

High concentration few-layer graphene sheets obtained by liquid phase exfoliation of graphite in ionic liquid†

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In the present work, the use of a commercial ionic liquid as a convenient solvent medium for graphite exfoliation in mild and easy conditions without any chemical modification is presented. To confirm the presence of few layer graphene, its dispersion, which exhibits Tyndall effect, was characterized by Raman and UV spectroscopies, and atomic force and field emission electron microscopies. It is noteworthy that, by gravimetric analysis, a graphene concentration as high as 5.33 mg ml⁻¹ was determined, which is the highest value reported so far in any solvent.

Introduction

Graphene is a one-atom thick two-dimensional molecule exclusively made of sp² hybridised carbon atoms. Obtained for the first time in 2004,¹ graphene can be formally considered as the basic building block of all sp² carbon allotropes including graphite, carbon nanotubes and fullerenes. In particular, graphite is a set of graphene sheets stacked one over the other and held together by weak van der Waals forces, while fullerenes and carbon nanotubes can be regarded as wrapped up and rolled graphenes, respectively.

The structure of graphene is free of defects, with all atoms of the same kind, linked together by strong and flexible bonds: this is the origin of the extraordinary properties of this material. Moreover, electrons can move throughout the graphene lattice without encountering obstacles due to structure imperfections or presence of heteroatoms. As a consequence, electrons can move much faster than what they do in metals or semiconductors.²

The outstanding properties of graphene include high values of: Young modulus (~1100 GPa),³ fracture strength (125 GPa),³ thermal conductivity (5 × 10³ W m⁻¹ K⁻¹),⁴ mobility of charge carriers (2 × 10⁵ cm² V⁻¹ s⁻¹)⁵ and specific surface area (2630 m² g⁻¹).⁶

Graphene and its derivatives are promising candidates as components in applications such as energy-storage materials,⁶ 'paper-like' materials,^{7,8} polymer composites,^{9,10} liquid crystal devices¹¹ and mechanical resonators.¹²

Both chemical and physical methods have been proposed for the preparation of graphene.¹³ They include: production from colloidal suspensions, electrochemical methods,¹⁴ micromechanical exfoliation,¹ chemical vapor deposition and epitaxial growth.^{15,16}

The obtainment of graphene from colloidal suspensions is advantageous in terms of simplicity and high volume production, and could be used for a wide range of applications; in particular, there are two ways to obtain graphene by this method: chemical modification of graphite (*i.e.* obtainment of graphite oxide and its reduction after exfoliation)¹⁷ and direct exfoliation without chemical modification in suitable organic solvents¹⁸ or surfactants.¹⁹ Unlike direct exfoliation, chemical modification results in considerable destruction of graphene electronic structure, thus compromising its unique properties.

Aim of the present work was to develop an easy and effective method for obtaining graphene through the direct exfoliation of graphite powder in ionic liquids (ILs).

ILs are organic or partially inorganic salts, liquid at temperature below 100 °C. Because of some of their properties, such as compatibility with a wide range of organic and inorganic solvents, low volatility, low risk of flammability and explosiveness, they are used in several alternative synthetic approaches²⁰ including those related to the green chemistry.²¹ In addition, ILs are recyclable and can be easily separated from other materials by liquid-liquid extraction (*i.e.* distillation) or solid phase extraction (*i.e.* ionic exchange). Other interesting applications are in the fields of conductive²² and stimuli responsive materials,^{23,24} namely in those cases in which the presence of a non-volatile solvent is required.

In 2003, Fukushima *et al.* observed that imidazolium-based ILs can be successfully used as solvents for untangling carbon

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nanotubes.²⁵ It was assumed that this process involves interactions between π electrons of the nanotube and the positive charge of the imidazolium ring. In 2008, Liu *et al.* reported the preparation of graphene nanosheets by electrochemical synthesis assisted by imidazolium ILs.¹⁴ In 2010, Zhou *et al.* reported the use of the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate as a solvent to disperse graphene, stabilized with a polymerized ionic liquid.²⁶ However, these latter two works deal with the use of ILs as media for the chemical synthesis and/or modification of graphene or graphite, respectively.

In the present work, stable graphene dispersions in a proper ionic liquid without any chemical modification nor any stabilizing additive are obtained.

Results and discussion

As described in the Experimental, graphene was obtained by grounding and sonicating graphite in 1-hexyl-3-methylimidazolium hexafluorophosphate (HMIH), which is the ionic liquid chosen for the present work. The dispersions of graphene appear as homogeneous gray to black viscous liquids, which were found to be stable for about three weeks. The occurrence of the Tyndall effect (see ESI†) confirmed the colloidal nature of the dispersions.

In a first series of experiments, a study on the effect of sonication time²⁷ on graphene concentration was performed by gravimetry and UV analysis. As can be seen in Table 1, graphene concentration increases considerably with sonication time going from 11 $\mu\text{g ml}^{-1}$, for 30 min of ultrasound application, to over 2.332 mg ml^{-1} for 24 h of sonication time. The visual difference between these two samples is shown in Fig. 1.

A second series of experiments was performed in order to determine the best initial graphite concentration that allows obtaining the highest graphene concentration (Fig. 2) by keeping constant the sonication time as determined in the previous series (24 h). Graphene concentration as high as 5.33 mg ml^{-1} was achieved, a value that is the highest reported so far for any solvent.^{27–30} On this respect, it should be noticed that, as already reported in the literature,²⁷ the final concentration of graphene is largely affected by various operational parameters, including reactor geometry and dispersion volume. (A thorough study on the effect of these parameters on graphene concentration and properties is in progress and will be reported soon.) The concentration values determined by gravimetry were used together with UV spectroscopy data in order to determine the actual absorption coefficient of graphene in HMIH, which was found to be $\alpha = 1172 \text{ ml mg}^{-1} \text{ m}^{-1}$, a value significantly lower than others reported in literature.^{18,28,31}

Table 1 Graphene concentration ($\pm 5.0\%$) as a function of sonication time for samples with 1.0 wt% of initial graphite

Sonication time/h	Graphene concentration/ mg ml^{-1}
0.5	0.011
6.5	0.238
14.5	1.640
24.0	2.332

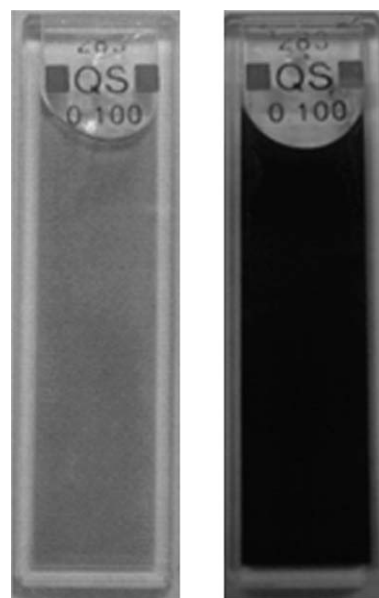


Fig. 1 Images of dispersions obtained after 0.5 h (left) and 24 h (right) of sonication time for samples with 1 wt% of initial graphite.

In order to characterize the graphene sheets, field-emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM) were carried out on drop-cast films obtained by removing the ionic liquid with chloroform. The presence of large flakes of ~ 3 to $4 \mu\text{m}$ in diameter (Fig. 3a) is clearly evident. A similar morphological aspect was obtained for the graphene films deposited from different initial graphite concentrations (see ESI†).

AFM is one of the most direct methods of quantifying the degree of exfoliation to graphene sheet level.^{32,33} Tapping mode AFM image of the deposited film is reported in Fig. 3b. Graphene flakes with average thickness of about 2 nm were observed.

The degree of exfoliation of the starting graphite flakes was also captured with Raman spectroscopy characterization. Indeed, Raman allows unambiguous nondestructive identification of single layer, bilayer, and few layer graphene flakes.^{31,34–36} Raman spectra were performed onto the samples analyzed by

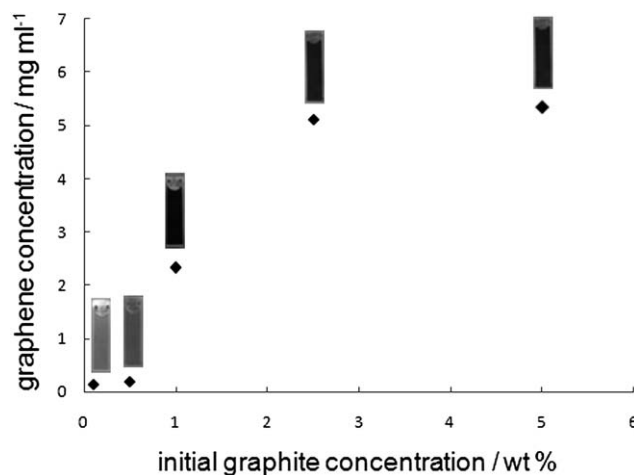


Fig. 2 Graphene concentration as a function of initial graphite concentration (sonication time = 24 h). For each sample, the visual aspect of the dispersion is shown.

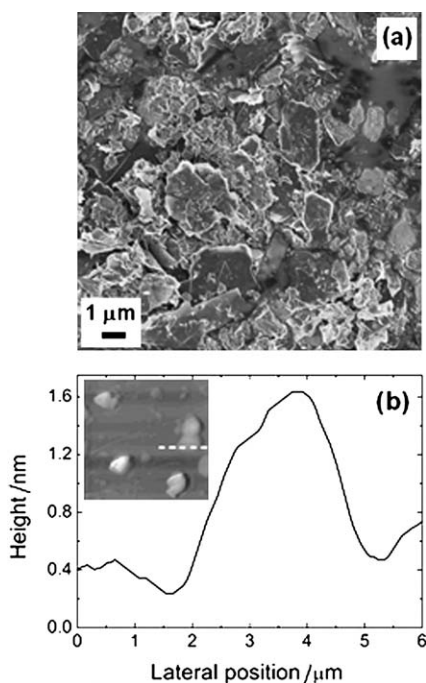


Fig. 3 (a) FE-SEM image and (b) 2D tapping-mode topography ($15\ \mu\text{m} \times 15\ \mu\text{m}$). AFM image and height profile of the graphene flakes obtained from 5.0 wt% dispersion of graphite in HMIH.

AFM. A representative Raman spectrum of the graphene flakes reported in Fig. 3 compared with pristine graphite is shown in Fig. 4a. The presence of the main peaks of graphene^{31,34–36} is clearly evident: the G band at $\sim 1570\ \text{cm}^{-1}$, the 2D band at $\sim 2690\ \text{cm}^{-1}$, and the disorder-related D peak at $\sim 1350\ \text{cm}^{-1}$. The 2D peak of graphite consists of two components and the main peak is upshifted to $2713\ \text{cm}^{-1}$. The disorder related D peak is present also in the initial graphite powder, but its intensity is higher for graphene; according to Sun *et al.*³⁷ we assign this finding to the edges of the submicrometre flakes we produce. As far as graphene spectrum is concerned, the wavelength of the 2D peak (full width at half maximum = $85\ \text{cm}^{-1}$) for the sample with 5.0 wt% of initial graphite is similar to that of bilayer graphene.³¹ Fig. 4b shows Raman spectra of samples obtained from the other initial graphite concentrations. The Raman spectra of the samples obtained from 0.1 wt% and 0.5 wt% of graphite in HMIM show a significant change in the shape of the 2D band signal; the 2D peak consists of two components at $2683\ \text{cm}^{-1}$ and $2705\ \text{cm}^{-1}$. The Raman spectra of the samples obtained from 1.0 and 2.0 wt% of graphite in HMIM show a single 2D peak; according to what reported in ref. 34, these data indicate the obtainment of a better exfoliation of the graphite sheets as higher the initial concentration is. The 2D band signal is broader than that reported by Green and Hersam,³¹ thus suggesting that the film structure consists of a stacking of layered graphene sheets.

Experimental

Materials

Graphite flakes, HMIH, methylene chloride, and chloroform were purchased from Aldrich and used as received without further purification.

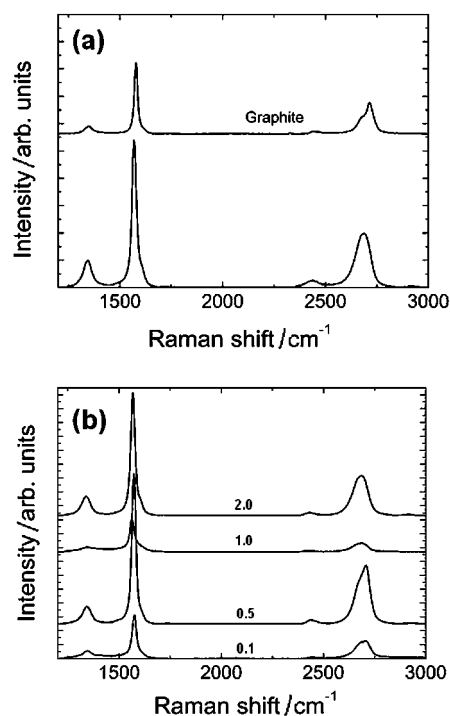


Fig. 4 (a) Raman spectra of graphene obtained by exfoliation starting from 5.0 wt% of graphite in ionic liquid; the Raman spectrum of graphite has been reported as reference. (b) Graphene spectra for samples obtained from 0.1, 0.5, 1.0, and 2.0 wt% graphite in HMIH.

Graphene dispersion in HMIH

General procedure: mixtures containing various amounts of graphite flakes and HMIH (5.00 g) were grounded in a mortar for 10 minutes; then, they were put in a tubular plastic reactor (i.d. 15 mm) and placed in an ultrasonic bath (0.55 kW, water temperature $\approx 25\ ^\circ\text{C}$) for 0.5, 6.5, 14.5 or 24 h. Finally, they were centrifuged for 30 min at 4000 rpm; the gray to black liquid phase containing graphene was recovered.

Best conditions: 3.5 ml of dispersion (5.0 wt% graphite in HMIH) was sonicated for 24 h. After centrifugation (see above) a graphene concentration as high as $5.33\ \text{mg ml}^{-1}$ was obtained.

Gravimetric and UV analyses

In order to determine the actual graphene concentration, the graphite dispersion was divided into two fractions having known volume. The first one was filtered through polyvinylidene fluoride filters (pore size $0.22\ \mu\text{m}$) in order to directly weigh the amount of dispersed graphene. The second one was analyzed by UV analysis by using a Hitachi U-2010 spectrometer (1 mm cuvette). The above gravimetric data allowed us to determine the absorption coefficient. In detail, from a known volume of initial dispersion several dilutions were done and the absorbance at a wavelength of $660\ \text{nm}$ ^{18,28,31} was measured. Absorbance plotted *versus* concentration (see ESI†) gave an absorption coefficient $\alpha = 1172\ \text{ml mg}^{-1}\ \text{m}^{-1}$.

FE-SEM and AFM analysis

AFM images were obtained in tapping mode. For the FE-SEM analysis, graphene dispersions were drop-cast onto carbon tape and washed with chloroform in order to remove the ionic liquid. Then, chloroform was allowed to evaporate at 50 °C for 30 min. For AFM analysis, a common transfer printing method from the carbon tape to Si substrate was adopted.

Raman spectroscopy

Graphene dispersion was washed three times with methylene chloride. The resulting HMIH-free graphene was deposited onto SiO₂ and the solvent was evaporated at 50 °C for 30 min. Raman analysis was performed by a Bruker Senterra Raman microscope, using an excitation wavelength of 532 nm at 5 mW. The spectra were acquired by averaging 5 acquisitions of 5 seconds with a 50× objective.

Conclusions

For the first time, an ionic liquid was used as a convenient method for dispersing graphite and easily obtaining graphene in high concentration. It is noteworthy that this method does not imply any chemical synthesis or modification, and allows obtaining values of graphene concentration (up to 5.33 mg ml⁻¹) that are the highest reported so far in any medium. It should be also pointed out that the use of an ionic liquid may suggest interesting applications in those cases in which a green chemistry approach and/or a non-volatile, stable solvent medium are required. Namely, by considering the unique properties of both graphene and ionic liquids, this dispersion could be used for applications in the field of solar cells, energy storage devices, catalysis and for nanocomposite materials, including polymers. Moreover, graphene powder can be easily obtained by washing the dispersion with organic solvents to eliminate the ionic liquid, which, thanks to its properties, can be easily purified and recycled, with great advantages in terms of cost.

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