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COMMUNICATION

Production of large graphene sheets by exfoliation of graphite under high power ultrasound in the presence of tiopronin†

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Under ultrasonication, the production of high quality graphene layers by exfoliation of graphite was achieved *via* addition of tiopronin as an antioxidant.

A number of sonochemical methods have been described for the production of stable dispersions of graphene.^{1–5} However, the chemical effects of high intensity ultrasound, which are usually accompanied by mechanical and physical effects, have not been clearly identified in graphene synthesis. Ultrasonication techniques employed for the production of graphene basically consist of the sonication of graphite in organic solvents able to colloidally stabilize graphene.⁶ During the process high pressures and high temperatures generated by the implosion of cavitation bubbles cause violent collisions between particles at very high speed. These extreme conditions in air-saturated sonicated solutions allow solvent dissociation into peroxy radicals.⁷ The radical reactions are usually destructive because ultrasonic treatments are very effective in breaking C–C bonds.⁸ Increasing the sonication time increases the concentration of graphene in dispersion. However, longer ultrasonication treatments result in graphene layers with a higher number of defects and reduction of the sheet size.⁹ These defects mostly consist of oxidized carbon atoms at the edges of graphene layers in the form of epoxy or carbonyl and carboxyl groups.

Recently, we reported the formation of Multi-Walled Carbon Nanotubes (MWNs) from graphite by addition of ferrocene aldehyde as a reducing agent during sonication treatments.¹⁰ Herein, we demonstrate that the damage created in graphene sheets during exfoliation of graphite in DMF can be considerably reduced by the addition of *N*-2-mercapto-propionyl glycine

(tiopronin), a molecule that inhibits reactions promoted by oxygen, peroxides and radicals (Fig. 1).¹¹ This protocol generates dispersions with a higher yield of larger graphene sheets containing less defects than those obtained by common sonication treatments.¹ Our results confirm that ultrasonication in organic solvents generates free radicals, which can enable or be involved in secondary reactions.

Samples were prepared using the ultrasonic tip processor GEX 750. All samples were sonicated in cycles of 30 s on/30 s off for 1 or 3 h periods of time at the lower power of the ultrasonic tip (20%, 112.5 W).

During ultrasonication, the samples were kept in an ice bath to avoid overheating. Initially, we produced **G-1**: 10 mg of graphite crystals were ultrasonicated in 30 ml of DMF for 1 h in order to induce partial exfoliation of graphite (ESI†). UV-vis spectroscopy was used to quantify the amount of graphene by measuring the absorption at 660 nm. The concentration of the final dispersion was calculated using the absorption coefficient $\alpha = 2460 \text{ ml mg}^{-1} \text{ m}^{-1}$, resulting in $0.031 \pm 0.003 \text{ mg ml}^{-1}$. The dispersed material was investigated by transmission electron microscopy (TEM), the micrographs can be found in ESI.† TEM analysis of **G-1** indicates the presence of graphene flakes with lateral size typically between 4–5 μm , consisting of several layers. Sonicated DMF was always removed by filtration and the wet precipitate was redispersed in 10 ml of fresh DMF. Following the preparation of **G-1**, as a control experiment, we sonicated **G-1** for 3 h (**G-DMF**). The concentration of the dispersions was calculated to be $0.027 \pm 0.002 \text{ mg ml}^{-1}$.

Fig. 1 Scheme of the graphite exfoliation under high power ultrasound in the presence of tiopronin as radical trap.

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G-DMF micrographs show graphene layers with lateral size typically smaller than 500 nm, shown in ESI†. The quality of the resulting material was further analysed by Raman spectroscopy (ESI†). The 2D band of **G-DMF** shows a low intensity band associated with damage to graphene.¹² The intensity of the D peak at 1332 cm^{-1} relative to the G peak ($\sim 1580\text{ cm}^{-1}$), D/G intensity ratio (I_D/I_G), was found to be 0.99, identifying **G-DMF** as a highly damaged material comparable to graphene oxide (GO).¹³ In a different set of experiments 40 mg of tiopronin (Sigma-Aldrich) was added to **G-1**. The dispersions were sonicated for 3 h, under the same experimental conditions, resulting in **D-Tio** (Fig. 1). The product was copiously washed by filtration with fresh DMF in order to remove tiopronin and byproducts. Samples were redispersed in an ultrasonicator bath (a few seconds) in 10 ml of fresh DMF. Centrifugation of all dispersions was carried out at 3000 rpm for 30 min. A liquid fraction of 5 ml of **D-Tio** dispersion was collected and analysed. After sonication and purification treatments described above, the concentration of **D-Tio** was calculated to be $0.030 \pm 0.005\text{ mg ml}^{-1}$.

TEM and HR-TEM micrographs of **D-Tio** reveal the presence of nanofibers. The formation of similar structures has been reported as being a result of the condensation of organic pieces of polyaromatics¹⁴ or the radical polymerization of conjugated carbon polymers.¹⁵ The nanofiber formation under sonication treatment indicates the occurrence of organic radical reactions close to the edges. We use tiopronin since it is a significant antioxidant¹¹ and has free terminal $-\text{SH}$ and $-\text{CO}_2\text{H}$ groups that can serve as ligands in the stabilization of gold nanostructures (Fig. 1).¹⁶ Thus, in order to verify where the reactions took place, Au nanorods (NRs) were later introduced into **D-Tio** as contrast markers (see ESI†).¹⁷ After the addition of 1 ml of **D-Tio** dispersion to 1 ml of Au NRs, TEM micrographs, presented in Fig. 2a and b, show Au NRs mainly attached to carbon nanofibers as sketched in Fig. 1. As an indication of the purity of the resulting graphene material, Au NRs were not found in the graphene sheets, nor at the edges. After separation by centrifugation at 900 rpm for 90 min, the lower part of the dispersion, named **G-Tio**, was analyzed by TEM showing mainly the presence of graphene layers with lateral sizes of 2–5 microns. A representative TEM micrograph is presented in Fig. 2c and additional micrographs are included in the ESI†. Further analysis was performed by HR-TEM (Fig. 2d). Compared to other techniques, such as Raman or AFM, HR-TEM allows the preparation of the sample from very diluted dispersions, keeping graphene sheets as monolayers or few-layers. Thus, the atomic structure of the graphene is visualized by exit wave reconstruction, which is an advanced TEM technique in which 10 to 30 HR-TEM images are acquired at different defocus values and combined into a complex wave of electrons at the exit plane of the sample. In order to prevent beam damage, these series of images were collected at 80 kV using an aberration corrected microscope. An example of a phase image of the exit wave of electrons when leaving a graphene sheet is presented in Fig. 2d. In contrast to single HR-TEM images, phase images enable one to interpret the contrast quantitatively and distinguish single and double graphene layers.¹⁸ The inset of Fig. 2d shows a defect-free graphene lattice, in which the positions of the individual carbon atoms can be recognized. This image clearly

Fig. 2 Carbon nanostructures produced with the addition of tiopronin. (a) TEM micrograph of a solution cast of **D-Tio**. (b) **CNF-Tio-Au**. (c) Representative TEM micrograph of **G-Tio**. (d) HR-TEM image of **G-Tio**.

indicates a single graphene sheet, as the AB stacking of a double sheet would lead to the presence of additional atoms in the center of the hexagons. The overview image shown in Fig. 2d furthermore shows that adsorbents are likely to be present at the surface of the graphene layer leading to the ripple-like contrast present in this image.

Raman comparison of the different nanostructures obtained by sonication with the addition of tiopronin molecules is shown in Fig. 3a. The Raman spectrum of **D-Tio** contains bands that are not correlated with the well-known 2D, G, and D bands of graphitic materials (Fig. 3a) which might originate from tiopronin or its fragments. The I_D/I_G ratio was calculated to be 0.87. The Raman spectrum of tiopronin is also shown for comparison, the spectrum shows the stretching band of $-\text{SH}$ at 2575 cm^{-1} typical of alkanethiol molecules.¹⁹ After separation by centrifugation, the Raman spectrum of **CNF-Tio** was extremely noisy, however after the addition of Au NPs the spectrum changed dramatically showing the appearance of Raman bands (**CNF-Tio-Au**). It is possible that Surface Enhanced Raman Scattering (SERS) is responsible for this effect.²⁰ The absence of the SH stretching in **CNF-Tio-Au** dispersion might indicate the chemisorption of tiopronin or tiopronin fragments onto

Fig. 3 (a) Comparison of the Raman spectra (excitation at 633 nm) of tiopronin, **CNF-Tio**, **D-Tio** and **G-Tio**. (b) C 1s XPS spectrum of **D-Tio**.

the Au NPs. Other relevant features are the C–C stretching signals between 1000 and 1150 cm^{-1} , CH_3 wagging at 1300 cm^{-1} and CH_3 deformations at 1450 cm^{-1} , while the band at 1566 cm^{-1} can be identified as amorphous carbon.²¹ The Raman features in **CNF-Tio-Au** corroborate that under sonication in DMF, tiopronin reacts with the graphene sheets close to the edges producing nanofibers, where Au NRs can remain attached. Instead, Raman analysis of **G-Tio** identified the presence of good quality graphene layers since the I_D/I_G ratio amounted to only 0.24. The concentration calculated for **G-Tio** was $0.027 \pm 0.003 \text{ mg ml}^{-1}$. Finally, the XPS analysis of **D-Tio** was performed by drop casting of the dispersion onto a clean Ag substrate. Spectra are shown in Fig. 3b. The C 1s core level region shows a contribution from carbon from the hexagonal lattice of graphite at 285.0 eV representing 67.2% of the total carbon intensity, as well as from carbon singly bound to oxygen and nitrogen at 286.1 eV, amounting to 21.8% of the total C intensity. Two more chemically shifted C contributions are found at 287.8 eV (12.3%) and 289.1 eV (3.3%), which are attributed to the carbonyl and carboxyl groups, respectively. As seen in Fig. SI-5(ESI†), the chemical shift of the S 2p core level XPS signal towards lower binding energies than those of free thiol testifies to the successful attachment of the Au nanoparticles to the functional molecules. One more indication of the interaction between Au nanoparticles and tiopronin or tiopronin fragments is the slight increase in the binding energy of the Au 4f_{7/2} core level peak from 83.9 eV of free Au to 84.5 eV (ESI†).

The proposed mechanism for the production of larger graphene layers in higher yields involves tiopronin as an effective superoxide and hydroxyl radical scavenger. The thiyl radical formed in radical ablation can be dissipated by mutual annihilation; however, under aerobic conditions the peroxy-sulfenyl radical may form. This radical is reported to be more reactive²² and might be implicated in different reactions. We suggest that during ultrasonication without addition of tiopronin, the formed radical species are strong enough to gradually oxidize the entire graphene sheet; this process might be initiated at the edges and inner defects, cutting the graphene sheets into small pieces. Instead by the addition of tiopronin, the formation of carbon nanofibers is most likely the result of controlled radical attack by tiopronin producing antioxidant derived-radicals which are able to attack graphene sheets at the edges. Perfect graphene has a very low reactivity but topological defects, such as Stone–Wales defects and vacancies close to the edges, which may promote the cutting of graphene layers in polyaromatics and amorphous carbon as Au NRs indicated. These fragments later aggregate in carbon nanofibers as they are insoluble in DMF.

In conclusion, the effect of adding tiopronin during exfoliation of graphite by ultrasonication in DMF was investigated and found to result in a considerable reduction of the degree of oxidation of the exfoliated graphene sheets as demonstrated by XPS and Raman spectroscopy analyses. Higher concentrations were calculated from the UV-vis absorption at 660 nm of the dispersions and larger graphene sheets were observed by

TEM. Finally HR-TEM confirmed a very low density of defects in the resulting graphene layers. These results are expected to be very useful in understanding why polar solvents are effective in exfoliating graphite (through the formation of radical species) and in furthering the design of higher yield experimental procedures for liquid-phase exfoliation of graphite.

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