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On the oxidation degree of few-layer graphene oxide sheets obtained from chemically oxidized multiwall carbon nanotubes

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ABSTRACT

Multiwall carbon nanotubes (MWCNT), generated by catalytic decomposition of methane using a Fe–Mo/MgO catalyst, were subjected to oxidation and exfoliation obtaining aqueous suspensions of few-layer graphene oxides (FLGO). FLGO with different oxidation ratios were obtained using a modified Hummers method by varying the amount of oxidizing agent ($KMnO_4$), followed by ultrasonic exfoliation. The exhaustive characterization of the resulting materials clearly showed surface functional groups evolution during oxidation and structural and morphological changes. Oxidation caused expansion and separation of the graphene layers by oxygenated groups formation and water intercalation. The full opening of the MWCNT resulted in FLGO as carbon nanoribbons and sheets from a $KMnO_4$/MWCNT ratio of 6.

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1. Introduction

Since Geim and Novoselov isolated and characterized a single layer of graphene in 2004 [1], graphene has become a subject of great scientific interest owing to its outstanding mechanical, electronic, optical, thermal and chemical properties [2,3]. Graphene is a 2-D hexagonal tessellation of sp^2-bonded carbon. The sp^2 hybridization leads to the formation of bonds to 120° between carbons with four electrons in the valence band, three in the sp^2 hybrids to form a planar network of covalent bonds, and one in a p-orbital perpendicular to the hybrids plane. Lateral overlapping of p orbitals creates π orbitals resulting in a giant delocalized molecular orbital on each side of graphene, which is the basic component of the structure of 3D graphite, where these orbitals are bonded by van der Waals forces. "Top-down" strategies for graphene obtention from graphite are based on the rupture of these van der Waals forces, resulting in the exfoliation of the graphene layers that compose the 3D structure [4,5].

To date, chemical oxidation of graphite with strong oxidizing agents and subsequent exfoliation is the most common approach to graphene materials production, being the Brodie [6], Staudenmaier [7] and Hummers [8] oxidation methods the most commonly used. Chemical methods allow large-scale graphene production, since the exfoliation of graphite oxide can be carried out in suspension [2,5,9], which is well-suited to chemical functionalization. Furthermore, the possibility of using different graphitic materials, including carbon nanotubes [5,10,11], different oxidation methods [12,13] and different subsequent reduction processes [14,15] widens the family of graphene products that can be produced, from monolayer graphene (Graphene) or few-layer graphene (FLG: 2–5 layers) to multi-layer graphene (MLG: 2–10) [16]. As a function of the number of layers, each type of graphene shows unique

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physical and vibrational properties [17,18], and properties similar to graphite when it is above 10 layers [19]. As a result of oxidation, the sp^2-bonded carbon in graphene oxide (GO) is disrupted by oxygenated functionalities such as hydroxyl and ether groups in basal planes and carboxylic and carbonyl groups in edges [20–22], which make it electrically insulating, highly hydrophilic and readily dispersible in water or organic solvents forming aqueous colloidal suspensions [23]. Hydrophilicity and electrostatic repulsions between GO layers allowed water intercalation in aqueous medium resulting in the exfoliation and dispersion by simple sonication [24] or by long-duration stirring [13].

Some authors used multiwall carbon nanotubes (MWCNT) unzipping to obtain graphene nanoribbons (GNR) with high height-to-width ratios and metallic or semiconducting transport [11,25]. Several chemical methods have been reported to unzip nanotubes, including Li intercalation in liquid NH_3 [26], Hummers-based reactions [8], cutting by metal nanoparticles [27] and selective plasma etching [28]. Unzipping method developed by Kosynkin et al. [10] is the most widespread used due to its simplicity, efficiency and scalability potential, obtaining graphene sheets and nanoribbons. Also platelets can be obtained from helical-ribbon carbon nanofibers using Kosynkin-based methods [29]. For samples with polydispersity in size, shape or number of layers, separation can be carried out by centrifugation [30], density-gradient separation [31] or pH-assisted selective sedimentation [32].

The use of MWCNT obtained by catalytic decomposition of methane (CDM) [33] as graphene based materials precursors is an interesting alternative to synthetic graphite, which is produced by graphitization of petroleum coke. Besides the expensive high temperature treatment needed (>2500 °C), coke is a byproduct of petroleum processing, which is a limited energy source and which inevitably entails a gradual increase of its market price.

In this work the direct obtention of homogeneous dispersions of sheets of few-layer graphene oxide (FLGO) were carried out by sonochemical unzipping of unpurified MWCNT produced by CDM. FLGO supernatant was separated at a high centrifugation speed of 4500 rpm removing completely unreacted MWCNT, generating an homogeneous dispersion when a high enough amount of $KMnO_4$ was used. A thorough characterization of the resulting materials obtained under different oxidation degrees, including XRD, Raman and XPS spectra deconvolution and full peak assignment, clearly showed surface functional groups evolution during oxidation and important structural and morphological changes. The facility and scalability of this route, together with the high edge/basal planes ratio of the resulting FLGO make these materials very promising for graphene-based composite materials manufacturing.

2. Experimental

2.1. MWCNT synthesis

MWCNT were synthetized via CDM in a rotary bed reactor. Set-up characteristics and synthesis conditions are summarized elsewhere [33,34]. MWCNT were obtained in 180 min runs with a feed of pure methane (99.99%) at 750 °C and with a weight hourly space velocity of 1.5 $L_N\ g_{cat}^{-1}\ h^{-1}$. A Fe–Mo/MgO catalysts (molar composition: 63.2:5.1:31.6) was used for MWCNT synthesis and led to the join formation of thin-walled carbon nanotubes (t-MWCNT) and bamboo type CNT, with a wide diameter distribution below 30 nm showing some tubular structures up to 100 nm in diameter, and an average of ca. 30 nanotube layers [33]. Raw MWCNT included metal particles (from the remaining catalyst), as Fe, metal carbides (Fe_3C and Mo_2C) and MgO which accounted for 40% by weight. This carbon materials exhibited similar structural properties to those of graphite, with an interlayer spacing of 0.3367 nm, and a surface area of 45.3 $m^2\ g^{-1}$.

2.2. FLGO obtention under different degrees of oxidation

FLGO with different degrees of oxidation were obtained using a modified Hummers method [8,9,24,25,35] by varying the amount of oxidizing agent ($KMnO_4$), followed by ultrasonic exfoliation. In a typical procedure, 0.5 g of as produced MWCNT, 0.5 g of $NaNO_3$ (purity $\geqslant$ 99.0%), and 23 mL of H_2SO_4 (96%) were stirred together in an ice bath. Under vigorous stirring, the required amount of $KMnO_4$ was slowly added to the mixture to obtain the desired ratio of $KMnO_4$ to as prepared MWCNT ($KMnO_4$/MWCNT; wt.%): 1, 3, 6, 9 or 12. Temperature was kept below 20 °C during mixing and then the solution was stirred at room temperature overnight. After oxidation, a brownish thick paste was formed. Then, 40 mL of deionized water was slowly added, and the solution was stirred for 30 min while the temperature was raised to 90 ± 5 °C. Subsequently, the mixture was diluted with 100 ml of deionized water, and 3 ml of H_2O_2 (33%) were added dropwise, turning the solution color to yellowish brown. Resulting material exfoliation was carried out for 20 min in mild sonication [36]. Product was filtered through a glass microfiber filter (Whatman) and washed with 200 ml of HCl (10%) and deionized water until neutral pH. The filter cake was dispersed in deionized water by 1 h sonication and centrifuged at 4500 rpm for 40 min to remove coarse particles (mainly unreacted MWCNT). Finally, the supernatant consisted of water dispersed FLGO of 1.4–4.6 mg/ml concentration. Final FLGO are hereafter denoted as R–X: R-01, R-03, R-06, R-09 and R-12, where X corresponds to the $KMnO_4$/MWCNT ratio.

2.3. Characterization techniques

Structural, chemical and morphological characterization of raw MWCNT and FLGO samples was carried out by X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and atomic force microscopy (AFM). As prepared MWCNT were used without further treatment. FLGO dispersions were either dried at 80 °C overnight for powder techniques such as XRD, RAMAN or XPS or redispersed ultrasonically in deionized water (3–5 mg/ml) for an hour for TEM and AFM analysis.

XRD patterns of raw MWCNT and dried FLGO were acquired in a Bruker D8 Advance Series 2 diffractometer. The angle range scanned was 3°–80° using a counting step of 0.02° and a counting time per step of 4 s. XRD data were fitted using the structure analysis software TOPAS (Bruker AXS) including subtraction of a second order Chebyshev

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