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Highly concentrated and stable few-layers graphene suspensions in pure and volatile organic solvents

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ABSTRACT

Highly stable graphene suspensions in pure organic solvents, including volatile solvents such as ethanol, tetrahydrofurane, chloroform, acetone or toluene have been prepared by re-dispersion of a graphene-powder. Such re-dispersable solid is produced by precipitation or solvent elimination from graphene suspensions obtained by sonication of graphite in several organic solvent–water mixtures. Re-dispersion is feasible in a wide range of pure organic solvents, obtaining high quality few-layers graphene flakes stable in suspension for months. As a proof-of-concept, on-glass spray deposition of some of these suspensions, *e.g.* ethanol or tetrahydrofuran, results on electrically conductive transparent coatings. These results suggest industrial potential use of the scalable technology here developed to fabricate low-cost devices with many different potential applications.

1. Introduction

Graphene has attracted much attention as a new nano-carbon form with a unique structure and exceptional physical properties [1]. Commercial applications for graphene are expected in many areas from high-frequency electronics [2] to smart coatings [3]. While some of those applications will require coverage of large areas with single layer graphene of high structural quality, many others such as printed electronics [4], transparent electrodes [5] or conductive coatings [6] will demand low-cost graphene suspensions able to be processed by simple methods in large quantities and in a wide range of media. In this context, liquid phase exfoliation (LPE) of graphite is expected to fill this gap [7,8]. However, the preparation of graphene suspensions is still very limited. Probably the most promising LPE procedure is based on the graphite exfoliation using N-methyl-2-pyrrolidone (NMP) as solvent [9]. Despite having high quality graphene layers in graphene-NMP suspensions, the stability of the suspensions and even industrial scale-up [10], are the main drawbacks due to the features of NMP, which is a non-green solvent [11] with a high boiling point that may prevent the processability of the graphene suspensions. Therefore, it seems obvious the need for the search of alternative solvents that could overcome these features. Following this idea, graphene dispersions in high boiling point solvents have been successfully transferred into volatile solvents by solvent exchange. However, these procedures yield to low concentration graphene suspensions [12]. In addition, a direct method based on sonication at very low power during long time of graphite in choloroform or isopropanol has allowed the formation of stable graphene suspensions with high graphene concentration [13]. Despite this interesting result, the long sonication time required to obtain the mentioned graphene suspensions limited the scalability of the process. Finally, recent reports showed the possibility of use mixtures acetone/water [14] and ethanol/water in graphite liquid phase exfoliation [15–17].

In a different approach, graphene suspensions have been obtained by reducing graphene oxide suspensions [18]. Although interesting, this is a not desirable strategy from different perspectives. In one hand, the atom economy of this approach is quite low which has a negative impact both environmentally and economically. On the other hand, commonly the physical properties of graphene are not completely restored after reduction of graphene oxide due to the defects produced in the chemical manipulation that results in a low quality graphene [19]. Thus, it is convenient to distinguish clearly those methods based on graphene oxide reduction and those that imply direct graphite

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exfoliation, which up to this date implied the use of a limited number of solvents and working conditions that hampered its massive application.

In this work we have produced, by a simple two-steps procedure, graphene powders readily re-dispersable in water-free volatile organic solvents such as ethanol, tetrahydrofurane, chloroform, acetone or toluene. These graphene powders offer an unprecedented tool to obtain highly concentrated few-layers graphene suspensions in a wide range of organic solvents. The stability of these suspensions *vs* time has been evaluated showing an excellent performance. As a proof-of-concept of the potential applications of these suspensions, spray-on technique has been used to prepare transparent and conductive glasses.

2. Materials and methods

The starting commercial graphite source (NGS Naturgraphit) is based on natural graphite with particles sizes <150 μm (100 mesh) up to <45 μm (325 mesh). Solvents were provided by commercial sources and used without further purification unless is stated otherwise.

Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer 1650 spectrophotometer in KBr pellets. Optical absorption spectroscopy (OAS) was measured on graphene-ink suspensions using an Agilent 8452 diode array recorded over a 190–1100 nm range. Graphene-ink concentration, C_G, was determined from $A/l = \alpha C_G$, where A was measured at 280 nm. The absorption coefficient, α, which is related to the absorbance per unit path length, A/l, through the Lambert–Beer law $A/l = \alpha C$, is an important parameter in characterizing any dispersion. In order to accurately ascertain the graphene concentration, the absorption coefficient, α, is determined experimentally (Fig. S1). Therefore, the absorption coefficient was obtained by measuring the absorbance, the dispersion volume and weight of the dried graphene residue of a large volume of graphene dispersions in THF–water mixture (4:1) at different concentrations. Powder X-ray diffraction measurements were carried out using a diffractometer PANalyticalX'Pert PRO theta/2theta primary monochromator and detector with fast X'Celerator. Transmission electron microscopy (TEM) images were obtained in a JEOL model Transmission Electron Microscope JEM 3000 F (field emission) with an accelerating voltage of 300 kV. Scanning electron microscopy (SEM) was performed using a microscope JEOL JM6400 equipped with a 40 kV microprobe. The substrates used for SEM were copper discs. Atomic force microscope (AFM) images were acquired in dynamic mode using a Nanotec Electronica system operating at room temperature in ambient air conditions. For AFM measurements, Olympus cantilevers were used with a nominal force constant of 0.75 N/m. The images were processed using WSxM software. All the samples of AFM were prepared with spraying the dilute suspensions of samples on SiO_2. For AFM measurements previously distilled THF (tetrahydrofuran) was used. Raman spectra were recorded on a WITec/Alpha 300AR Raman confocal microscope at ambient conditions. The laser wavelength and power were 532 nm and 0.7 mW, respectively. Maps of Raman spectra of the entire graphene flakes were acquired to ensure the homogeneity of the flake. Thermal gravimetric analyses (TGA) were performed in a TGA TA instruments Q-500 analyzer. The temperature program was from 25 to 1000 °C, with a temperature rate of 5 °C min^{-1} under a nitrogen flow.

Spray coating. The substrates were sprayed on glass substrates using a Meinhard TR-30-K1 nebulizer with a flow of argon 0.3 L/min. The film thickness can be controlled by spraying time and the suspension concentration. Transparency was measured at a wavelength of $\lambda = 550$ nm after annealing the conductive films at 350 °C for 15 min. Optical transmission spectra of the films deposited on glass slides were recorded on a UV–vis spectrometer (Agilent 8452) with a glass slide as reference.

Sheet resistance measurements, R_s, were measured by a KDY-1 two-probe resistivity test system (GuangZhou KunDe) at 300 K on samples with contact made with graphite conductive paste at room temperature.

Determination of optimal solvent–water mixture. Graphene dispersion is prepared by sonicating 50 mg graphite in 10 mL of mixtures having different S:water (S = tetrahydrofurane, ethanol, acetone and acetonitrile) ratios, during 90 min at 310 W with 40 Hz, followed by centrifugation at 550 × g for 60 min. Several ratios of S and water mixtures were explored to determine the optimum mixing S:water ratio (Table S1). The graphene concentration, C_G, was calculated by measuring the absorption at 270 nm, being the corresponding, experimentally determined, extinction coefficient $\varepsilon_{270\mathrm{nm}} = 3180\ \mathrm{L\ g^{-1}\ m^{-1}}$.

Preparation of THF–water suspension. 50 mg graphite were sonicated in 10 mL of THF-water (4:1) for 90 min at 310 W with 40 Hz, followed by centrifugation at 550 × g for 60 min (named as suspension **B**). Table S2 and SI shows conditions to form other suspensions. Different suspensions were obtained depending on centrifugation procedure (time and g force).

Preparation of graphene powders. The graphene suspension **B** was selected as starting material to isolate the so-called graphene powders. We have used two different experimental procedures: (i) *Dried graphene powder* is obtained upon complete vacuum dryness of a THF–water (4:1) suspension **B**. (ii) *Precipitated graphene powder* is isolated by adding diethylether to the initial THF–water (4:1) suspension provoking a fast precipitation of graphene powder. Addition of 1 mL diethyl ether to 4 mL freshly sonicated THF–water suspension **B** results in fast precipitation of a black powder that can be easily collected by using centrifuge with high speed (16,000 × g for 3 min) and washed several times with only distilled THF and then completely dried under vacuum.

Preparation of graphene suspensions in anhydrous media. Dried graphene powder and *precipitated graphene powder* can be re-dispersed in a variety of organic solvents including ethanol, tetrahydrofurane, chloroform, acetone or toluene. Typically, 1 mg of graphene powder was suspended in 10 mL of solvent, and sonicated for 90 min at 310 W, then the mixture was centrifuged at 550 × g for 15 min. It is observed that the *precipitated graphene powder* is more efficiently re-dispersed than *dried graphene powder*. The concentration of graphene incorporated to the suspension was evaluated by UV measurements as in Section S1 (Tables S3 and S4).

3. Results and discussion

A general scheme of the whole procedure to generate high concentrated and stable graphene suspensions in pure volatile organic solvents is shown in Scheme 1.

A first step consists on initial liquid phase graphite exfoliation, which is optimal when sonication occurs in a mixture THF/H_2O 1:4. Exfoliated graphene in suspension can be collected as solid powders (*vide infra*) which can be re-dispersed by sonication on several organic volatile solvents. In particular, in this work is shown that solid obtained by precipitation after addition of diethyl ether, affords higher graphene concentrations in suspension in a variety of pure organic solvents where direct exfoliation of graphite is not feasible. In addition, such precipitated graphene powder generates highly stable solutions that can remain unaltered over, at least, two months. Therefore, the isolation of a graphitic solid with a high degree of exfoliation (in particular the *precipitated graphene powder*) allows setting up protocols to prepare graphene suspensions in an unprecedented range of organic solvents.