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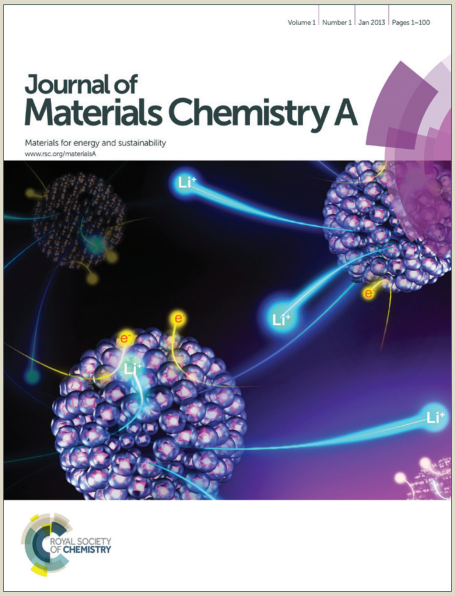

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ARTICLE TYPE

A facile and fast electrochemical route to produce functional few-layer graphene sheets for lithium battery anode application

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A simple approach for the production of polymer functionalized graphene sheets is reported. The resulting polyacrylonitrile chemisorbed on graphene sheets are made of 1 to 5 layers, with a large majority of single-layer graphene sheets. This novel functionalized graphene exhibits good rate capability as anode in the Li-ion batteries without added conductive additive or binder.

Graphene, a monolayer sheet of sp^2-hybridized carbon atoms with two dimensional hexagonal lattice structure,[1] attracts great research interest due to its intrinsic characteristics such as physical, mechanical and electrical properties since the discovery of its freestanding form in 2004.[2] Due to its superior electrical conductivity,[3] excellent mechanical flexibility,[4] and high surface area of over 2600 m^2.g^{-1},[5] graphene is therefore a promising materials for application in energy storage devices such as lithium-ions batteries (LIBs)[6] or super-capacitors.[7] Graphene has been already proved as a reliable anode materials for LIBs, demonstrating enhanced capacity and increased high rate performance due to large reversible lithium storage ability.[8-10] The development of scalable methods for generating functional graphene sheets for LIBs is therefore of great interest because currently available electrode materials may not meet the high-energy demands for electronic devices and electric vehicles. To produce graphene sheets, many methods have already been developed such as the micro-mechanical[11] and liquid-phase exfoliation of graphite,[12] chemical vapour deposition (CVD),[13] epitaxial growth[14] as well as reduction of graphene oxide (GO).[15] Electrochemical exfoliation of graphite represents a promising alternative for large-scale production of graphene sheets. Compared to previously reported techniques and methods, this electrochemical process has several advantages such as simplicity, high productivity with short processing times and is economically viabile.[16] Electrochemical exfoliation of graphite into graphene has been performed mainly using aqueous acid and salt electrolytes as well as using ionic liquids.[17-18] Exfoliation of graphite using acidic electrolytes produces graphene flakes with large lateral size but with significant oxygen-containing functional groups. Indeed, the corrosive acid and high potential conditions cause the occurrence of oxidative side reactions and the introduction of a considerable amount of structural defects in graphene.[19] Recently, Wang *et al*.[20] and Zhong *et al*.[21] reported electrochemical expansion of graphite by electrolysis in a propylene carbonate (PC)/Li$^+$ (or/and tetra-n-tetrabutylammonium (TBA) salt) electrolyte without using oxidative agents. The applied high potentials (-15V) activated the intercalation of Li$^+$/PC (or/and TBA/PC) into graphite, promoting its exfoliation, and leading to the recovery of graphene sheets. Nevertheless, the prolonged sonication and high working voltage still produces a defect rich material.

A recent work from Mao *and co-workers.*[22] reports a promising strategy, wherein, Few Layer Graphene (FLG) flakes were synthesized from both a graphite anode and a graphite cathode in protic ionic liquids at a low polarization potential (3 V). However, the graphene flakes obtained from the cathode were relatively small, displayed moderate electrical conductivity (1.11 S.cm^{-1}) and with no specific/pre-designed surface functionality. Furthermore, the graphene obtained from the anode was found to be fully oxidized.

This communication describes an original new method for the preparation of high quality and chemically functionalized few-layer graphene sheets in one pot process by electrochemical exfoliation of graphite at low working potentials using an acid-free and oxidant-free electrolyte. The electrochemical procedure for the exfoliation of HOPG is also accompanied by *in-situ* functionalization with chemically grafted polymer chains. The developed process allows us to intercalate simultaneously the electrolyte ammonium cation and a vinyl monomer (acrylonitrile, AN) into HOPG (Figure 1a). Subsequently, electropolymerization of AN leads to the exfoliation and stabilization of the graphene sheets by the so-produced polyacrylonitrile (PAN).

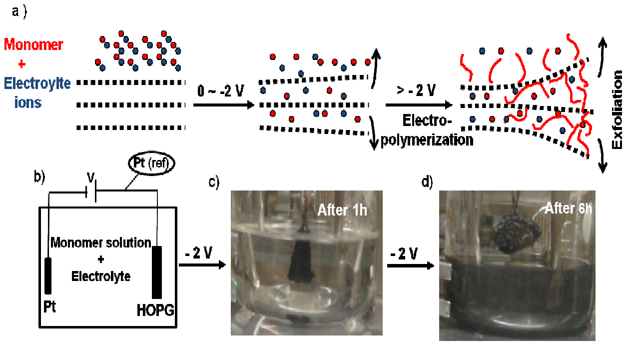

Fig. 1: Schematic illustration of (a) the exfoliation mechanism of HOPG and (b) of the experimental setup used. (c) Images of the HOPG electrode after electrochemical exfoliation after 1h and (d) 6h at an applied bias of -2 V.

The chemisorbed PAN at the surface of graphene is exploited for boosting the electrical conductivity of graphene films upon appropriate thermal treatment. The lithium storage capabilities of PAN-functionalized graphene sheets have been also evaluated. A binder-free anode material with a high specific capacity and good cycling stability was successfully prepared.

The experimental set-up for the electropolymerization assisted exfoliation of HOPG is shown in Figure 1b. In a typical experiment, the HOPG working electrode is immersed into a DMF electrolyte containing AN monomer and tetraethyl ammonium perchlorate as supporting salt under nitrogen atmosphere and at room temperature.[23-25] Subsequently, HOPG is cathodically polarized (0 ~ - 2,2 V) using a classical three-electrode setup and platinum as a reference electrode. Under these conditions, the onset of the AN electropolymerization was detected at about -2 V. Fig.1a depicts the underlying exfoliation mechanism, the whole process being resumed to two main steps: (1) the ammonium cations are driven by the electric field into the interlayer between the graphene layers;[26,27] (2) the graphene is slightly exfoliated due to the insertion of cations (Fig. 1c) permitting the intercalation of AN and therefore the electropolymerization between the graphite layers, resulting on the full exfoliation of the HOPG electrode after long exposure (Fig. 1d). Part of these electropolymerized PAN chains are chemisorbed at the surface of the exfoliated graphene sheet by surface initiated polymerization of AN that enhances the stability of graphene suspension. Suspension of those modified graphene at 1mg/mL in DMF are stable for few weeks without stirring.

Fig. S1 shows a typical voltametric curve for the AN electropolymerisation. The current increase observed between -1.75 and -2 V corresponds to the electropolymerization of intercalated AN between graphene layers.[28] Complete exfoliation of the HOPG electrode was observed within six hours of electrode polarization at -2V (Fig.1d). A short ultrasonication treatment was applied to fully disperse the expanded HOPG chunk. The dispersed graphene sheets were subsequently recovered by filtration and washed several times by DMF to remove the physisorbed PAN chains produced during the electropolymerization process. Complete removal of PAN by solvent washing was not achieved, significative of strong covalent binding to graphene sheets.

Exfoliated graphene was subjected to thermogravimetric analysis (TGA, Fig. 2a) to probe and quantify the amount of chemisorbed PAN. The weight loss corresponding to the degradation of the polymer observed between 220 and 500°C represents only 15 wt.% of the exfoliated material. In a control experiment, PAN was subjected to TGA analysis performed in similar conditions resulting in about 65% mass loss (Fig. S2 in ESI†), the remaining residue (35wt%) being carbonaceous materials. As such, the content of PAN in Gr-*g*-PAN composite is estimated to 20 wt.%. The low polymer content is significative of efficient and high surface density grafting chemisorption process.

Raman spectroscopy is a technique that provides information about the crystallography and carbon defects of the as-prepared materials.[29-31] Indeed, the weak D band at 1350 cm^{-1} indicates the disorder of the edge carbons whereas the G band at 1580 cm^{-1} is related to the ordered in-plane sp^2 carbon atoms. Therefore, the intensity ratio (I_D/I_G) is generally accepted to represent the defective carbon fraction. Fig. 2b,c and d present the Raman spectra of pristine HOPG, exfoliated graphene (Gr-*g*-PAN) and the thermally annealed Gr-*g*-PAN at 250°C under air. The I_D/I_G intensity ratio (before and after thermal annealing) of 0.06 indicates the low-level of defects of Gr-*g*-PAN compared to those obtained from GO which is typically above 0.8.[32] This very low defect density supports the beneficial effect of the electrochemical exfoliation of HOPG that occurs at low operation voltage (-2V). Moreover, we also notice small peaks around 1450 cm^{-1} and 2240 cm^{-1} that are assigned to the vibrations chains of nitrile function of PAN.[33] These peaks disappear after the thermal annealing at 250°C (Fig. 3d) due to the stabilization of PAN into condensed heterocyclic structure.[34,35] These results further confirm the presence of PAN in our exfoliated graphene sheets.

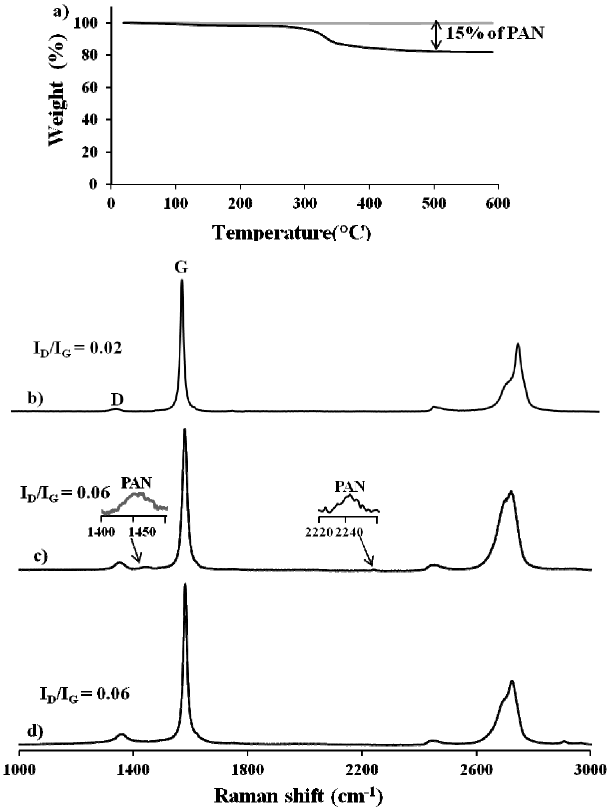

Fig.2: a) TGA thermogram of exfloliated graphene (Gr-*g*-PAN; dark) and pristine HOPG (grey). Raman spectra (647.1 nm laser excitation) for b) pristine HOPG, c) exfoliated Gr-*g*-PAN, d) exfoliated Graphene-PAN film annealed at 250°C under air conditions for 1 hours.

Figs. 3a and 3b show AFM images of the exfoliated graphene sheets spin coated onto mica substrate. The graphene sheets are recognizable from both, topographic (Fig. 3a) and phase (Fig. 3b) signals. The lateral size of graphene flakes ranges from 0.5 to 6 µm (see also Fig. S3 in ESI† for a large-area AFM scan). The statistical analysis (Fig. 3c) shows that the large majority of the graphene sheets have a thickness comprised between 0.5 and 1.5 nm. Therefore, the number of layers in the exfoliated graphene sheets ranges from 1 to 2 layers, with a large majority of single layer graphene.

We notice on the topogaphic images (Fig. 3a) the presence of a few PAN aggregates (white spots) onto the surface and between the graphene sheets. AFM phase images (Fig. 3b) also reveal the presence of holes in the graphene sheet. Fig. 3d shows a TEM image of a smaller graphene sheet with 500 nm lateral size.

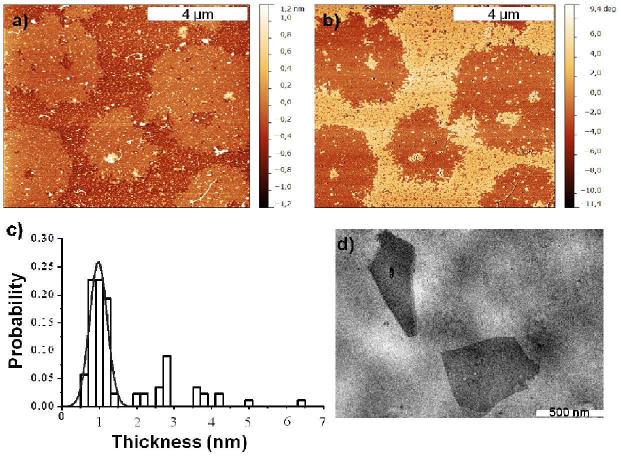

Fig. 3. Height (a) and phase (b) acoustic intermittent contact mode AFM images of exfoliated graphene sheet solution (0.1 mg/mL in DMF) spin-coated onto a mica substrate. c) Statistical thickness analysis of the graphene sheets. d) TEM image of small exfoliated graphene sheet.

X-ray diffraction (XRD) is a suitable technique for evidencing the exfoliation of HOPG[20] and is therefore used for characterizing our modified graphene sheets (Gr-*g*-PAN). Fig. S4 shows the reflection characteristic of the π-π stacked layers for the original HOPG. This reflection almost completely vanishes for Gr-*g*-PAN, supporting the exfoliation of the graphene layers of HOPG during the electropolymerization process.

To probe the electrical conductivity, a thin film of exfoliated Gr-*g*-PAN was deposited on a glass substrate. For that, a dispersion of Gr-*g*-PAN in DMF (1 mg/mL) was drop-casted on the substrate, followed by the addition of a small amount of water, a non-solvent for PAN (see methods in ESI). Graphene sheets aggregated onto glass due to the precipitation of PAN covering the graphene surface. The solvent was then evaporated by heating the modified substrate at 140°C for a few minutes under air. The obtained film presented high homogeneity as observed by SEM (Fig. S6 in ESI†). The thickness of the film measured by AFM was about 370 nm. The electrical conductivity of the prepared film was measured by the method of volume resistivity (measurement method described in ESI†). The measurements were performed onto rectangular (4 mm × 7 mm) graphene sheet film deposited on glass substrate. Films exhibit linear I-V behavior (Fig. S7 in ESI†), confirming ohmic contact between the graphene film and the electrodes. The electrical conductivity (σ) of the film is high with a value of 8.1 S.cm^{-1}. Importantly, the annealing of the film at 250°C under air boosted the electrical conductivity of the composite by a factor of 20 ($\sigma = 182.1$ S.cm^{-1}), whereas the measured conductivity of composite reduced GO/PAN (10% of PAN) treated in the same condition is only about 64.4 S.cm^{-1}. This exceptional increase in conductivity is the result of the stabilization of chemisorbed-PAN into condensed conjugated heterocyclic structure at the surface of graphene sheets that improves contacts between graphene sheets.

The electrochemical lithium storage behavior of the Gr-*g*-PAN sheets was finally evaluated with no added conductive additive or polymer binder. Indeed, most of the research efforts have used polymeric binders in the anode that degrade the specific capacity, and the power performance of the LIBs.[36] Our PAN grafted graphene dispersed in DMF were directly employed and coated on Cu foil (cathode preparation and measurement method described in ESI†). Fig. 4 shows the capacity retention and the voltage curves of the PAN functionalized graphene sheets cycled between 0.01 and 2V cycled at a current density of 50mA/g. The charge discharge profiles show the characteristic features of the carbon based anodes. A low voltage plateau typical to graphene-based lithium anodes is observed at 0.2 V. The first discharge curve (inset to Fig. 4a) shows an irreversible plateau at 0.7 - 0.8V corresponding to the solid electrolyte interphase (SEI) formation.[37] This is a common behavior observed in carbon based anodes and is associated to the decomposition of the electrolyte and formation of a passivation layer composed of mixed organic and inorganic compounds. The irreversible capacity observed at the first cycle could be attributed to high specific surface area of the exfoliated graphene flakes and electrolyte decomposition. SEI formation is also observed during the second discharge cycle although to a lesser extent. The lithium reaction at the graphene surface could involve degradation of the graphene - PAN interface, leading to exposure of fresh graphene surface where new SEI will form. Optimization is being underway in order to stabilize the PAN functionalized graphene sheets and reduce the irreversible capacity loss at the first cycle. Nevertheless, a reversible capacity of 300mAh/g is obtained after more than 200 cycles evidencing the good stability of the Gr-*g*-PAN electrode material.

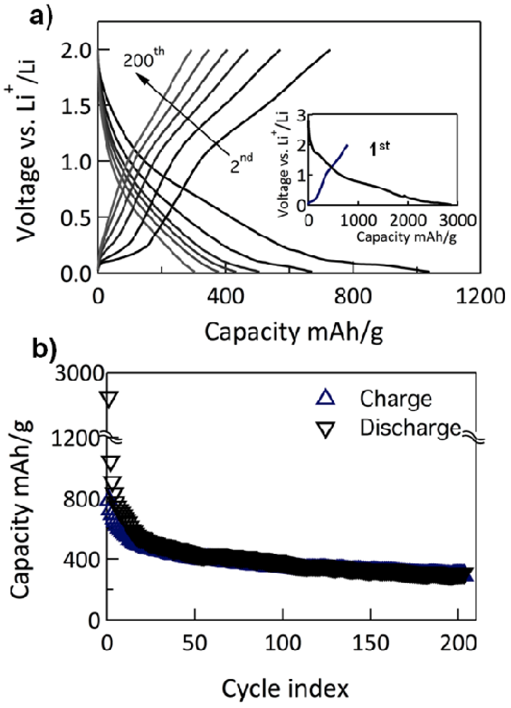

Fig 4: (a) Discharge and charge profiles and (b) cycling performance of the Gr-g-PAN composite. Inset in (a): first cycle charge discharge plots.

In conclusion, we have developed a simple and efficient one-pot electrochemical method for the exfoliation and functionalization of graphene sheets with polyacrylonitrile. Under low cathodic working potentials (~ - 2V), we were able to intercalate and electropolymerize acrylonitrile between the graphite layer. The PAN growing chains trigger the exfoliation of HOPG electrode, leading to functionalized graphene sheets (Gr-*g*-PAN) containing 20 wt% PAN. The low working voltage reduces considerably the degradation of graphene sheets as evidenced by Raman analysis. Homogeneous films containing these modified graphene were formed onto glass and displayed high electrical conductivities (8.1 S.cm^{-1}). Importantly, an appropriate thermal annealing boosts the electrical conductivity of the prepared films by 2000%, leading to highly conductive thin-film material (~ 182.1 $S.cm^{-1}$). The Gr-g-PAN composite displays enhanced lithium storage performance delivering a capacity of 300 $mAhg^{-1}$ for more than 200 cycles at the current density of 50 mAg^{-1}. This work provides an efficient approach to obtain high-quality, cost-effective, and scalable production of "functional graphene inks", which may pave the way toward future applications in flexible electronics and energy storage applications in thin film batteries.

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Notes and references

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A facile and fast electrochemical route to produce functional few-layer graphene sheets for lithium battery anode application

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Abstract:

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