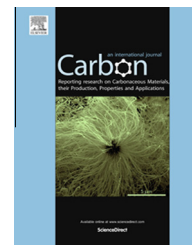


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Effect of oxidation debris on spectroscopic and macroscopic properties of graphene oxide

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ABSTRACT

Oxidation debris (OD) and graphene oxide (GO) before and after OD removal were characterized by Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, mass spectroscopy, X-ray diffraction, transmission electron microscopy and potentiometric titration, respectively. OD removal decreased GO absorption intensity in UV/Vis spectra, caused changes in peak position and absorption intensity in FTIR spectra, and resulted in the decrease of I_D/I_G in Raman spectra. OD was amorphous and had higher content of acidic groups than purified GO. OD contributed 10–25% of overall surface charge density to unpurified GO in spite of small amount (ca. 1% mass). OD removal decreased significantly GO dispersibility in aqueous solution, but increased obviously the electrical conductivity of reduced graphene oxide (rGO) and the apparent density of compacted rGO. The removal of OD was necessary because of its striking effects on both GO spectroscopic and macroscopic properties. Batch desorption in NaOH solution was recommended for OD removal from as-prepared graphite oxide because of slow OD desorption kinetics.

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1. Introduction

Graphene and graphene oxide (GO) have been attracted great attention because of their unique structures and remarkable electronic, mechanical and optical properties [1]. To further explore these carbon nano-materials, surface functionalization is a necessary step [2–4], and oxidation is usually used as a precursor reaction [4,5]. In addition, oxidation is a common purification method for carbon nanotubes (CNTs) and also a popular exfoliation approach for GO preparation from graphite [6,7]. A number of surface functional groups, such as carboxyl, hydroxyl and epoxy, are produced on GO by oxidation, which enables follow-up reactions possible [8–10]. The oxidation reactions occur at surface reactive sites, such as two sides of CNTs, surface defects and edges of graphene, and improve hydrophilicity of the carbon nano-materials in aqueous solutions [11–14]. However, oxidation also produces

oxygen-containing debris which strongly adheres to oxidized CNTs and GO, and affects their dispersibility, thermal stability and further functionalization of the carbon nano-materials [11,12,14,15]. Recently, striking effects of oxidation debris (OD) on other GO properties have been reported. For example, OD removal from as-prepared GO improves dramatically GO catalytic activity for the oxidative coupling of amines to imines [16], increases significantly the adsorption of 1-nitriprylene on GO [17], influences greatly the kinetics of the association between GO and silver nanoparticles [18], affects significantly electrochemical behaviors of both GO and reduced graphene oxide (rGO) [19], and influences obviously the property of GO Langmuir–Blodgett film [20].

The amount of OD is generally dependent on oxidation levels which are controlled by the type of oxidant, concentration, temperature, and reaction time et al. [7,8,11,21]. Up to 43% surface functional groups on unpurified oxidized

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multiwalled carbon nanotubes (MWCNTs) were found to be due to OD coating on surfaces of MWCNTs [13]. In the case of oxidized single-walled carbon nanotubes (SWCNTs), OD amount was about 2% of total mass, and OD atomic ratio of C to O was comparable to that of oxidized SWCNTs [8]. The amount of OD in as-produced GO was reported to be roughly one-third by mass and independent of oxidation method [14,22]. However, the value varied significantly in the literature. For example, a commercially available GO synthesized by a modified Hummers method [23] was found to be 16.2% by accurately weighing [18], whereas no impurities were detected for GO product from the same company by another group [24]. It seems that purification method also contributes somewhat to the observed OD amount in addition to oxidation level.

Many studies indicated that OD from oxidized CNTs was amorphous carbonaceous materials [25,26] and thus known as carbonaceous fragments in literature. In addition, OD was found to be similar to fulvic acid (FA) occurring in natural environment [13]. Low molecular weight carboxylated carbons from nitric acid treated SWCNTs were also isolated and identified [25]. Small organic fragments with m/z between 200 and 900 were found by mass spectroscopy for OD from GO [14,22]. Although potential effects of OD on the properties of CNTs and GO were realized in some investigations [e.g., 12–14,25,26], numerous studies ignored OD and included few purification steps for OD removal. The ignorance might increase research uncertainty and even lead to different conclusions for the same question [11,25]. OD desorption kinetics which is of importance for efficient OD removal has been seldom studied, although it has been commonly observed that OD can be removed by basic solutions [12,14,25,27]. In the present paper, we studied OD desorption kinetics from as-prepared graphite oxide, isolated OD, characterized OD and GO before and after purification, and investigated OD influences on GO spectroscopic and macroscopic properties.

2. Experimental

2.1. Materials

Natural graphite flake powder (purity >99.8%) was purchased from Alfa Aesar. All other chemicals were analytical grade and used as received without further purification except for zinc powder which was washed with HCl to remove zinc oxide.

2.2. Methods

2.2.1. Characterization

Solid-state Fourier transform infrared (FTIR) spectra were recorded from 400 to 4000 cm^{-1} on a NEXUS 670 5-DX 170SX spectrometer (Nicolet Instrument Corporation). Raman spectra from 500 to 4000 cm^{-1} were collected on an inVia-Reflex Raman scope using a 632.8 nm He–Ne laser (Renishaw). X-ray diffraction (XRD) pattern was scanned from 5° to 60° on X'Pert PRO X-ray diffractometer (Panalytical). Fluorescence emission spectra were recorded with a FLSP 920 fluorescence spectrometer (Edinburgh Instruments Ltd.). Transmission

electron microscopy (TEM) was examined using a Tecnai-G2-F30 Field Emission Transmission Electron Microscope (FEI Corporation). UV–Vis absorbance spectra were measured on a LAMBDA 35 UV/visible spectrophotometer (Perkin Elmer). Mass spectra were examined using an Esquire6000 ion trap mass spectrometer (Bruker Daltonics). Elemental analysis was performed on a vario EL Cube elemental analyzer (Elementar Analysensysteme GmbH).

2.2.2. GO and rGO preparation and OD isolation

Graphite oxide was prepared from natural graphite by a modified Hummers method [23]. The as-prepared graphite oxide was purified by OD desorption in 0.1 M NaOH solution. The desorbed OD was isolated and purified on a column of XAD-8 resin and then transformed into H^+ -form by a column of H^+ -saturated cation exchange resin. GO was obtained by ultrasonication of graphite oxide suspension in water. All samples of GO and OD for spectroscopic measurements were in H^+ -form unless otherwise specified. Reduced graphene oxide (rGO) was prepared by zinc powder reduction according to Mei and Ouyang's method [28]. GO from as-prepared graphite oxide was named as unpurified GO and that from purified graphite oxide was named as purified GO hereafter for convenience. Experimental details of GO preparation and OD isolation can be found in the [Supplementary Materials](#).

The B.E.T. specific surface areas of purified and as-prepared graphite oxide determined by nitrogen adsorption isotherms are 165.0 and 211.6 m^2/g , respectively. Elemental compositions of purified and unpurified GO determined by elemental analysis are very similar, i.e., unpurified GO: C, 56.33; H, 1.86; purified GO: C, 55.60; H, 2.08.

2.2.3. OD desorption kinetics

OD desorption kinetics from as-prepared graphite oxide was performed in NaOH solutions at different concentrations (0.01, 0.1 and 1 M, respectively). Aliquot of graphite oxide suspension was sampled from time to time and centrifuged at 18,000 g for 30 min. OD concentration in the supernatant was spectrometrically measured. Experimental details for desorption kinetics can be found in the [Supplementary Materials](#).

2.2.4. Potentiometric titration

To characterize the surface charge densities (ΔQ , mol/g) of purified and unpurified GO, potentiometric titrations were performed under argon atmosphere. GO proton excess which was equal to the surface charge density was determined by subtracting the titration curve of the background electrolyte solution (blank) from that of GO suspension. In general, a suspension of 2.0 g GO in 50 mL NaCl solution (0.1 M) was titrated with a standard NaOH solution (0.05 M) up to pH ~ 10 at 25 °C. Experimental details for potentiometric titration can be found in the [Supplementary Materials](#).

2.2.5. rGO volume resistivity

0.300 g rGO was compressed at 10 MPa pressure to obtain a flake with the diameter of 13.00 mm and the volume resistivity was measured with the flake on an SX1934 type digital four-point probe meter.

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