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Abstract

Electrochemical exfoliation of graphite is an emerging approach to provide large scale, low cost, efficient and reliable production of high quality, low defect and solution-processable graphene. The use of a sulphuric acid electrolyte allows rapid and efficient anodic graphite exfoliation. However, the highly oxidative process in this electrolyte promotes hydroxyl radicals. These degrade the carbon lattice structurally, hence compromising the quality of graphene produced. Here, we report a simple and effective way to overcome this challenge; the use of an additive to scavenge hydroxyl radicals. The addition of a small volume percentage of ethylene glycol acts to scavenge hydroxyl radicals. Furthermore, it is readily adsorbed onto the intercalated graphite surface, and therefore also serves as an oxidative prevention layer. As a result, the damage on the graphitic structure is greatly minimized, resulting in a low defect and high quality few layers graphene, with high yield (>80%) and a low degree of oxidation with a C/O ratio of 16.9. The graphene solution-processability is readily tuned and improved with stable dispersions up to 5 mg/mL in dimethylformamide. This new strategy of a simple and low cost dual purpose additive in scavenging hydroxyl radicals and providing an oxidative prevention layer to efficiently tune the graphene quality and solution-processability; holds promise in industrial scale mass production of high quality graphene.

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Tunable solution-processable anodic exfoliated graphene

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Keywords: graphene; electrochemical exfoliation; ethylene glycol; low defect

Abstract

Electrochemical exfoliation of graphite is an emerging approach to provide large scale, low cost, efficient and reliable production of high quality, low defect and solution-processable graphene. The use of a sulphuric acid electrolyte allows rapid and efficient anodic graphite exfoliation. However, the highly oxidative process in this electrolyte promotes hydroxyl radicals. These degrade the carbon lattice structurally, hence compromising the quality of graphene produced. Here, we report a simple and effective way to overcome this challenge; the use of an additive to scavenge hydroxyl radicals. The addition of a small volume percentage of ethylene glycol acts to scavenge hydroxyl radicals. Furthermore, it is readily adsorbed onto the intercalated graphite surface, and therefore also serves as an oxidative prevention layer. As a result, the damage on the graphitic structure is greatly minimised, resulting in a low defect and high quality few layers graphene, with high yield (> 80 %) and a low degree of oxidation with a C/O ratio of 16.9. The graphene solution-processability is readily tuned and improved with

stable dispersions up to 5 mg/ml in dimethylformamide. This new strategy of a simple and low cost dual purposes additive in scavenge hydroxyl radicals and providing an oxidative prevention layer efficiently tuning the graphene quality and solution-processability; holds promise in industrial scale mass production of high quality graphene.

1.0 Introduction

Over the past 10 years, intensive research reveals outstanding physical and chemical properties of graphene; this two-dimensional carbon material shows considerable promise in a wide range of applications including: electronics, energy conversion/storage, catalysis and biomedicine [1-4]. The performance of the graphene-based devices is known to vary significantly depending on the quality of the material [4-6]. As such, bypassing a key bottleneck associated with developing applications for this material depends upon finding methods to produce high quality graphene at low cost and high volume.

Among the top-down approaches, direct liquid exfoliation of graphite in the liquid phase by ultrasonication and shear forces can produce a very high quality, defect-free graphene, but it suffers from a very low exfoliation yield [7-9]. Chemical exfoliation of graphite to graphene oxide, based on the widely employed modified Hummers method, provides an attractive means of producing large quantities of graphene oxide and reduced graphene oxide [10-11]. However, harsh chemical oxidation resulting in graphitic lattice typically contains significant structural defects and oxygen groups. In comparison, electrochemical exfoliation offers a method that allows both mass production of graphene, with a relatively lower number of surface defects [12-15].

Surface defects in graphene produced by anodic exfoliation are induced by the generation of highly oxidative hydroxyl and oxygen radicals, which attack the graphitic

structure and introduce oxygen-containing functional groups; hence counter strategies focus on how to mitigate such effects. Attempts have been made in raising the pH of the electrolyte either by exfoliation in basic solutions or by lowering the pH of acidic solutions by the addition of base [16-17], but this process results in slower rate of exfoliation and a lower yield. Similar observation as is the case with the exfoliations in ionic liquids [18, 19] and surfactant such as sodium dodecyl sulfate [20]. More recently, Parvez et. al. used neutral pH inorganic salts such as $(\text{NH}_4)_2\text{SO}_4$ as the electrolyte [21]. The use of reducing agents, in particular (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO), as an additive to the $(\text{NH}_4)_2\text{SO}_4$ was found to further inhibit the oxidation and structural degradation of the graphene lattice [22]. Munuera et. al. have used sulfonated aromatic hydrocarbons which facilitate graphite exfoliation in addition to preventing oxidation [23], with disodium naphthalene-1,5-disulfonate (SNDS) was found to be the best performing electrolyte.

However, those two most effective electrolyte/additive (i.e. TEMPO and SNDS) are complex and relatively expensive. For practical, and low cost mass production; it is highly desirable if the electrolyte and oxidative-preventing reagents are made from a widely available, low cost and simpler compounds. From an economical and industrial perspective, an acidic electrolyte such as H_2SO_4 which offers a faster and efficient exfoliation, is preferable to a neutral or alkaline counterpart. Here, we propose the use of inexpensive and widely available ethylene glycol (ETG) as an effective additive to the H_2SO_4 electrolyte. ETG is attractive as it is a simple organic compound with only hydroxyl groups as the active moiety. ETG has been widely employed for various electrochemical experiments [24-26]. We demonstrate that an addition of 2 vol % ETG in 0.5 M H_2SO_4 solution dramatically lowers the defect density of the graphene structure, and greatly enhances the graphene dispersibility in DMF with a stable dispersion up to 5 mg mL^{-1} . Comparatively, melamine as an additive in H_2SO_4 electrolyte was only capable of attaining a stable dispersion in DMF of 0.2 mg mL^{-1} [27].

2.0 Results and discussion

Figure 1 illustrates the strategy we have employed to produce low-defect electrochemically exfoliated graphene flakes in H_2SO_4 electrolyte. Upon applying a highly oxidative potential during the exfoliation process, the water electrolysis process generated radicals such as $\text{HO}^\bullet$, and these are destructive to the graphitic structure. Such radicals result in a high density of defects consisting of oxygen-containing functional groups, compromising the quality of the exfoliated graphene. With the introduction of a few vol. % of ETG as an additive (Figure 2a), we propose that $\text{HO}^\bullet$ radicals instead will be consumed via the oxidation of ETG, generating CO_2 and water. ETG is known to be a $\text{HO}^\bullet$ scavenger, whereby it is oxidised by multiple $\text{HO}^\bullet$ to form intermediates such as glycol-aldehyde, glycolic acid, oxalic acid and formic acid, before conversion to CO_2 and water [28-32]. Furthermore, ETG is readily and efficiently adsorbed onto the intercalated graphene layer and forms a protective layer preventing oxidation of the graphene by $\text{HO}^\bullet$ and $\text{O}_2^\bullet$. Hence, the presence of ETG in both surface-confined and in solution-phase offers dual protection and results in production of a low-defect anodic exfoliated graphene.

To validate our proposed concept, we first examined the cyclic voltammograms of the intercalated graphite foils in contact with different concentrations of ETG in 0.5 M H_2SO_4 solution (Figures 2b-c). The voltammograms were recorded by a potentiostat in a two-electrode setup, which was identical to that performed in constant-voltage anodic exfoliation with a dc power supply. Up to 3.0 V, the intercalated graphite remained intact with a minimal exfoliation. The presence of ETG resulting in the peaks corresponding to adsorption/desorption processes. Detailed examination of the peaks in Figure 2c shows that the addition of 1 vol. % ETG results in the appearance of an adsorption peak at ~ 1.15 V in the forward scan. Increasing the ETG concentration to 2 and 3 vol. % not only shows the expected increase in the area of this peak but also shifts the potential ~ 0.15 V less positive for each increment in ETG. This also indicates

favourable adsorption of ETG on the graphite electrode. The backward desorption peaks also appear but with a smaller peak area indicating that the consumption of ETG occurred during the water oxidation process. A control experiment in the absence of ETG (0ETG) did not observe such peaks. The efficient adsorption of ETG on graphite is shown by the appearance of those peaks even at fast scan rates (see Figure S1). Comparatively, electro-oxidation of ETG in H₂SO₄ using a platinum electrode did not exhibit adsorption behaviour as in graphite foil (Figure S2).

In an acidic medium, the complete electro-oxidation of ETG involves oxidation to CO₂ with 10 electrons per glycol molecule as shown in equation 1 [33].

Therefore, apart from acting as a hydroxyl radical scavenger (as shown in Figure 1), the presence of ETG that adsorbed on the intercalated graphite surface also serves as a buffer layer allowing electro-oxidation of ETG as in Eq. 1, which suppresses the water oxidation process that generates hydroxyl radicals. This is further verified by the current-time profile as a function of different concentrations of ETG during the exfoliation process in H₂SO₄ electrolyte (Figure 2e). The significant drop in current after 2 min in 0.5 M H₂SO₄ solution was as a result of graphite foil being exfoliated to graphene flakes and dispersed in the solution. A complete exfoliation (see photograph at Figure 2e) occurs within ~ 3 min in 0.5 M H₂SO₄ solution. Since the foil is still in electrical contact with the electrolyte, therefore some current remained. With the increased ETG concentration from 1 to 2 vol. %, prolonged exfoliation duration is seen. Slower exfoliation is particularly obvious at 2 vol. % where the current recorded a slight increase at the first 9 mins, with slower releases of exfoliated graphene flakes in comparison to 0ETG and 1ETG. At 3 vol. %, the exfoliation efficiency significantly dropped and a much longer time is required for exfoliation with complete exfoliation is unattainable. In a control experiment in pure ETG, as expected, no exfoliation or graphite intercalation was

shown as ETG is not a charged species (see Figure 2d). Electrolytes containing 25 % and 50 % ETG also did not observe exfoliation. Our data and control experiments therefore identify the roles of ETG as a HO[•] scavenger, and buffering/controlling the reaction rate of the intercalation and exfoliation processes. The buffering capacity and concentration dependency of ethylene glycol are consistent with the believe that radicals play essential role in opening graphitic structure that facilitate intercalation of anions [21]. At 2 vol % of ethylene glycol, excessive radicals generated at a high voltage of 10V would be captured which still allow the complete of exfoliation process at a slower rate. Nevertheless, excessive ethylene glycol at 3 vol %, retard the exfoliation process as insufficient radicals would be available to open graphitic structure for subsequent anions intercalation.

Since ETG is miscible in water, it is readily removed and washed from the exfoliated graphene by immersion in deionized water under gentle stirring (Figure 2a). The water was replaced several times before vacuum filtration, and the graphene was then dried. Moreover, graphene with residual ETG was found to have a very poor dispersibility in DMF (Figure S3). As poor exfoliation process at 3 vol % ETG, we have selected mainly the exfoliated graphene produced from solution of 2 vol % ETG in 0.5 M H₂SO₄ (henceforth denoted as H₂SO₄ + 2ETG) for further characterization. The well-washed and dried graphene power obtained from H₂SO₄ + 2ETG was dispersed in DMF by mild sonication for 30 min. Concentrations of graphene used were 1, 2.5, 5, and 7.5 mg per ml of DMF. Comparison was made with graphene exfoliated in 0.5 M H₂SO₄ (Figure 3a). For H₂SO₄ + 2ETG a homogeneous dispersion of graphene (5 mg/ml) was stable for several weeks without apparent agglomeration. In contrast, 0.5 M H₂SO₄ without ETG (2.5 mg/ml) shows poor dispersibility, with agglomeration apparent after just 1 day and in the case of the 1 mg/ml the dispersion is only stable for several days. The graphene flakes of H₂SO₄ + 2ETG were found to have average sizes of 0.5 to 2 μm, with the majority

having a thickness of 1-4 layers (Figures 3b-d), and obtained at a high exfoliated yield of > 80 %. Each single layer is corresponding to $\sim 0.7 \pm 0.1$ nm of graphene on silicon wafer [34].

To examine the influence of ETG in lowering the defect concentration in the graphene, we acquired Raman spectra (Figure 4a) with a 632 nm excited laser from exfoliated graphene obtained via H_2SO_4 as well as $\text{H}_2\text{SO}_4 + 2\text{ETG}$. The ratio of the D to G peak (I_D/I_G) of graphene produced from $\text{H}_2\text{SO}_4 + 2\text{ETG}$ was 0.18 ± 0.05 , being much lower than that for pure H_2SO_4 (0.9 ± 0.1). The lower intensity ratio of I_D/I_G indicates the graphene has a fewer defects. X-Ray diffraction (XRD) patterns in Figure 4b suggest that $\text{H}_2\text{SO}_4 + 2\text{ETG}$ contained fewer functional groups, with a peak at 26.54° (nearer to the XRD peak obtained for graphite foil at 26.6°). Furthermore, the XRD peak obtained from the H_2SO_4 derived material (26.47°) is broader and shifted to the lower angles compared with a pure graphite foil. This indicates that the exfoliated graphene from H_2SO_4 only electrolyte has a higher concentration of functional groups [21].

X-ray photoelectron spectroscopy (XPS) was used to determine the chemical composition and variation of the exfoliated graphene; Figures 4c-d show the C1s core level spectra of H_2SO_4 and $\text{H}_2\text{SO}_4 + 2\text{ETG}$ -derived materials respectively. Deconvolution of the C1s spectra results in an asymmetric primary peak at 284.5 eV corresponding to C=C bonding, along with the associated $\pi-\pi^*$ shakeup peak at approximately 291 eV. Additional peaks associated with undesired functional groups are located at binding energies of 286.3 (C-OH, C-O-C), 287.8 (C=O) and 288.9 (O-C=O) eV. Peak fitting reveals the $\text{H}_2\text{SO}_4 + 2\text{ETG}$ sample produced less signal from the various O-containing groups as compared with the H_2SO_4 -derived graphene. The former material thus has a higher quality graphitic network, further evidenced by a C/O ratio of 16.9, as compared to 9.2 for the H_2SO_4 -derived material (see Table S1). FTIR data for 0, 1 and 2 vol % ETG-derived graphene shows how ETG additions reduce the concentration of oxygen functional groups (Figure S4). The STEM data shown in Figs 4e-4f and Fig. S5 is fully consistent with the above characterization, whereby the sample anodized

in H₂SO₄ showed a much lower uniformity in thickness (1-12 monolayers of graphene), compared with the 2ETG-derived material (1-3 monolayers). Graphene exfoliated in the presence of ETG (Figure 4f) has a lower surface defect concentration and a much smoother surface. All these investigations indicate that the presence of 2 vol% of ETG in 0.5 M H₂SO₄ electrolyte improves significantly the quality of the graphene by producing a less defective graphene, containing a greatly reduced concentration of oxygen functional groups.

We have evaluated functional applications of the synthesized graphene. Graphene produced in H₂SO₄-2ETG is well dispersed in DMF (Figure 3a), readily used as a highly conductive graphene-based ink and can be drop-cast directly onto a gas diffusion layer electrode such as a carbon paper. This modified structure provides enhanced surface area and conductivity for electrocatalyst loading, whilst allowing efficient diffusion of liquid/gas phase reactant/product (Figures 5a, S6). The highly conductive nature of graphene allows homogeneous electrodeposition of the H₂ evolution catalyst cobalt phosphide [35], with an 160 mV overpotential (η) for the hydrogen evolution reaction at 10 mA cm², in comparison to bare carbon paper with η = 280 mV (Figure 5b, Figure S6). This is further supported by in-situ electrodeposition of a cobalt phosphate water oxidation catalyst [36], at 1.2 V (vs Ag/AgCl 3M NaCl) resulting in more than 3-fold enhancement in the electrocatalytic current (inset in Figure 5c) with the carbon paper loaded with graphene ink in comparison to carbon paper alone (Figure 5c, Figure S7).

Another benefit of the optimized exfoliation process to enhance solution-processability is a reduction in the quantity of organic solvent required to produce advanced materials such as graphene papers; which is highly desirable from both economical and environmental perspectives. A stable graphene dispersion in DMF that we obtained is the highest concentration (5 mg/mL) reported to date using H₂SO₄ as an anodic bath. This concentrated ink enables the fabrication of flexible and conductive ($10 \pm 2 \Omega \text{ sq}^{-1}$) graphene papers (Figure

5d) at various thicknesses. This value is comparable to paper coated with exfoliated graphene [21], and carbon nanotube paper [37]. Such graphene papers can be employed directly in a solid-state supercapacitor with a layer of poly(vinyl alcohol)/sulphuric acid as a solid gel electrolyte (Figure 5d); achieving an excellent areal capacitance of 44 mF cm^{-2} at 2 mV s^{-1} , which is much higher value than $\sim 11.3 \text{ mF cm}^{-2}$ reported based on electrochemically exfoliated graphene ink coated paper [21].

3.0 Conclusions

In summary, we present a general strategy to produce low-defect electrochemically exfoliated graphene with significantly enhanced solution-processability. We demonstrate a first example of the use of a new dual purposes additive; ethylene glycol in scavenging hydroxyl radicals, and acting as a protective buffer layer to reduce excessive electrochemical oxidation of the graphene. This cheap and widely available additive can effectively tune anodic exfoliation of graphite in an acidic electrolyte, offers a new strategy to meet industry demand of low cost, large scale and efficient production of high quality graphene. This new concept of an additive as an oxidative radical scavenger is extendable and applicable to other electrochemical reactions, where controlling oxidative reaction is essential in obtaining desirable chemical and physical properties of the synthesized nanomaterials.

Conflicts of interest

There are no conflicts to declare.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at

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FIGURE CAPTIONS

Figure 1 Schematic illustration of the role of ethylene glycol (ETG) in buffering the attack of the hydroxyl radicals on the carbon lattice, hence minimizing the creation of defects in the exfoliated graphite. A simplified equation shows the conversion of ethylene glycol to carbon dioxide and water by hydroxyl radicals. Note that apart from the presence of ETG in the electrolyte, it is readily adsorbed onto the graphite surfaces, forming an oxidative protection layer to minimising attack from hydroxyl and oxygen radicals.

Figure 2 (a) Schematic of electrochemical exfoliation experimental setup, with ethylene glycol (ETG) was added to the H_2SO_4 electrolyte (i); the exfoliated graphene was gently washed with deionised (DI) water under stirring, and the DI water was replaced several times to remove ETG; the graphene flakes were obtained by filtration and left drying (iii); and the dried graphene is readily dispersed in DMF solvent (iv). (b) Cyclic voltammograms recorded on graphite foils in the presence of different vol % (indicated by number) of ETG (the rest of vol % is 0.5 M H_2SO_4), at 100 mV s^{-1} . (c) Detail of the adsorption and desorption peaks of ETG up to 2.2 V. (d) Cyclic voltammograms of 25, 50 and 100 % of ETG, at 100 mV s^{-1} . (e) The current-time profile upon electrochemical exfoliation of graphite foils performed at 10 V in 0.5 M H_2SO_4 solution and with ETG as an additive. Inset shows the photographs of graphite foils after anodization with increased vol % (left to right) of ETG presence in 0.5 M H_2SO_4 .

Figure 3 (a) The DMF dispersibility test of electrochemically exfoliated graphene prepared from 0.5 M H_2SO_4 , with and without 2 vol. % ETG, after left for 3 days, (b) SEM image of electrochemically exfoliated graphene prepared from H_2SO_4 with 2 vol. % ETG, and

the corresponding AFM image of graphene on Si (c) with inset showing the layer thickness, and (d) distribution profile of the graphene sheet thicknesses.

Figure 4 Raman (a), X-ray diffraction (b), X-ray photoelectron spectroscopy (c, d) and STEM colorised high angle annular dark field images (HAADF, left half) and bright field (BF, right half) images comparing electrochemically exfoliated graphene in 0.5 M H₂SO₄ only (c, e) and H₂SO₄ + 2ETG (d, f). The colorised HAADF images in which the contrast is a function of thickness. The BF images show atomic resolution. The addition of ETG results in a much more uniform graphene product. The full field view of these images are shown in Figure S4.

Figure 5 (a) Impedance spectra of carbon paper (CP, blue), and CP loaded with graphene (red) performed in 0.5 M H₂SO₄. Inset shows a SEM image of CP modified with graphene, (b) The linear sweep voltammograms for a platinum foil (black); and cobalt phosphine (CoP) on CP (blue) or graphene modified CP (red). (c) Cyclic voltammograms (CVs) of the CP with (red) and without (black) loaded with graphene in 0.5 mM Co(NO₃)₂ in 0.1 M potassium phosphate pH 7.0. Inset shows *i-t* profile recorded for the subsequent in-situ electrodeposition of CoPi at 1.2 V (vs Ag/AgCl 3M NaCl). (d) CVs of solid-state graphene supercapacitor recorded at different scan rates. Inset shows a flexible graphene paper prepared from the loading of 30 mg graphene from 5 mg/ml graphene ink in DMF.

FIGURES

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5