org/accounts
10.1021/ar300141s

constitutive graphene flakes. In order to perform the full exfoliation of all the individual (graphene) layers, the process has to be done in a liquid in order to stabilize the individual flakes. We will come back to this point. The core problem is to overcome the large $\pi-\pi$ extended interactions between the constitutive layers of a piece of graphite, and dissolve (or disperse?) large pieces of material (from a molecular point of view), of several micrometers in lateral size if not more. These two problems are related. It is by being able to actually dissolve (rather than disperse) graphene flakes, that is, reduce the free energy of the system in the process, that the adhesive interaction between graphene layers can be truly overcome (vide infra).

Liquid Formulations of Graphene

Intense research efforts have been directed toward obtaining liquid formulations of graphene. The graphite oxide route represents the largest share of the available literature:[3] graphite is oxidized to a water dispersible oxygen-rich species with fully exfoliated layers. These graphite oxide layers can then be reduced to what's been called reduced graphene oxide (RGO) with restored sp^2 carbon network, albeit with still a significant oxygen fraction of several atomic percent. A variety of attempts have been made at dispersing neutral pristine graphite. These include dispersions in organic solvents,[9−15] aqueous dispersions stabilized by surfactants,[16] π stacking pyrenic acid,[17] hydrophobins,[18] long alkyl amines,[19] polyvinylpyrrolidone,[20] and superacid formulations.[21] This list is not exhaustive, and new papers are continuously appearing. Shih et al. have modeled the dispersion of graphene in organic solvents showing that the best graphene solvents are *N*-methylpyrrolidone (NMP), dimethyl sulfoxide (DMSO) and dimethylformamide (DMF). However, after 3 months of storage, only about 5% of the dispersed material was composed of graphene and double layer flakes.[11]

Dissolve or Disperse?

In a solution, a (molecular) solute is surrounded by solvent molecules.[22] A dispersion on the other hand consists of finely dividing a solid into the smallest possible particules in a solvent in order to increase the importance of Brownian motion and counterbalance, at least for a certain amount of time, aggregation. Reducing solute−solvent interfacial energy by adding a surfactant increases the stability of the dispersion. However, the resulting dispersion is still metastable and the system will eventually return to the biphasic state

Graphite and carbon nanotubes dispersions have been prepared in water with surfactant molecules to lower surface energy.[16−20,23] Another way of getting carbon nanotubes or graphite into a liquid is by choosing a solvent with more affinity for graphitic surface than water.[24−29] The resulting enthalpic penalty of replacing graphitic surface self-interaction by solvent−surface interaction is lowered and dispersions with reasonable metastability can be obtained. For aqueous and organic solvent based dispersions, high shear mixing or sonication is usually required. This has a drawback: carbon nanotubes or graphene sheets are cut into smaller pieces, reducing the particle anisometry. This has been well documented[30,31] and even used to control final particle size.[32] The interested reader is referred to the review of Cravotto and Cintas about the interaction of sound waves and graphene.[33] Although the deleterious anisometry reduction can be diminished by using lower sonicating power and longer times (up to weeks), the metastability is an inherent characteristic of carbon nanotubes or graphene dispersions in water or most organic solvents.

Carbon nanotubes and graphene are macromolecular objects, difficult to dissolve. What seems like a formidable challenge for a material scientist might seem trivial to a polymer scientist, used to soluble polymers. A common class of soluble macromolecules are polyelectrolytes, that is, polymers bearing electrical charges. Indeed, a rigid inorganic polyelectrolyte $Mo_6Se_6^{2-}$ had been shown to be soluble in polar solvents back in 1985[34] and was the inspiration behind our mild solubilization of carbon nanotubes alkali metal salts[35] in 2005.[36] This has been recently formalized in a study of the solubility of reduced (negatively charged) nanotubes as a function of their charge. It was shown that the free energy of mixing an alkali metal salt of nanotubes and DMSO is negative up to ca. 0.5% volume fraction. Hence, the resulting system is a true solution in the thermodynamic sense.[37]

Graphite Intercalation Compounds

Unlike carbon nanotube salts,[38] graphite intercalation compounds (GICs) have been there forever, or so it seems. GICs exist in different stages, identified by *n*, the number of graphene layers between two consecutive intercalant layers. Hence, stage 1 compounds are the most doped GICs with the maximum amount of charge per carbon atom (1/8 for KC_8) and only one layer of graphene between two intercalant layers. GICs were the subject of intense research in the 1970s and 1980s as synthetic metals, and have recently gained renewed interest both due to the discovery

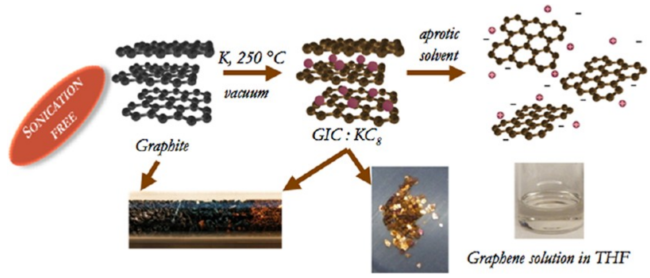


FIGURE 1. Schematics of graphite liquid deconstruction via GICs dissolution.

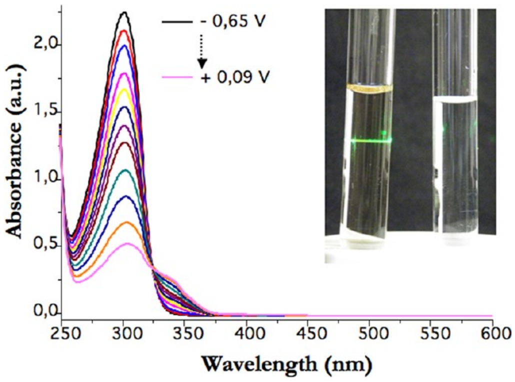


FIGURE 2. Absorption spectra of an NMP solution of negatively charged graphene flakes from KC_8 dissolved in NMP. Black: starting solution. All other spectra were recorded while raising the electrochemical potential of the solution to less negative potentials. The intensity of the 300 nm peak could be fitted using the Nernst equation and yielded a reduction potential of $+22$ mV vs SCE for graphene. Inset: The graphene solution scatters light from a laser beam, indicating the presence of particles of colloidal size (Tyndall effect), whereas the same laser is invisible through the pure solvent. Images and legend adapted from ref 47.

of a superconductor with a relatively high critical temperature of 11.5 K[39] and because of the graphene activity. Reviews[40] and textbooks[41] about GICs abound. GICs are important in relation with graphene for at least two aspects. They provide a readily exfoliable material (vide infra) and they constitute a model system for the electronic properties of doped graphene, because the graphene layers are electronically decorrelated, as has been recognized by Pichler et al.[42,43]

Dissolution of Graphite Intercalation Compounds

In GICs, the graphene layers are effectively separated and the $\pi-\pi$ interactions between them have been replaced by electrostatic interactions.[38] The trick is then to dissolve those two-dimensional anions, much the same way carbon nanotube salts had been dissolved. Exposing $K(THF)C_{24}$, a stage 1 compound[44] where THF is tetrahydrofuran, to NMP leads to spontaneous dissolution (Figure 1), and, after mild centrifugation to remove nonsolubilized material, very weakly absorbing solutions of up to 0.15 mg/mL of dissolved material are obtained.[45] To simplify the system, we turned our attention to the paradigmatic GIC KC_8:[46] KC_8 is synthetized by reacting potassium and graphite at 250 °C, in an evacuated glass tube.[46,47] No other reactant is involved in the synthesis. KC_8 was found to be soluble in NMP, up to 0.7 mg/mL, leading to fully transparent (in the visible) solutions if rigorously dry NMP is used (Figure 2).[47]

GICs have long been used to exfoliate graphite. Expanded graphite, an industrial brand of graphite, is obtained by suddenly exposing an intercalated graphite[48] to temperatures of ca. 1000 °C. The volatilization of the intercalants violently expands the graphene layers, resulting in a 200 fold gain in volume. Along its *c* axis, expanded graphite has between 1 and 100 layers per domain. These characteristics do not appear to be very different from what has been referred as "graphene by the ton".[49] Thus, the liquid exfoliation described here should be seen as a mild variation of this long-known temperature driven GICs exfoliating capabilities. However, this liquid exfoliation leads to fully exfoliated graphene flakes (vide infra), which is not the case of expanded graphite.[50] There's a price to pay for this sonication-free, graphene dissolution method: The GICs and the resulting solutions of graphene salts are strong reducing agents, similarly to the carbon nanotube salts solutions[51] and must be handled under strict inert atmosphere conditions. In passing, by controlled oxidation of these solutions of fully exfoliated (vide infra) reduced graphene flakes, spectroelectrochemical analysis allowed to determine the reduction potential of graphene ($E_{red} = +22$ mV vs SCE, Figure 2).[47] Converted in energy units (-4.7 eV), this result is quite close to the experimental work function of undoped graphene of -4.57 eV.[52]

Other groups have aimed at graphene liquid formulations by a GIC route.[53-59] Most interesting is the pre-2004 literature. Besides Kaner et al.'s preparation of nanoscrolls by sonicating KC_8 in ethanol,[60] Shioyama, as early as 2001, reported the *cleavage of graphite to graphene* by a simple and elegant polymerization of isoprene within KC_8.[61]

Nomenclature: Graphenide Solutions

It did not take long after the discovery of fullerenes to name the $C_{60}{}^{n-}$ ions fullerides,[62] the same way chloride means a chlorine atom with a negative charge. Although nanotubes salts have been around since 1997 (see review in ref 38), it was not until very recently that Shaffer et al. named them

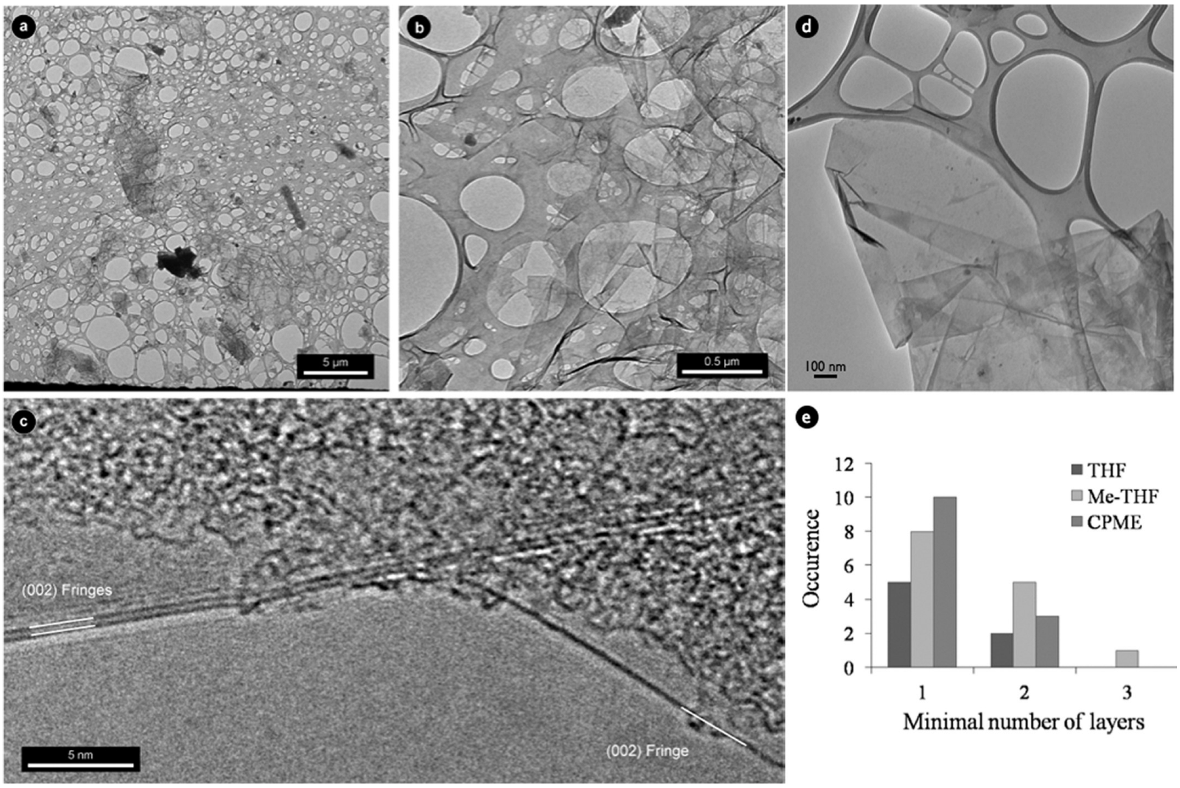


FIGURE 3. TEM analysis of graphene flakes deposited from the solutions described in this Account. (a) Low-magnification TEM image showing a number of graphene flakes. Very little unexfoliated material remains after centrifugation and several crumpled flakes of several micrometers are present. (b) Higher magnification TEM image showing in more detail one of the multiple folded flakes on the holey carbon film. (c) High-resolution TEM image of folded mono- and bilayer borders, where lattice fringes from (002) graphite are highlighted. (d) Low resolution image showing multiple folding of a flake. Images (a–c) are from THF solutions, image (d) from NMP solution. (e) Results of the analysis of the thickness of the membranes. The histogram shows the occurrence of the minimal border thickness measured at the folded borders for the three solvents indicated (THF, Me-THF, CPME). Images and legend adapted from ref 65.

nanotubides.[63] This 12-year delay compared to fullerides has probably to do with (un)aesthetic wording. At the time of writing of this Account, R. Hauke, J. Englert, J. Malig (from or linked to A. Hirsch's group[64]), M. Shaffer, and one of us (A.P.) were all attending ChemOnTubes'2012 Conference in Arcachon, France and it was agreed to call those negatively charged graphene sheets graphenides. Hence, dissolution of GICs gives graphenide solutions.

Graphenide Solutions in Low Boiling Point Solvents

NMP has long been recognized as an efficient solvent for graphitic material,[25,26,28] but it has two drawbacks: (i) its boiling point is high, 202 °C so it is difficult to remove; (ii) it has recently been classified as CMR 1B reagent, that is, a reagent suspected of carcinogenic activity. Thus, substitute solvents, if possible of low boiling point, are needed. NMP solutions containing up to 0.7 mg/mL dissolved material are transparent to the naked eye, although a laser shone through them would reveal the presence of particles that scatter light (see Figure 2). That means that the naked eye is not a good detector to judge the solubility of KC_8 in a given solvent. It was found by TEM analysis that KC_8 is soluble in THF, Me-tetrahydrofurane (Me-THF) and cyclopentylmethylether (CPME).[65]

It is noteworthy that graphenide salts are found to be soluble in THF and other low boiling point ethers which fail to solubilize CNT salts. A qualitative rationale may be proposed for that, in terms of the larger number of degrees of freedom of graphene in solution compared to carbon nanotubes (vide infra).

Soluble All-Carbon 1D and 2D Polyelectrolytes

At constant temperature and pressure, a spontaneous process involves the reduction of the Gibbs free energy ($\Delta G < 0$). For the case of mixing (e.g., dissolving), two energy terms are relevant. The first is related to the entropy of mixing (ΔS_{mix}), which always acts in favor of dissolution. The second term (ΔH_{mix}) measures the enthalpy change during the mixing process (the solvent–solute interaction compared with solvent–solvent and solute–solute interactions); it can be favorable or not. Thus, the question of whether the mixing will be spontaneous will be determined by the combination of both terms: $\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}$.

The process of dissolving small molecules entails large ΔS_{mix}: the solute molecules have a larger number of accessible states in solution; the entropy of mixing of large objects (per unit mass) is less significant. For example, ΔS_{mix} of a polymer is largely reduced compared with free monomers: the chemical bonds between the segments reduce the number of accessible states upon dissolution. For this reason, when ΔH_{mix} is unfavorable, polymers are usually less soluble than ordinary liquids of similar chemical nature. The scenario is different for the case of charged macromolecules (polyelectrolytes). The favorable entropic contribution due to the release of the small counterions is largely responsible for their enhanced solubility in solvents of high dielectric constant.

Similar considerations can be used to understand the behavior in solution of reduced CNTs or GICs. As we have recently shown,[37] the solubility of reduced CNTs can be well-described by a simple thermodynamic model including the favorable entropic contributions of counterions and dispersed CNTs (ΔS_{mix}) and the unfavorable ΔH_{mix}. ΔH_{mix} can be estimated from the CNT–solvent interfacial energy, which is proportional to the external area of the CNTs. Analogously, solubility of GICs is determined by the balance between the enthalpic term (resulting from the cohesive energy of the GIC lost upon solvation and the solvation energy of both potassium counterions and charged graphene flakes) and the entropic term concerning counterions and undulating graphenide plates.[47] As a consequence of the intercalation, the distance between the graphite layers is increased (and the interplane interaction energy is greatly reduced) compared with the case of graphite. The cohesive energy of GICs is then dominated by their Madelung energy. Several points deserve further consideration.

In both cases (CNTs or GICs), counterion condensation needs to be considered, as it may substantially reduce their contribution to ΔS_{mix}. This process results from the balance between the entropy loss due to immobilization of the counterions, which drives dissociation, and the electrostatic attraction between the ions and the charged species, which drives counterion association. We have recently shown that a simple model of ion condensation properly describes the solubility of CNTs.[37]

CNTs can be likened to stiff polymers, with a persistence length between 30 and 170 μm,[66] that is, large compared to their length. This stiffness largely diminishes the contribution to ΔS_{mix} of individualized CNTs. The case of graphene may be different. Finite temperature induces thermal fluctuations of the flakes at different length scales, increasing their configurational entropy. This fluctuations increase ΔS_{mix}, favoring dissolution. Although the presence of the charges on the graphenide plate will probably augment its rigidity (the problem of the effect of ionic distribution and electrostatic forces on membrane shape is extremely complex), TEM/AFM images evidence that graphene can indeed be twisted, rolled, and crumpled (Figure 3b and d), suggesting a much shorter persistence length than for CNTs. Thus, the entropic contribution of graphene flakes upon dissolution is much larger than the one of CNTs, allowing dissolution of GICs in a larger variety of solvents than CNT salts. In addition, undulations have a stabilizing role due to the steric repulsion of entropic origin between individual graphenides. This aspect is the subject of further research in our group.

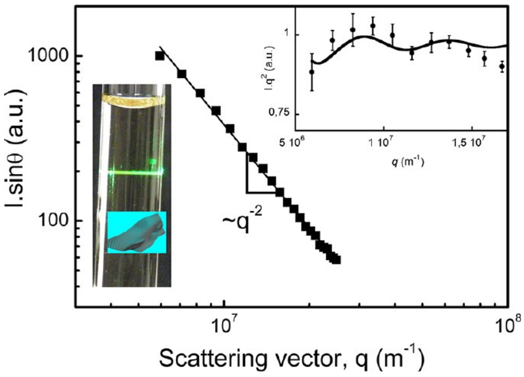


FIGURE 4. Static light scattering intensity *I* (corrected by the variation of scattering volume) versus angle of scattering θ for a THF–graphene solution. The square power-law decay of the intensity is a sign of the presence of large flat species in solution. Inset: variation of Iq^2 with wave-vector q. The nonmonotonic behavior of the intensity of scattering can be used to estimate the mean particle size. The solid line corresponds to a crude estimate of *I* for disk-size particles of 660 nm, which closely matches more precise results from DLS measurements. Inset: a THF graphenide solution with an artist's view of a graphene sheet. (Image and legend adapted from ref 65.)

The Exfoliation Issue

How exfoliated is the dissolved material? It would certainly be a great advantage to have at hand a method to analyze the dissolved material in situ. As we will see below, we are now able to analyze dimensionnality and lateral size in solution.[65] Milner et al. have recently demonstrated full exfoliation of GICs in ammonia by neutron scattering.[59] Degree of exfoliation has been measured by counting number of fringes in HRTEM.[65,67] Let us summarize the whole process: (i) A certain amount of graphite is reacted

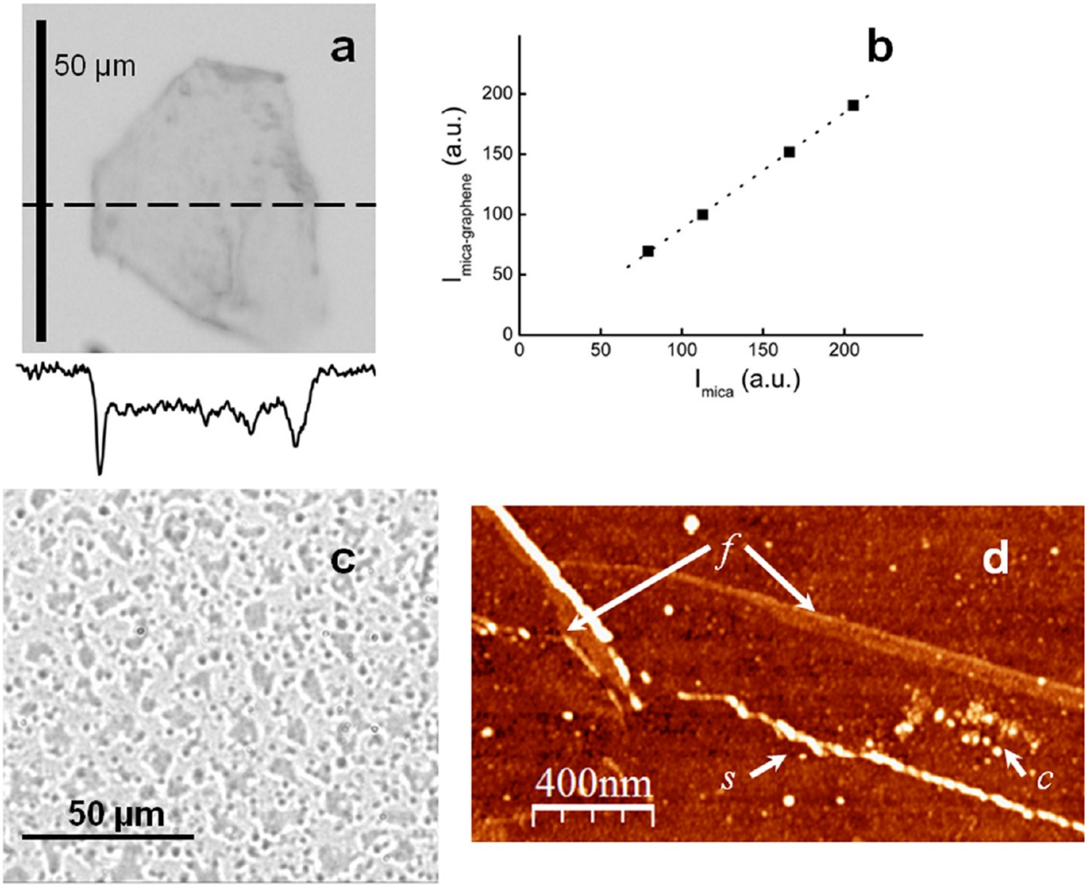


FIGURE 5. Deposits from graphene solutions. (a) Optical microscopy image of a large graphene flake deposited on mica by dip-coating. The lower graph shows the transmitted light intensity profile corresponding to the dashed line. The darker zones in the edge of the flake suggest local rolling up. (b) Measurements of the difference of light transmitted inside and outside the graphene piece in (a) can be used to estimate the thickness of the deposited flake (2–3 layers in the shown example). (c) Optical microscopy image of mica coated with graphene flakes by spin coating from a THF solution. The contrast is enhanced to allow easy visualization of the deposited graphene flakes. The thickness and composition of deposited films can be easily controlled using this technique. (d) AFM image of mica coated by dip-coating. Flat (f), crumpled (c), and swirling (s) pieces are observed. The thickness of the flat pieces can be determined by AFM; single layer graphene is regularly observed.

with a stoechometric quantity of potassium to give KC_8. (ii) A few milligrams of KC_8 are exposed, under inert atmosphere, to a few milliliters of solvent and left stirring for a few days. (iii) Mild centrifugation is performed and the supernatant kept. (iv) Dry extract of the supernatant allows one to measure concentration. Up to 0.8 mg/mL of dissolved material is obtained for a starting weight of 2 mg KC_8/mL. (v) A few drops of the solution are then deposited on a TEM grid and rinsed under ambient air with water, acetone, and isopropanol.

In images such as those of Figure 3,[65] none or very few large aggregates can be observed, in agreement with the fact that the solution is clear and presents no detectable particles. The grids are covered with very thin, weakly contrasting folded sheets of similar opacity. The ubuquitous folding of graphene can be used for counting the number of layers: under the electron beam, a folded edge appears as a darker wall, very much like CNT walls. Every time a flake folds, one is able to count the number of fringes and, hence, the number of folded layers. Reality is more complex, and multiple folding (i.e., in various places) is the rule in our observations (Figure 3). By close examination of the edges of one object and finding the minimum number of fringes observed in a local folding, it is possible to determine the thickness of a flake. Thickness distribution statistics have been obtained for solutions of KC_8 in different solvents: NMP,[67] THF, Me-THF, and CPME[65] (Figure 3e). None of the flakes were observed to have more than three layers. The distribution is highly peaked toward single layers, although only a small number of flakes have been analyzed, due to the time-consuming counting procedure. In view of the fundamentally different nature of GICs dissolution compared to graphite dispersions (vide supra), this result is not surprising. The liquid exfoliation described in this Account is based on the negative free energy of mixing between GICs and the solvent.[47] Contrary to metastable dispersions, this spontaneous exfoliation has no reason to stop before reaching the ultimate exfoliation stage, that is, graphene.

Probing Graphene Solutions

Reliable high-throughput methods of characterization of the dissolved material are necessary for particular applications. The scattering of light by graphene species in solution mentioned before can be used for this purpose, as static (SLS) and dynamic light scattering (DLS) are well established and easy to use tools. In a typical DLS experiment, the diffusion coefficient D of dissolved particles is derived from the autocorrelation function of the intensity of scattering. The size of the particles in solution is then calculated from D. Customarily used data analysis strategies, which consider small scatterers, must be avoided for the case of graphene solutions because the typical flake size is of the order of visible light wavelength. Fortunately, the scattering of light by large disk-shaped particles, determined by two characteristic diffusion coefficients (translational and rotational), has been thoroughly described in the literature.[68] This treatment can be applied for accurate determination of dissolved graphene lateral size, to assess the quality and long-term stability of the solutions. Similarly, SLS can be used to readily determine the mean size of graphene flakes in solution, as illustrated in Figure 4.[65] On the contrary, it is impossible to evaluate the thickness of dissolved graphene by using scattering of visible light. A rough estimate of the graphene thickness could be obtained by using radiation of much smaller wavelength (e.g., small-angle neutron scattering). However, graphene flakes in solution will not adopt a flat configuration: thermally induced fluctuating ripples will be present at finite temperatures. More precise determination of graphene thickness can be obtained ex-situ, for example, by HRTEM (as described before), or by characterization of deposits using AFM or optical microscopy.

Deposits

Graphene deposits and coatings can be readily obtained from these thermodynamically stable solutions by spin coating, solvent casting, electrophoresis, dip coating, inkjet printing, or spray coating. Some examples are presented in Figure 5.

Concluding Remarks

Central in this Account are the *solutions* of graphene salts. By providing the scientific and industrial communities with well-defined graphene solutions, their use will become possible. This includes (i) composites, either for mechanical or electrical properties, much like carbon nanotubes, but also antioxydant coatings, due to the two-dimensionnal nature of graphene, (ii) cheap, transparent conducting films, (iii) high surface area materials and coatings, and (iv) structured deposits. Certainly, a lot of questions remain to be answered, with one of the most interesting ones in our view being finding an in situ probe for graphene in a liquid or matrix.

Most of the experimental work described here has been performed by Dr. C. Vallés, Dr. A. Catheline, and Dr. D. Voiry, in collaboration with the group of Prof. F. Paolucci from the University of Bologna (in particular, Dr. M. Marcaccio, Dr. M. Iurlo, Dr. G. Valenti, and Dr. S. Rapino) and with Dr. L. Ortolani and Dr. V. Morandi (CNR, Bologna). Dr. M. Monthioux (CEMES, Toulouse) and Dr. C. Furtado (CDTN, Belo Horizonte) as well as Prof. M. Pimenta, Dr. A. Righi, and Dr. C. Fantini are also gratefully acknowledged as well as all the researchers and students from the "carbon nanotubes and graphene" team at CRPP. Support from the Agence Nationale de la Recherche (TRICOTRA and GRAAL Projects) is acknowledged. This work has been performed within the framework of the GDR-I 3217 "graphene and nanotubes".

BIOGRAPHICAL INFORMATION

Alain Pénicaud obtained his Ph.D. form the University of Rennes in 1988. After spending two years at the University of Southern California, he has worked, first in Mexico (UNAM, then CINVESTAV) then in Bordeaux, using redox chemistry to crystallize soluble fullerenes or to dissolve novel carbon nanoforms.

Carlos Drummond received his Ph.D. from the University of California, Santa Barbara (1999), and has been a CNRS research fellow since 2003. His research interests include Surface Forces, Nanotribology, and Responsive Functional Surfaces.

FOOTNOTES

*To whom correspondence should be addressed. E-mail: penicaud@crpp-bordeaux.cnrs.fr.
The authors declare no competing financial interest.

REFERENCES

1 Dekens, O. *Derrida, pas à pas*; Ellipses: Paris, 2008 (in French).

2 Novoselov, K. S.; Geim, a K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. Electric field effect in atomically thin carbon films. *Science* **2004**, *306*, 666–669.

3 Park, S.; Ruoff, R. S. Chemical methods for the production of graphenes. *Nat. Nanotechnol.* **2009**, *4*, 217–224.

4 Allen, M. J.; Tung, V. C.; Kaner, R. B. Honeycomb carbon: a review of graphene. *Chem. Rev.* **2010**, *110*, 132–145.

5 Gengler, R. Y. N.; Spyrou, K.; Rudolf, P. A roadmap to high quality chemically prepared graphene. *J. Phys. D: Appl. Phys.* **2010**, *43*, 374015.

6 Tkachev, S. V.; Buslaeva, E. Y.; Gubin, S. P. Graphene: A novel carbon nanomaterial. *Inorg. Mater.* **2010**, *47*, 1–10.

7 Cui, X.; Zhang, C.; Hao, R.; Hou, Y. Liquid-phase exfoliation, functionalization and applications of graphene. *Nanoscale* **2011**, *3*, 2118–2126.

8 Soldano, C.; Mahmood, A.; Dujardin, E. Production, properties and potential of graphene. *Carbon* **2010**, *48*, 2127–2150.

9 Blake, P.; Brimicombe, P. D.; Nair, R. R.; Booth, T. J.; Jiang, D.; Schedin, F.; Ponomarenko, L. A.; Morozov, S. V.; Gleeson, H. F.; Hill, E. W.; Geim, A. K.; Novoselov, K. S. Graphene-based liquid crystal device. *Nano Lett.* **2008**, *8*, 1704–1708.

10 Hernandez, Y.; Nicolosi, V.; Lotya, M.; Blighe, F. M.; Sun, Z.; De, S.; McGovern, I. T.; Holland, B.; Byrne, M.; Gun'Ko, Y. K.; Boland, J. J.; Niraj, P.; Duesberg, G.; Krishnamurthy, S.; Goodhue, R.; Hutchison, J.; Scardaci, V.; Ferrari, A. C.; Coleman, J. N. High-yield production of graphene by liquid-phase exfoliation of graphite. *Nat. Nanotechnol.* **2008**, *3*, 563–568.

11 Shih, C.-J.; Lin, S.; Strano, M. S.; Blankschtein, D. Understanding the Stabilization of Liquid-Phase-Exfoliated Graphene in Polar Solvents: Molecular Dynamics Simulations and Kinetic Theory of Colloid Aggregation. *J. Am. Chem. Soc.* **2010**, *13*, 14638–14648.

12 Qian, W.; Hao, R.; Hou, Y.; Tian, Y.; Shen, C.; Gao, H.; Liang, X. Solvothermal-assisted exfoliation process to produce graphene with high yield and high quality. *Nano Res.* **2009**, *2*, 706–712.

13 Malik, S.; Vijayaraghavan, A.; Erni, R.; Ariga, K.; Khalakhan, I.; Hill, J. P. High purity graphenes prepared by a chemical intercalation method. *Nanoscale* **2010**, *2*, 2139–2143.

14 Bourlinos, A. B.; Georgakilas, V.; Zboril, R.; Steriotis, T. a; Stubos, A. K. Liquid-phase exfoliation of graphite towards solubilized graphenes. *Small* **2009**, *5*, 1841–1845.

15 Geng, J.; Kong, B.-S.; Yang, S. B.; Jung, H.-T. Preparation of graphene relying on porphyrin exfoliation of graphite. *Chem. commun.* **2010**, *46*, 5091–5093.

16 Lotya, M.; Hernandez, Y.; King, P. J.; Smith, R. J.; Nicolosi, V.; Karlsson, L. S.; Blighe, F. M.; De, S.; Wang, Z.; McGovern, I. T.; Duesberg, G. S.; Coleman, J. N. Liquid phase production of graphene by exfoliation of graphite in surfactant/water solutions. *J. Am. Chem. Soc.* **2009**, *131*, 3611–3620.

17 An, X.; Simmons, T.; Shah, R.; Wolfe, C.; Lewis, K. M.; Washington, M.; Nayak, S. K.; Talapatra, S.; Kar, S. Stable aqueous dispersions of noncovalently functionalized graphene from graphite and their multifunctional high-performance applications. *Nano Lett.* **2010**, *10*, 4295–301.

18 Laaksonen, P.; Kainlauri, M.; Laaksonen, T.; Shchepetov, A.; Jiang, H.; Ahopelto, J.; Linder, M. B. Interfacial engineering by proteins: exfoliation and functionalization of graphene by hydrophobins. *Angew. Chem., Int. Ed.* **2010**, *49*, 4946–4949.

19 Zheng, J.; Di, C.-an; Liu, Y.; Liu, H.; Guo, Y.; Du, C.; Wu, T.; Yu, G.; Zhu, D. High quality graphene with large flakes exfoliated by oleyl amine. *Chem. Commun.* **2010**, *46*, 5728–5730.

20 Bourlinos, A. B.; Georgakilas, V.; Zboril, R.; Steriotis, T. a.; Stubos, A. K.; Trapalis, C. Aqueous-phase exfoliation of graphite in the presence of polyvinylpyrrolidone for the production of water-soluble graphenes. *Solid State Commun.* **2009**, *149*, 2172–2176.

21 Behabtu, N.; Lomeda, J. R.; Green, M. J.; Higginbotham, A. L.; Sinitskii, A.; Kosynkin, D. V.; Tsentalovich, D.; Parra-Vasquez, a N. G.; Schmidt, J.; Kesselman, E.; Cohen, Y.; Talmon, Y.; Tour, J. M.; Pasquali, M. Spontaneous high-concentration dispersions and liquid crystals of graphene. *Nat. Nanotechnol.* **2010**, *5*, 406–411.

22 Cabane, B.; Hénon, S. *Liquides, Solutions, dispersions, émulsions, gels*; Belin: Paris, 2007 (in French).

23 Grossiord, N.; Loos, J.; Regev, O.; Koning, C. E. Toolbox for dispersing carbon nanotubes into polymers to get conductive nanocomposites. *Chem. Mater.* **2006**, *18*, 1089–1099.

24 Ruoff, R. S.; Tse, D. S.; Malhotra, R.; Lorents, D. C. Solubility of C60 in a Variety of Solvents. *J. Phys. Chem.* **1993**, 3379–3383.

25 Ausman, K. D.; Piner, R.; Lourie, O.; Ruoff, R. S.; Korobov, M. Organic Solvent Dispersions of Single-Walled Carbon Nanotubes: Toward Solutions of pristine nanotubes. *J. Phys. Chem. B* **2000**, *104*, 8911–8915.

26 Furtado, C. A.; Kim, U. J.; Gutierrez, H. R.; Pan, L.; Dickey, E. C.; Eklund, P. C. Debundling and dissolution of single-walled carbon nanotubes in amide solvents. *J. Am. Chem. Soc.* **2004**, *126*, 6095–6105.

27 Ham, H. T.; Choi, Y. S.; Chung, I. J. An explanation of dispersion states of single-walled carbon nanotubes in solvents and aqueous surfactant solutions using solubility parameters. *J. Colloid Interface Sci.* **2005**, *286*, 216–223.

28 Detriche, S.; Zorzini, G.; Colomer, J. F.; Fonseca, A.; Nagy, J. B. Application of the Hansen Solubility Parameters Theory to Carbon Nanotubes. *J. Nanosci. Nanotechnol.* **2008**, *8*, 6082–6092.

29 Coleman, J. N. Liquid-Phase Exfoliation of Nanotubes and Graphene. *Adv. Funct. Mater.* **2009**, *19*, 3680–3695.

30 Badaire, S.; Poulin, P.; Maugey, M.; Zakri, C. In situ measurements of nanotube dimensions in suspensions by depolarized dynamic light scattering. *Langmuir* **2004**, *20*, 10367–10370.

31 Lucas, A.; Zakri, C.; Maugey, M.; Pasquali, M.; Schoot, P. V. D.; Poulin, P. Kinetics of Nanotube and Microfiber Scission under Sonication. *J. Phys. Chem. C* **2009**, *113*, 20599–20605.

32 Khan, U.; O'Neill, A.; Lotya, M.; De, S.; Coleman, J. N. High-concentration solvent exfoliation of graphene. *Small* **2010**, *6*, 864–871.

33 Cravotto, G.; Cintas, P. Sonication-assisted fabrication and post-synthetic modifications of graphene-like materials. *Chem.—Eur. J* **2010**, *16*, 5246–5259.

34 Tarascon, J. M.; DiSalvo, F. J.; Chen, C. H.; Carrol, P. J.; Walsh, M.; Rupp, L. First example of monodispersed $(Mo_3Se_3)_\infty^{-1}$ clusters. *J. Solid State Chem.* **1985**, *58*, 290–300.

35 Petit, P.; Mathis, C.; Journet, C.; Bernier, P. Tuning and monitoring the electronic structure of carbon nanotubes. *Chem. Phys. Lett.* **1999**, *305*, 370–374.

36 Pénicaud, A.; Poulin, P.; Derré, A.; Anglaret, E.; Petit, P. Spontaneous dissolution of a single-wall carbon nanotube salt. *J. Am. Chem. Soc.* **2005**, *127*, 8–9.

37 Voiry, D.; Drummond, C.; Pénicaud, A. Portrait of carbon nanotube salts as soluble polyelectrolytes. *Soft Matter* **2011**, *7*, 7998.

38 Pénicaud, A.; Petit, P.; Fischer, J. E. Doped Carbon Nanotubes. In *Carbon Meta-Nanotubes: Synthesis, Properties and Applications*; Monthioux, M., Ed.; John Wiley & Sons: Chichester, UK, 2012; pp 41−111.

39 Emery, N.; Hérold, C.; d'Astuto, M.; Garcia, V.; Bellin, C.; Marêché, J.; Lagrange, P.; Loupias, G. Superconductivity of Bulk CaC_6. *Phys. Rev. Lett.* **2005**, *95*, 1–4.

40 Dresselhaus, M. S.; Dresselhaus, G. Intercalation compounds of graphite. *Adv. Phys.* **1981**, *30*, 139–326.

41 Enoki, T.; Suzuki, M.; Endo, M. *Graphite Intercalation Compounds and Applications*; Oxford University Press: New York, 2003.

42 Grüneis, A.; Attaccalite, C.; Rubio, A.; Vyalikh, D.; Molodtsov, S.; Fink, J.; Follath, R.; Eberhardt, W.; Büchner, B.; Pichler, T. Electronic structure and electron-phonon coupling of doped graphene layers in KC_8. *Phys. Rev. B* **2009**, *79*, 205106–205109.

43 Grüneis, A.; Attaccalite, C.; Rubio, A.; Vyalikh, D.; Molodtsov, S.; Fink, J.; Follath, R.; Eberhardt, W.; Büchner, B.; Pichler, T. Angle-resolved photoemission study of the graphite intercalation compound KC8: A key to graphene. *Phys. Rev. B* **2009**, *80*, 075431–075435.

44 Stein, C.; Poulenard, J.; Bonnetain, L.; Golé, J. Nouvelle méthode de préparation de composés d'insertion de métaux alcalins dans le graphite. *C. R. Acad. Sci.* **1965**, *260*, 4503–4505.

45 Vallés, C.; Drummond, C.; Saadaoui, H.; Furtado, C. a; He, M.; Roubeau, O.; Ortolani, L.; Monthioux, M.; Pénicaud, A. Solutions of negatively charged graphene sheets and ribbons. *J. Am. Chem. Soc.* **2008**, *130*, 15802–15804.

46 Fredenhagen, K.; Cadenbach, G. Die Bindung von Kalium durch Kohlenstoff. *Z. Anorg. Allg. Chem.* **1926**, *158*, 249–263.

47 Catheline, A.; Vallés, C.; Drummond, C.; Ortolani, L.; Morandi, V.; Marcaccio, M.; Iurlo, M.; Paolucci, F.; Pénicaud, A. Graphene solutions. *Chem. Commun.* **2011**, *47*, 5470–5472.

48 Enoki, T.; Suzuki, M.; Endo, M. *Graphite Intercalation Compounds and Applications*, Oxford University Press: New York, 2003; pp 403−413.

49 Segal, M. Selling graphene by the ton. *Nat. Nanotechnol.* **2009**, *4*, 612–4.

50 Falcao, E.; Blair, R.; Mack, J.; Viculis, L.; Kwon, C.; Bendikov, M.; Kaner, R.; Dunn, B.; Wudl, F. Microwave exfoliation of a graphite intercalation compound. *Carbon* **2007**, *45*, 1367–1369.

51 Lorençon, E.; Ferlauto, A. S.; de Oliveira, S.; Miquita, D. R.; Resende, R. R.; Lacerda, R. G.; Ladeira, L. O. Direct production of carbon nanotubes/metal nanoparticles hybrids from a redox reaction between metal ions and reduced carbon nanotubes. *ACS Appl. Mater. Interfaces* **2009**, *1*, 2104–2106.

52 Yu, Y.-J.; Zhao, Y.; Ryu, S.; Brus, L. E.; Kim, K. S.; Kim, P. Tuning the graphene work function by electric field effect. *Nano Lett.* **2009**, *9*, 3430–3434.

53 Widenkvist, E.; Boukhvalov, D. W.; Rubino, S.; Akhtar, S.; Lu, J.; Quinlan, R. A.; Katsnelson, M. I.; K, L.; Grennberg, H.; Jansson, U. Mild sonochemical exfoliation of bromine-intercalated graphite: a new route towards graphene. *J. Phys. D: Appl. Phys.* **2009**, *42*, 112003.

54 Kwon, J.; Lee, S. H.; Park, K.-H.; Seo, D.-H.; Lee, J.; Kong, B.-S.; Kang, K.; Jeon, S. Simple preparation of high-quality graphene flakes without oxidation using potassium salts. *Small* **2011**, *7*, 864–868.

55 Fu, W.; Kiggans, J.; Overbury, S. H.; Schwartz, V.; Liang, C. Low-temperature exfoliation of multilayer-graphene material from $FeCl_3$ and CH_3NO_2 co-intercalated graphite compound. *Chem. Commun.* **2011**, *47*, 5265–5267.

56 Wang, J.; Manga, K. K.; Bao, Q.; Loh, K. P. High-yield synthesis of few-layer graphene flakes through electrolyte. *J. Am. Chem. Soc.* **2011**, *133*, 8888–8891.

57 Alanyahoglu, M.; Segura, J. J.; Oro-Solé, J.; Casañ-Pastor, N. The synthesis of graphene sheets with controlled thickness and order using surfactant-assisted electrochemical processes. *Carbon* **2012**, *50*, 142–152.

58 Shih, C.-J.; Vijayaraghavan, A.; Krishnan, R.; Sharma, R.; Han, J.-H.; Ham, M.-H.; Jin, Z.; Lin, S.; Paulus, G. L. C.; Reuel, N. F.; Wang, Q. H.; Blankschtein, D.; Strano, M. S. Bi- and trilayer graphene solutions. *Nat. Nanotechnol.* **2011**, *6*, 439–445.

59 Milner, E. M.; Skipper, N. T.; Howard, C. A.; Shaffer, M. S. P.; Buckley, D. J.; Rahnejat, K. A.; Cullen, P. L.; Heenan, R. K.; Lindner, P.; Schweins, R. Structure and morphology of charged graphene platelets in solution by small angle neutron scattering. *J. Am. Chem. Soc.* **2012**, *134*, 8302–8305.

60 Viculis, L. M.; Mack, J. J.; Kaner, R. B. A Chemical Route to Carbon nanoscrolls. *Science* **2003**, *299*, 90095.

61 Shioyama, H. Cleavage of graphite to graphene. *Carbon* **2001**, 499–500.

62 Allemand, P.-M.; Srdanov, G.; Koch, A.; Khemani, K.; Wudl, F. The unusual electron spin resonance of fullerene C_{60}. *J. Am. Chem. Soc.* **1991**, *113*, 2780–2781.

63 Fogden, S.; Howard, C. A; Heenan, R. K.; Skipper, N. T.; Shaffer, M. S. P. Scalable method for the reductive dissolution, purification, and separation of single-walled carbon nanotubes. *ACS Nano* **2012**, *6*, 54–62.

64 Englert, J. M.; Dotzer, C.; Yang, G.; Schmid, M.; Papp, C.; Spiecker, E.; Hauke, F.; Hirsch, A.; Gottfried, J. M.; Steinrück, H.-P. Covalent bulk functionalization of graphene. *Nat. Chem.* **2011**, *3*, 279–286.

65 Catheline, A.; Ortolani, L.; Morandi, V.; Drummond, C.; Zakri, C.; Pénicaud, A. Viewing Graphene in Solution: Light Scattering Analysis of Solutions of Graphene in Tetrahydrofurane. *Soft Matter* **2012**, *8*, 7882–7887.

66 Duggal, R.; Pasquali, M. Dynamics of Individual Single-Walled Carbon Nanotubes in Water by Real-Time Visualization. *Phys. Rev. Lett.* **2006**, *96*, 1–4.

67 Ortolani, L.; Catheline, A.; Morandi, V.; Pénicaud, A. Transmission Electron Microscopy Study of Graphene Solutions. In *GraphITA 2011: Selected papers from the Workshop on Fundamentals and Applications of Graphene*; Ottaviano, L., Morandi, V., Eds.; Series: Carbon Nanostructures; Springer: Berlin Heidelberg, 2012; pp 157−164.

68 Xu, R.; Chu, B. Dynamic light scattering of thin disks: Coupling of diffusive motions. *J. Colloid Interface Sci.* **1987**, *117*, 22–30.