Carbon 111 (2017) 83–93

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Functionalization of graphene sheets by the diazonium chemistry during electrochemical exfoliation of graphite

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A R T I C L E I N F O

Article history:
Received 13 April 2016
Received in revised form
23 September 2016
Accepted 25 September 2016
Available online 28 September 2016

A B S T R A C T

Graphene sheets were spontaneously functionalized with anthraquinone molecules in a one-pot process, during the oxidative electrochemical exfoliation of a graphite electrode in a 0.1 M H_2SO_4 solution containing anthraquinone diazonium ions. This counterintuitive process involves the electrochemical oxidation of graphite and reduction of diazonium ions and functionalization occurs by spontaneous reaction of freshly generated graphene sheets with diazonium ions. This reaction is faster than the common approach based on the reaction of diazonium ions with pre-exfoliated graphene sheets. Indeed, the grafting yield of our one-pot process is higher than that of a two-step procedure based on functionalization of already produced graphene sheets, presumably due to the higher reactivity of freshly generated graphene sheets during electrochemical exfoliation. As a result of functionalization, the water dispersibility of graphene sheets was improved and an increase of the BET specific surface area was observed. The presence of anthraquinone molecules was confirmed by Fourier transform infrared spectroscopy, electron microscopy, X-ray photoelectron spectroscopy and cyclic voltammetry. Thermogravimetric analysis, Raman spectroscopy and electronic conductivity measurements are consistent with the covalent bonding of anthraquinone on the graphene sheets. Thermogravimetric analysis and cyclic voltammetry data allowed the evaluation of the loading of anthraquinone groups on the graphene sheets.

1. Introduction

Graphene, a two-dimensional honeycomb sp^2 lattice with exceptionally high electrical conductivity, elasticity, electron mobility [1], thermal conductivity [2], high specific surface area [3] and mechanical strength [4,5] has received a great deal of attention for its potential application in the future generation of nanoelectronic devices [6,7], composite materials [8] and energy storage systems [6,9]. The production of high-quality graphene has been carried out by, micromechanical cleavage [1], chemical vapor deposition [10] and thermal desorption of Si from a SiC substrate [11]. However, these methods provide high-quality material in relatively small quantity, useful only for selected applications [1,12]. For large-scale production, graphene is obtained by reduction of graphene oxide, itself prepared by the Hummer's method [13], and by either chemical [14–17], thermal [18] or electrochemical [14] techniques [19]. All these methods result in abundant structure defects and surface functional groups on the graphene sheets that significantly affect their electronic properties [2] and their electrochemical behavior [20]. Existing methods to minimize these issues, such as electrochemical expansion [21,22], solvent and surfactant-assisted liquid-phase exfoliation [23] and graphite intercalated compounds [24] required extensive sonication processes which can limit the size and yield of thin graphene layer [6,24]. Finally, the large-scale synthesis of high-quality graphene by electrochemical exfoliation of graphite into graphene sheets has been recently developed by using non-aqueous [21,22] and aqueous electrolytes [6,7,25–27]. Electrochemical exfoliation from aqueous media is environmentally benign, low-cost in comparison to other procedures and can be used for the large scale production of high-quality and high-purity graphene sheets [25]. Even if graphene itself is an attractive material, its large-scale application usually requires further functionalization to obtain useful material with tailored properties. Functionalization of graphene [28,29] (and its derivatives) with organic molecules by covalent and non-covalent interactions has been reported by using classical chemistries previously used for other carbon materials [30,31]. Among

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http://dx.doi.org/10.1016/j.carbon.2016.09.063
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these, modification of graphene by spontaneous reduction of diazonium ions is attracting a lot of interest due to its versatility. Such covalent functionalization of graphene has been already reported for epitaxial graphene [32], graphene nanoribbons [33], chemically converted graphene [34,35] mechanically exfoliated graphene [35,36] as well as chemical vapor deposited graphene [35,37–40]. The functionalization occurred via a spontaneous reduction of diazonium ions that involves the generation of a radical by electron transfer from the carbon substrate to the aryldiazonium ion and subsequent formation of a covalent bond between carbon and the aryl group [41]. Another possible grafting mechanism is based on the spontaneous reaction of a cation generated by heterolytic dediazoniation or the reaction of the diazonium cations with the substrate [42]. Noteworthy that in all these previous studies, the grafting was performed on surface deposited graphene-based film [40,43–45] or graphene dispersed in solution [30,38,46].

In this work, we developed a convenient method to functionalize graphene sheets during the oxidative electrochemical exfoliation of graphite in the presence of diazonium cations (Fig. 1). This counterintuitive process, which involves the electrochemical oxidation of graphite and a reduction step, (diazonium ions reduction) occurs by spontaneous reaction of freshly generated graphene sheets with diazonium ions. To demonstrate the proof-of-concept, electroactive anthraquinone molecules were grafted [47–51]. The resulting materials were characterized by Raman spectroscopy, Fourier transform infrared spectroscopy, thermogravimetric analysis, scanning electron microscopy, transmission electron microscopy and electrochemistry to demonstrate that functionalization by anthraquinone molecules occurred during electrochemical exfoliation.

2. Experimental

2.1. Materials and reagents

Graphite foil (0.5 mm thick, 99.8%) was obtained from Alfa Aesar and was natural graphite with crystallite size of 16 nm, determined from the Scherrer equation from the 200 peak of the X-ray diffraction pattern. 2-aminoanthraquinone (2-aminoAQ) (97%) and *tert*-butyl nitrite (90% solution in acetonitrile) were purchased from Aldrich. Unless otherwise stated, all others reagents were obtained from Aldrich and were used without further purification. Millipore water (18.2 MΩ cm) obtained from a Milli-Q water purification system was used for sample rinsing and preparation of all aqueous solutions.

2.2. Electrochemical exfoliation

For electrochemical exfoliation, a graphite foil (7.5 cm × 2 cm × 0.05 cm (thickness)) used as anode (connected to the positive terminal of a DC power supply) with a Pt mesh (4 cm^2) as cathode, were immersed into the 0.1 M H_2SO_4 electrolyte. Table 1 presents experimental conditions used for electrochemical exfoliation. The distance between the graphite foil and the Pt electrode was kept constant (≈4 cm). An electrochemical exfoliation was also carried out by using a Nafion membrane to isolate the negative and positive electrode compartments (Supporting Information). Electrochemical exfoliation starts immediately after applying a DC voltage of 10 V (Fig. 2a). After a 1 h electrolysis, the exfoliated graphene sheets were collected by vacuum filtration through a polytetrafluoroethylene (PTFE) membrane filter with 0.47 μm pore size and washed several times with Nanopure water to remove residual acid. Typically, a mass of 500 mg is obtained in these experimental conditions. The electrochemically exfoliated graphene sheets powder was then dispersed in dimethylformamide (DMF) by ultrasonication for 10 min. The dispersion was left standing still 24 h for the precipitation of some thick graphitic flakes and only the upper part of the dispersion was used thereafter for all characterization. Following vacuum filtration, the obtained powder was dried in vacuum at 70 °C overnight before a heat treatment at 200 °C under an inert atmosphere of argon for 1 h to remove solvent trapped in the material. Graphene sheets flakes (Fig. 2b) are recovered in good yield (70%) and used for characterization. These graphene sheets can form a good dispersion in DMF (Fig. 2c) as well as a self-supporting film (Fig. 2d).

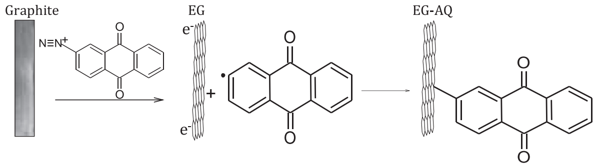

Fig. 1. Spontaneous functionalization of electrochemically exfoliated graphene sheets (EG) anthraquinone during electrochemical exfoliation of graphite in a one-pot process.

2.3. In situ electrochemical grafting

The diazonium ions solution was prepared by dispersing 2-aminoanthraquinone (5 mmol) in 100 mL of acetonitrile by strong sonication (Bransonic 3510, Branson) for 30 min and keeping the solution under stirring and heating at 50 °C for about 12 h until complete dissolution of the quinone derivative [52]. Then, the mixture was cooled at room temperature and 5 mmol of tert-butylnitrite was added and the mixture was stirred for 30 min to generate in situ the anthraquinone-2-diazonium cations. In order to functionalize graphene sheets during the exfoliation process, the saturated diazonium ions solution was added to 200 mL of 0.15 M H_2SO_4 to obtain a final H_2SO_4 concentration of 0.1 M (Table 1). A potential (DC voltage) of 10 V was applied for 1 h. The electrolysis also yielded graphene flakes floating at the surface of the initially dark brown solution (Fig. 2e). The dispersion was then collected with a polytetrafluoroethylene (PTFE) membrane filter with 0.47 μm pore size and washed successively with Nanopure water, acetonitrile, methanol, dimethylformamide (DMF) and acetone. Each solvent was used three times to remove ungrafted moieties. Finally, the obtained powder (~350 mg) was dried in vacuum at 70 °C overnight before undergoing a thermal treatment at 200 °C under an inert atmosphere (Ar) for 1 h to remove solvent trapped in the materials. The resulting modified graphene sheets exhibited a better dispersibility than unmodified electrochemically exfoliated graphene sheets. This is demonstrated by optical photographs of the anthraquinone-modified graphene sheets dispersion that remains stable over a period of 1 h, unlike the unmodified graphene dispersion for which sedimentation is observed (Supporting Information, Fig. S1). A set of control experiments were also performed and include: i) pre-exfoliation of graphite in 200 mL of 0.1 M H_2SO_4 during 1 h and subsequent reaction with in situ generated diazonium ions (solution same as above) added to the 0.1 M H_2SO_4 solution for 1 h (Table 1); ii) electrochemical exfoliation of graphite in 0.1 M H_2SO_4 containing anthraquinone (16 mM) for 1 h and iii) electrochemical exfoliation in 0.1 M H_2SO_4 in the presence of 2-aminoanthraquinone (16 mM).

2.4. Characterization techniques

Thermogravimetric analysis was carried out with a thermogravimetric analyzer (TA Instruments TGA (Q500)/Discovery MS).