Electrochemical synthesis and the functionalization of few layer graphene in ionic liquid and redox ionic liquid

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Electrochemical reductive exfoliation of graphite to few layered graphene (FLG) in presence of 1-ethyl-2,3-dimethyl imidazolium bis(trifluoromethylsulfonyl) imide ionic liquid and redox ionic liquid based ferrocene has been investigated. Thus, by applying a mild negative potential (−2.7 V vs. Fc/Fc$^+$) to carbon electrode in ionic liquid graphene flakes could be generated. The generated materials have been characterized by X-ray photoelectron spectroscopy, Raman spectroscopy, high resolution transmission electron microscopy and atomic force microscopy. XPS and Raman analysis show that the electrochemical reductive exfoliation provides the formation of FLG. The thickness of the resulting FLG was found to be ranged between 4 and 1 nm. HR-TEM images reveal the formation of few graphene layers and in some cases single graphene layer was observed. Moreover, this electrochemical route conduces to the formation of ionic liquid functionalized FLG. Finally, the reductive exfoliation was further investigated in the presence of redox ionic liquid. XPS and electrochemical measurements confirm the presence of ferrocene.

electrochemistry, reductive exfoliation, ionic liquid, graphene

1   Introduction

During the past decade, graphene has attracted a tremendous attention and has been proposed as a promising material for potential applications in nanoelectronics, polymer composite materials, sensors, batteries, catalysis and supercapacitors [1–3]. Graphene is an atomically thick, two-dimensional sheet composed of sp^2 carbon atoms arranged in a honeycomb structure. It has been viewed as the building block of all other graphitic carbon allotropes of different dimensionality [4,5]. For example, graphite (3D) is made of graphene sheets stacked on top of each other and separated by 0.33 nm. The 0D carbon allotrope, fullerenes (buckyballs), can be made by wrapping a section of graphene sheet. The 1D carbon nanotubes and nanoribbons, can be made by rolling and slicing graphene sheets, respectively.

Several methods have been proposed for graphene preparation, such as micromechanical cleavage, chemical vapor deposition, chemical processing, liquid phase exfoliation of graphite, ultrasonic or thermal exfoliation, and electrochemical exfoliation of graphite [6–9]. However, most of the used methods provide graphene oxide (GO) which is an electrical insulator due to the presence of oxygen functional groups causing the inevitable disruption of long-range con-

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jugation. Another drawback is related to the need of additional chemical or thermal reduction treatments on the GO to recover electrical conductivity [6]. In this article, electrochemistry has been proposed to be an effective tool for preparing graphene but also to modify its electronic states through adjusting the applied potential to change the Fermi energy level of electrode material surface. The synthesis of graphene nano-sheets by electrochemical reduction of exfoliated GO or by the electrochemical exfoliation of graphite have been reported [10,11]. Electrochemical synthesis of few layer graphene (FLG) was developed and considered as a straightforward strategy. So far, the electrochemical approaches occur mostly at the anode in aqueous electrolytic media and the produced materials are always contaminated by graphene oxide and other undesired carbonaceous species [8,9]. Other groups report on the formation of FLG after graphite oxidation in ionic liquids [12,13]. To produce FLG flakes based on electrochemical strategies, a high voltage was employed during the electrochemical process (10 to 20 V), and as consequence the generated graphene plates were oxidized and produced oxygen functionalities in addition to the presence of a high level of disorder [14]. In addition, the use of high voltage may intrigue unexpected reactions and introduce more impurities as well as defects. Therefore it is desirable to improve the stated electrochemical synthesis of FLG flakes. Recently, FLG has been obtained using electrochemical reduction process based on ion intercalations and organic solvents [15–17].

More recently, the functionalization of graphene with organic and inorganic molecules has been reported providing a new properties to the graphene [18–20]. Modification of partially reduced GO with imidazolium derivatives was reported and the resulting material was easily dispersed in aqueous and organic solvents [21]. Functionalization of GO by imidazolium derivatives through amide bonds has also been reported [22,23]. Subsequently, the heterocyclic ring was transformed to its ionic imidazolium analogue. The counter ion of the imidazolium ring can be substituted by other ions, providing new composite materials with interesting properties.

Interest in room temperature ionic liquids (RTILs) has increased dramatically in the past decade as their unique properties have been exploited. The RTILs present large potential interest as solvents for electrochemical applications because they can be used without the need of any added supporting electrolyte thanks to their intrinsic ionic conductivities [24]. However, only few works report on the reductive electrochemical exfoliation of graphene materials in tasks specific ionic liquid media [12,25,26].

In this communication, we report on the synthesis of few layer graphene (FLG) using electrochemical reductive exfoliation in 1-ethyl-2,3-dimethylimidazolium bis(tri-

fluoromethylsulfonyl) imide ([EdMI]-[TFSI]) ionic liquid. The electrochemical exfoliation of graphite electrode to graphene was performed in classical three electrodes setup and by applying mild negative potential, −2.7 V vs. Fc^+/Fc. The generated graphene was characterized by X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), Raman spectroscopy and high-resolution transmission electron microscopy (HR-TEM). Furthermore, FLG were generated using reductive exfoliation in the presence of 1-ferrocenylethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([FcEMIM][TFSI]), a redox ionic liquid. In this article, the generated materials were characterized by XPS and electrochemical measurements.

2   Experimental

2.1   Ionic liquid

1-Ethyl-2,3-dimethylimidazolium bis(trifluoromethane) sulfonimide, EdMI-TFSI, ionic liquid was prepared according to standard procedures [27]. Redox ionic liquid 1-ferrocenylethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide, was prepared according to standard procedures [28]. Prior to each experiment, vacuum pumping carefully dried RTILs overnight and the amount of residual water was measured with Karl Fischer titration (Karl Fischer 652 Metrohm).

2.2   Electrochemical experiments

For the electrochemical experiments a conventional three-electrode cell was used. Platinum wire was used as counter electrode, and polypyrrole coated Pt (Pt/PPy) as reference electrode [29]. All the potentials were reported versus Fc^+/Fc redox couple. Graphite rod (2 mm diameter and 3 cm length from Sodipro, France) was used as working electrode. The electrochemical methods were carried out on CHI 660C (CH instruments, USA). Before any electrochemical measurements the solutions were deoxygenated by bubbling argon gas for 30 min, during the experiment the electrochemical cell remain under argon.

2.3   Few layer graphene suspension

To prepare the FLG suspension, the ionic liquid solution was mixed with 20 mL ethanol. The suspensions were centrifuged at low rotation speed (1000 r/min) for 15 min to remove large agglomerates. The graphene sheets were cleaned using acetonitrile and ethanol, respectively. Next, the generated materials were re-suspended in pure ethanol and this suspension was drop-casted on Au surface for surface analysis.

2.4   Surfaces analysis

The few layer graphene dispersed in ethanol was coated onto Au substrate and subjected to surface analysis. X-ray photoelectron spectra measurements were performed using a Thermo VG Scientific ESCALAB 250 system fitted with a microfocused, monochromatic Al Kα (hv=1486.6 eV, USA) 200 W X-ray source. Data acquisition and processing were achieved with the Avantage software, version 4.67. Raman spectra were recorded at room temperature using a triple spectrometer Jobin Yvon T64000 and a LABRAM HR spectrometer with a solid-state laser (λ=532 nm). TEM studies were performed with a JEOL (JEM-100CX-II, Japan) instrument, operating at 100 keV. AFM experiments, tapping mode, were recorded at room temperature with a Molecular Imaging PicoPlus.

3   Results and discussion

First, the few layered graphene was synthesized by the electrochemical reductive exfoliation in EdMI-TFSI ionic liquid. Figure 1 shows the recorded cyclic voltammetry (CV) at graphite electrode, between 0 to −2.7 V vs. Fc/Fc$^+$, in [EdMI]-[TFSI] ionic liquid.

   The CV shows a reduction process starting at −2 V and oxidation peak at around −1 V attributed to the reversible formation of the carbon-organic phase. The electrochemical system observed in the ionic liquid could be ascribed, by analogy with the previous works [30–33], to the reversible formation of the reduced phase of carbon with a general formula [C$^-$, Cat$^+$, CatA], where Cat$^+$ and A$^-$ represent the cation and anion of the ionic liquid, respectively. This electrochemical process involves an electron transfer coupled with the insertion of the electrolyte cation, imidazolium EdMI$^+$, and leads to the formation of solid phases. In our case, the reduction process is accompanied with the insertion of the ionic liquid cation. Such phenomena have been already demonstrated and are accompanied by a morphological change of the electrode interface [32,34].

   Following that, the graphite electrode was polarized at potential −2.7 V for 4000 s. During the chronoamperometry, black pieces became visible in the ionic liquid solution and the graphite electrode was heavily expended. Scheme 1 illustrates the proposed electrochemical approach for the generation of FLG in ionic liquid media.

   Next, the sediment graphene in ionic liquid was mixed in ethanol, sonicated and then centrifuged at 8000 r/min for 20 min. For surface analysis the FLG in ethanol was spin-coated onto a pre-cleaned Au substrate. XPS is a versatile tool for accurately analyzing the surface chemical composition for a given material. Figure 2 shows the high resolution XPS spectra at the C (1s), N (1s), S (2p) and F (1s) core level
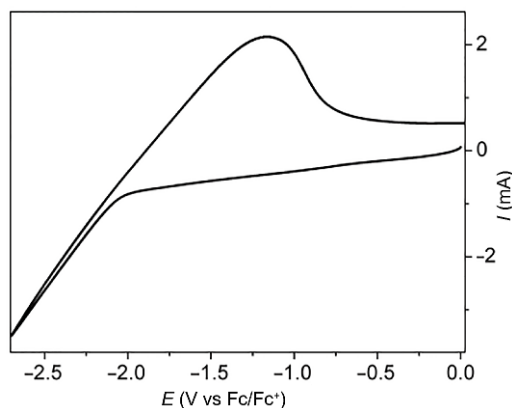
Figure 1   CV of graphite electrode in EdMI-TFSI ionic liquid, scan rate 0.1 V/s.
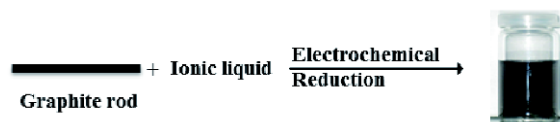
Scheme 1   Electrochemical reductive exfoliation of graphite in ionic liquid.
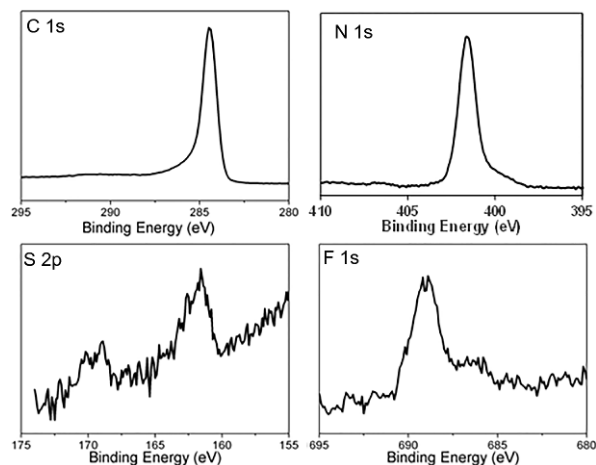
Figure 2   XPS high resolution spectra of FLG deposited on Au of C (1s), N (1s), S (2p) and F (1s).

of the FLG deposited onto an Au surface.

   The C (1s) core level spectrum shows the presence of three peaks components at binding energies of about 284.5, 286.2 and 291.3 eV. The peak centred at 284.5 eV corresponds to sp^2 C=C, and the sharp shape of this peak is characteristics of single-phase, pristine graphene. The peak at 286.2 eV is attributable to amide C–N bands. In addition, small peak at 291.3 eV is observed and attributed to C–F component [35]. The presence of C–N and C–F peaks can be unambiguously assigned to the presence of imidazolium and TFSI anion. The main N (1s) signal appears at 401.7 eV and attributed to imine group from imidazolium ring [36]. Additional peaks at

169 and 687.6 eV are observed and attributed to S (2p) and F (1s), respectively [37]. The presence of these peaks prove that the ionic liquid is linked to the exfoliated FLG. In addition, the atomic ratio of C and O of FLG are 89.3% and 6.4%, respectively. Since, the generated FLG was assisted by the electrochemical reduction in dry ionic liquid and under argon atmosphere, the FLG had low oxygen functionalities, such as carbonyl, epoxide and carboxylic acid group.

Raman spectroscopy is a powerful non-destructive tool to distinguish ordered and disordered crystal structures of carbon. The major Raman features, common to all chemically processed graphene samples, are the D band at 1330 cm^{-1}, G band at 1580 cm^{-1}. The D band is related to the structural defects and partially disordered structures of sp^3 carbon, while the G band is related to vibrational mode of sp^2 carbon atoms [38]. Figure 3(a) shows the Raman spectra of FLG deposited onto an Au substrate. The intensity of the D band is lower when compared to the intensity of the G band. The intensity ration I_D/I_G of the generated graphene is lower than 0.1 suggesting the presence of low density defects. The obtained ratio is in agreement with the reported results in the literature for the generated FLG using various exfoliation methods [11,12,15]. In addition, the presence of a broad and sharp peak at 2720 cm^{-1}, which originates from two phonon double resonance (2D), is a fingerprint for the presence of low defects and also the formation of few layer graphene [39]. The 2D peak at 2720 cm^{-1} is slightly shifted when compared to single or bilayer graphene which could be attributed to the intercalation of the imidazolium cation within the electrochemically exfoliated graphene.

Figure 3(b) shows the AFM image and the cross section profile of FLG. The image reveals the presence of graphene nano-flakes of various thicknesses and with different lateral dimension. The cross-section, realized at different FLG, exhibits a lateral size in the range of few micrometers (1 to 2 μm). The thickness of the FLG is ranged from 4 to 1 nm indicating the presence of few graphene layers. In some cases, the overall thickness is a result of a stacked graphene layer and a step high of about 0.5 nm is observed which could be assigned to the presence of single-layer graphene.

In order to obtain the structural information about the generated FLG, HR-TEM was performed (Figures 3(c, d)). The folded structure of graphene edges leads to evaluate the thickness and the interlayer spacing. Unlike graphite, for multilayer graphene, the adjacent graphene layers derived from electrochemical exfoliation are not parallel but uneven. Figures 3(c, d) clearly reveal the presence of few graphene layers and single graphene layer, respectively, with shallow crumples and lattice spacing of 0.34 nm. In the case of FLG, the interlayer spacing was found to be around 0.5 nm, which is larger than the reported value for reduced graphene. Based on the XPS investigations, this spacing increase is probably due to the presence of ionic liquid intercalated between the
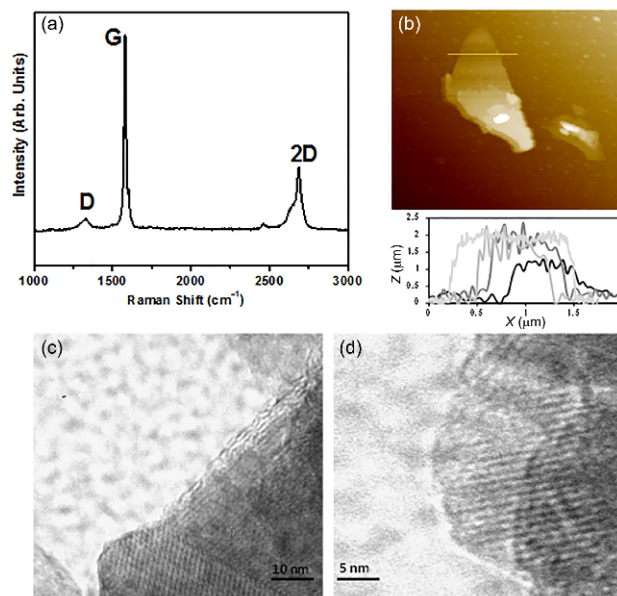

Figure 3 (a) Raman spectra of graphene electrochemically exfoliated in ionic liquid; (b) AFM image of FLG (image size 5×5 μm^2) and the cross section of four different FLG; (c, d) HR-TEM images of the FLG end flakes (color online).

graphene layers. Collectively, the above results confirm the achievement of electrochemical reductive exfoliation of graphite to FLG in ionic liquid. The concentration of the FLG dispersion generated after polarization at −2.7 V during 4000 s was estimated through UV-Vis absorption and found to be in the range of 0.08 mg/mL. The overall yield of FLG was estimated to be in the range of 8 wt%, but this value depends on the applied potential and the polarization time during the reductive exfoliation.

These investigations were complemented by preparing FLG based on the same procedure as described above, but in the presence of redox ionic liquid. Indeed, the graphite electrode was immersed in 1-ferrocenylethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [FcEMIM] [TFSI], and the electrode was polarized at −2.7 V during 4000 s. The use of ferrocenyl based ionic liquid as media for the electrochemical exfoliation leads to generate electroactive functional graphene layer and facilitate the characterization by following the electrochemical signal of the intercalated ferrocenyl moieties. Next, the generated FLG was deposited onto ITO electrode and was characterized by cyclic voltammetry in electrolytic solution (Figure 4(a)) and by XPS (Figure 4(b)).

The electrochemical characterization reveals a redox signal at 0.42 V vs. SCE corresponding to Fc$^+$/Fc redox couple. The presence of this signal confirms the presence of redox ionic liquid on the generated FLG. Moreover, the electrochemical signal exhibits a fast electron transfer as attested by the low peak potential separation suggesting the high con-
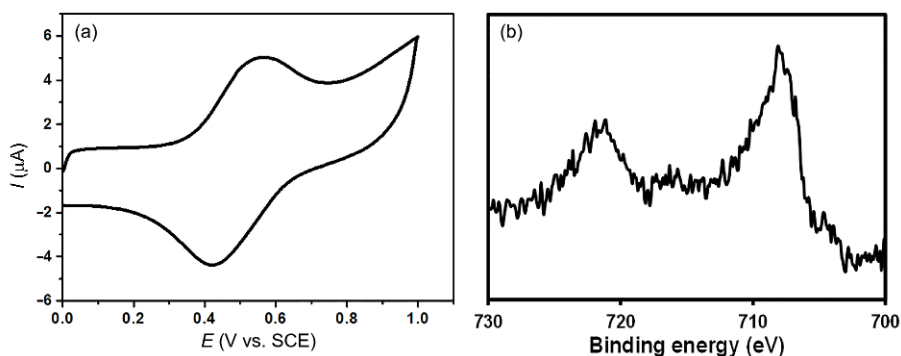
Figure 4   (a) CV response of FLG deposited onto ITO electrode in electrolytic solution (acetonitrile containing 0.1 M Bu₄NBF₄); (b) Fe(2p₃/₂) XPS spectrum of FLG generated in redox ionic liquid.

ductivity of the generated FLG. The Fe (2p) high resolution spectrum (Figure 4(b)) displays two peaks at 708.2 and 720.8 eV attributed to the Fe (2p₃/₂) and Fe (2p₁/₂), respectively. The presence of these peaks at these binding energies values is in agreement with those previously reported for immobilized ferrocenyl moieties onto electrode surface and corresponds to ferrocenyl in its reduced state [40]. In addition to the Fe signal, the XPS investigations exhibit similar spectra as shown in Figure 2 highlighting the presence of the redox ionic liquid and low oxygen functionalities present onto the FLG generated through reductive exfoliation in redox ionic liquid.

4   Conclusions

In summary, few layer graphene has been prepared by electrochemical reductive exfoliation of graphite in ionic liquid and redox ionic liquid using mild negative potential. The graphite electrode was heavily expended after intercalation of the ionic liquid cation into graphite electrode. According to the XPS analysis the proposed method produce FLG containing ionic liquid and prevents high levels of oxidation. Moreover, Raman spectroscopy proves the defectless nature of the graphene flakes. The thicknesses of the generated FLG are ranged from 4 to 1 nm highlighting the formation of few graphene layers as confirmed by HR-TEM images. Finally, the reductive exfoliation was further investigated in presence of redox ionic liquid leading to the formation of redox functionalized FLG.

Conflict of interest   The authors declare that they have no conflict of interest.

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