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Graphene from electrochemical exfoliation and its direct applications in enhanced energy storage devices†

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Graphite was electrochemically exfoliated in mixtures of room temperature ionic liquids and deionized water containing lithium salts to produce functionalized graphenes and such an electrochemical exfoliation technique can be directly used in making primary battery electrodes with significantly enhanced specific energy capacity.

Graphene-based materials are intriguing from the perspective of fundamental science and technology because they are non-toxic, chemically and thermally tolerant, and mechanically robust. Graphene exhibits superior electrical conductivity, high charge carrier mobility (20 $m^2\ V^{-1}\ s^{-1}$),[1,2] high surface area (2600 $m^2\ g^{-1}$)[1,2] and a broad electrochemical window that may be particularly advantageous for its applications in energy storage devices. In addition, graphene can offer both transparency and good conductivity at the same time.

Many methods have already been developed to produce graphene.[3–5] In 2004, Geim and co-workers[4] first reported graphene sheets prepared by mechanical exfoliation (repeated peeling) of highly oriented pyrolytic graphite (HOPG). This method, called the scotch-tape method, is still widely used in many laboratories to obtain pristine perfect structured graphene layers for basic scientific research and for making proof-of-concept devices. However, it is not suitable for mass production. Graphene can also be prepared by thermal decomposition of a SiC wafer under ultrahigh vacuum conditions.[6] However, these samples are composed of a multitude of domains, most of them submicrometre in scale, and are not spatially uniform in number or size over larger length scales. Chemical Vapour Deposition (CVD) is a popular technique for growing graphene. It has been used to grow graphene on metal substrates.[5] CVD has the potential to enable large scale graphene production for electronics applications such as thin film transistors, solar cells and touch panels which require large area graphene sheets in the order of tens of centimetres but always involve transfer of graphene to a desired substrate. Similar to thermal decomposition of SiC, CVD is also an expensive process. Alternative cost-effective ways of graphene synthesis using solution based processes are from chemical reduction of graphene oxide (GO)[3] and liquid phase exfoliation.[7] These methods offer the scope to produce large quantities of graphene cheaply. Particularly, chemical reduction of GO is a simple process and sheets as large as 50 microns have been made and they can then be subsequently chemically modified. Within the chemical methods, recently developed electrochemical exfoliation is regarded as a green method that allows easy tenability of the obtained products by varying the applied potential.[8,9] Sheet resistance of a film is expressed as the number of Ohms of resistance per square of material. Sheet resistance of graphene from chemical reduction of GO is in the range of 1 K to 100 K Ohm sq^{-1} with transmittance below 80%[10,11] or from 31 K to 18 M Ohm sq^{-1} at 95% transmittance,[12,13] while in contrast, sheet resistance of the electrochemical exfoliation of graphite is in the range of 0.015 to 0.21 K Ohm sq^{-1} at 96% transparency.[8,9] Electrochemical exfoliation happens in a mixture of solvents containing liquid with a narrow electrochemical window (*e.g.* water) and liquid with a large electrochemical window, for example, room temperature ionic liquid (RTIL). By choosing different RTILs in an aqueous system, the following theory to explain the RTIL-assisted electrochemical exfoliation of graphite was proposed by Lu *et al.*:[14] (1) electrolysis of water at the electrode produces hydroxyl and oxygen radicals; (2) the oxygen radicals start corroding the graphite anode on edge sites, grain boundaries and defect sites, which results in the opening up of edge sheets; (3) the RTIL anions intercalate within the edge sheets and initiate the electrode expansion; (4) the precipitation of some sheets results in the creation of graphene sheets in solution. These procedures do not necessarily take place in a sequential order, but it is rather the interplay between the electrolysis of water and the intercalation of RTIL ions that are responsible for the production of the sheets. It transforms the nearly plain surface of a graphite foil sheet into a wrinkled and curled morphology. Choice of narrow-electrochemical-window liquid is not limited to water, organic solvents can also be used.[8,9]

In this communication, graphite was electrochemically exfoliated in aqueous solvents containing hydrophilic RTIL, 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF_4]). It is found that addition of lithium salts can facilitate the exfoliation and fluorescent graphene flakes were produced in the solution. The solid part of exfoliated graphite can be directly

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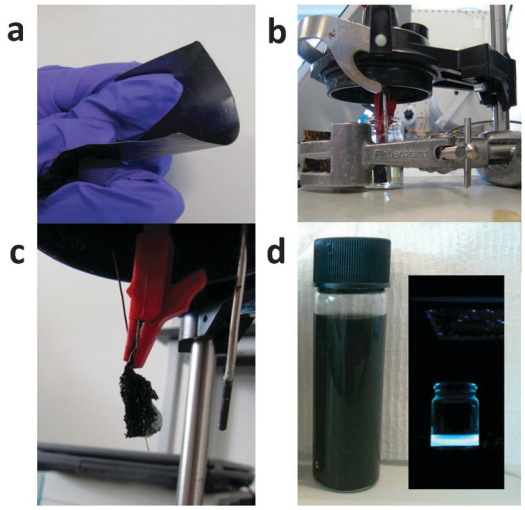

Fig. 1 Electrochemical exfoliation of graphene. (a) Flexible graphite electrode used to exfoliate, (b) electrochemical set-up for the experiment, (c) electrode after exfoliation, (d) final solution with graphene flakes in water solution and UV-induced luminescence from such RTIL functionalized graphenes.

used in primary lithium batteries and shows enhanced specific energy capacity.

All electrochemical exfoliation experiments were carried out by Autolab potentiostats. Flexible graphite (Fig. 1a) was used as a working electrode; a Pt rod was employed as a counter electrode and an Ag/AgCl electrode as a reference within a 3-electrode cell setup as shown in Fig. 1b. At the end of experiments graphite sheets will be exfoliated to a sponge shape electrode as shown in Fig. 1c and the colour of solution will change from transparent to dark brown containing graphene flakes. Graphene flakes were separated and dissolved in water solution and UV-induced luminescence from the graphene solution was observed (Fig. 1d). It was proved that the remaining RTIL is chemically bonded to the graphene flakes and the blue fluorescence upon irradiation with 254 nm UV light may be from the RTIL group.[14]

DI water is necessary to catalyse the sheet unzipping performed by the RTIL anoins (*e.g.* BF_4^- from [BMIM][BF_4]). Exfoliation of graphite in pure [BMIM][BF_4] turned the end product into 'bucky gel', an extremely viscous medium that makes isolation of the products very difficult. In addition, the graphite electrode will not be exfoliated to the expanded volume as the ones from solvents containing DI water. Increasing the water content can increase the radicals and gases generated during water electrolysis and lower the viscosity of solutions to improve the diffusion of RTIL ions penetrating the graphite. However, too much percentage of water will reduce the conductivity of the end product and more GO instead of graphene will constitute the final products. In these series of experiments we optimised the water percentage to 50% in volume. It is believed that anions of the RTIL also influence the exfoliation. 1-Butyl-3-methylimidazolium dicyanamide [BMIM][$N(CN)_2$] was also studied as an exfoliation solvent with various percentages of DI water, but no obvious electrochemical exfoliation was observed under the same experimental conditions. Both [BMIM][BF_4] and [BMIM][$N(CN)_2$] have a broad and stable electrochemical window, and the only difference lies in the size of their anions. The anion size may determine the success of the RTIL ions insertion. Smaller inorganic anions like $BF4^-$ may be more preferable in the exfoliation reaction to bulky anions like $[N(CN)_2]^-$ because they have less steric hindrance and can be intercalated into the graphite more efficiently.

Fig. 2 shows the 50th cycle of cyclic voltammogram during electrochemical exfoliation. Imidazolium based RTIL, [BMIM][BF_4], is very stable across a broad electrochemical window of 5 V (from −2 V to 3 V).

During exfoliation, the graphite electrode grows over time, reaching a final volume that is several times of its initial dimensions. It also leads to the dispersion of micro- and nano-sized carbon species. Colour of the solutions changes from transparent to black, which was associated with graphene suspensions in the literature.[14] Reduction peaks at around −0.8 V and 0.5 V indicate the level of exfoliation. It was noticed that bubbling from working and Pt counter electrodes appears at the voltage of 0.5 V during the reduction scan from 3 V to −2 V. This may be associated with electrolysis of water. With cycle number increases, graphite was exfoliated gradually and the peak at −0.8 V became more and more pronounced and it may be correlated to the level of exfoliation. Influence of lithium salts was studied by addition of 0.5 M $LiClO_4$ into the exfoliation solvents. It has been shown that addition of lithium salt, $LiClO_4$, facilitates the electrochemical exfoliation and intensities of both peaks at −0.8 V and 0.5 V increase as shown in Fig. 2. Exfoliation in solvents containing lithium salts is more efficient and effective and this may be partly due to the improved ionic conductivity of the solvents. By dissolving lithium salts such as $LiClO_4$ into the RTIL aqueous solution, it is expected that both the lithium ions and the RTIL anions will intercalate the graphitic material. Solvated Li^+ will enter the inter-graphene layers by decomposition of the solvent; leading to lithium-rich graphitic material.

Lithium ions (Li^+) are the second smallest cations to protons (H^+), and are the essential mobile ions in lithium batteries. Graphenes have been tried in different energy storage devices.[15,16] Electrochemical exfoliation may provide us a solution to fabricate a high-energy density battery electrode in

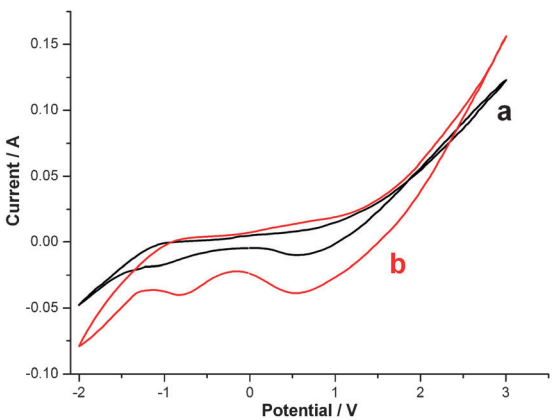

Fig. 2 Cyclic voltammogram of electrochemical exfoliation of graphite. (a) Exfoliation in the 1 : 1 (v/v) mixture of [BMIM][BF_4] and DI water. (b) Exfoliation in the 1 : 1 (v/v) mixture of [BMIM][BF_4] and DI water containing 0.5 M $LiClO_4$. Voltage *vs.* Ag/AgCl.

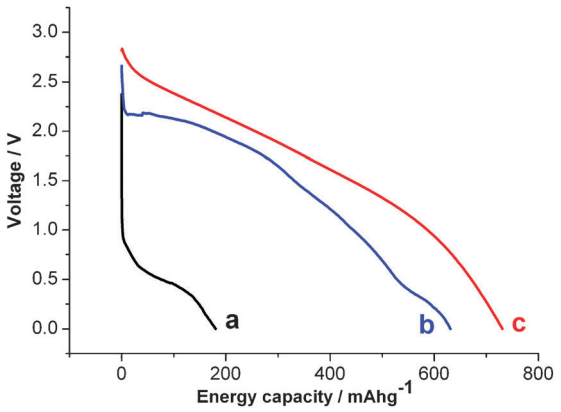

Fig. 3 Discharge curve of the primary batteries made of (a) graphite, and of exfoliated graphene from (b) the 1 : 1 (v/v) mixture of [BMIM][BF_4] and DI water, (c) 1 : 1 (v/v) mixture of [BMIM][BF_4] and DI water containing 0.5 M $LiClO_4$.

one step by intercalating Li^+ ions into the graphitic material during exfoliation, leading to the fabrication of a lithium battery electrode in its charged state. To prove this concept, the sponge-shape exfoliated electrodes were directly used as electrodes in lithium batteries. The assembled coin cells were discharged with a Maccor battery tester at a constant current density of 100 mA g^{-1} and Fig. 3 compares the discharge behaviour of primary batteries with different carbon based cathodes made from pure flexible graphite, exfoliated graphene from the 1 : 1 (v/v) mixture of [BMIM][BF_4] and DI water and from the same solution containing 0.5 M $LiClO_4$.

Batteries made from graphite have a specific capacity of about 200 mA h g^{-1}, and the voltage drops quickly during the discharging process to reach a plateau at about 0.5 V. When using exfoliated graphene from RTIL, the specific capacity improves to about 640 mA h g^{-1} and the voltage of plateau increases to 2 V. This may be due to the increased effective surface areas created during electrochemical exfoliation. Specific capacity reaches the highest to about 750 mA h g^{-1} when using the graphene exfoliated from an RTIL–DI water mixture containing 0.5 M $LiClO_4$. In addition, open circuit voltage of the cell is further improved to 2.8 V as compared with 2.2 V of the cell made from pure flexible graphite. This indicates that intercalated lithium ions also reduce the internal resistance of the battery.

In conclusion, electrochemical exfoliation has the benefits of cost-effectiveness as a chemical reduction method but provides graphenes with higher conductivity. The reduction level of graphene, exfoliation level and size of graphene flakes can be controlled by applying different electrochemical parameters and/or by choosing various RTIL solutions. UV-induced luminescence from the exfoliated graphene can be observed. By adding lithium salts into exfoliation solvents, lithium ions can facilitate the exfoliation process, inserted into graphite, and specific energy capacity increases 4 times compared with a pure graphite electrode. Thus, this method can make the enhanced primary battery electrode in one step. The highly conductive property and enormous active area of graphene may enable it as both a lithium ion and an electronic conductor to reduce both size and weight of batteries without sacrificing the energy capacity. Graphene provides high conductivity and transparency at the same time and it is a flexible building block to make construction of transparent or semi-transparent energy storage devices feasible in the future.

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