



Preparation of graphite derivatives by selective reduction of graphite oxide and isocyanate functionalization



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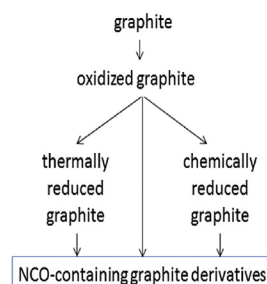
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HIGHLIGHTS

- Preparation of GO by Marcano's method results in defined interlayer spacing.
- Treatment of GO with diisocyanate widens the interlayer spacing to 1.3 nm.
- Chemical reduction of GO with benzyl alcohol is effective in defect repair.
- Electrical conductivity increases by 9 orders of magnitude during chemical reduction.
- The isocyanate functionalization is stable under chemical reducing conditions.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 9 July 2015

Received in revised form

1 July 2016

Accepted 10 July 2016

Available online 28 July 2016

Keywords:

Graphite oxide

Surface modification

Conductive nanoparticles

Reduction

Isocyanate modification

ABSTRACT

Heavily oxidized and ordered graphene nanoplatelets were produced from natural graphite by oxidation using a mixture of phosphoric acid, sulphuric acid, and potassium permanganate (Marcano's method). The atomic percentage of oxygen in the graphite oxide produced was more than 30% confirmed by XPS studies. The graphite oxide produced had intact basal planes and remains in a layered structure with interlayer distance of 0.8 nm, analyzed by WAXS. The graphite oxide was treated with 4,4'-methylenebis(phenyl isocyanate) (MDI) to produce grafted isocyanate functionalization. Introduction of these bulky functional groups widens the interlayer distance to 1.3 nm. In addition, two reduction methods, namely benzyl alcohol mediated reduction and thermal reduction were carried out on isocyanate modified and unmodified graphite oxides and compared to each other. The decrease in the oxygen content and the sp^3 defect-repair were studied with XPS and RAMAN spectroscopy. Compared to the thermal reduction process, which is connected with large material loss, the benzyl alcohol mediated reduction process is highly effective in defect repair. This resulted in an increase of conductivity of at least 9 orders of magnitude compared to the graphite oxide.

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1. Introduction

Future application prospects of graphene and graphene-like materials have triggered much interest and studies of novel ways to tailor the surface properties of graphene. Pristine graphene is made of sp^2 carbon network and has a single atom thickness, arranged in a honeycomb structure of hexagons with excellent mechanical, electrical, and thermal properties [1–6]. A very promising approach for nano-engineering the surface of graphene is the chemical functionalization, where oxidation and reduction reactions can be used to create and exploit the defects in graphene. The graphite oxide which is made of layers of oxidized graphene sheets is often referred as graphene oxide [7]. The oxidation of graphite is commonly carried out by Hummer's method [8] using concentrated sulphuric acid, sodium nitrate and potassium permanganate, but this involves the evolution of some toxic gases during the oxidation and safe handling is needed. Hence, we used Marcano's improved method [9] which results in intact and homogeneous graphite oxide without formation of toxic gases during the process. Beside the one used in this work, other improvement of Hummer's method have been developed recently [10].

Recent model suggests that GO is made of planar graphene interlinked with cyclohexane like rings of chair configuration [11]. The presence of oxygen containing groups in GO like epoxy and hydroxyl groups in the basal plane and carbonyl and carboxyl groups located at edges alters the van der Waals interactions between the layers of graphite oxide and render them hydrophilic, thus facilitating the hydration and exfoliation in aqueous media [12–14]. The interlayer distance between the graphene sheets increases due to the addition of oxygen functionalities to ~1 nm while in pristine graphite it is 0.34 nm due to Van der Waals forces. Isocyanate modification of graphite oxide was demonstrated by Stankovich et al. [15], where mono-isocyanates were used to react with the oxygen functionalities, which in turn help in exfoliation of the modified graphite oxide in polar aprotic solvents. The use of diisocyanates for modification of graphene oxide and its interactions to polymers results in crosslinked materials with improved strength [16–20]. We used diisocyanate to study the possibility for creating isocyanate-containing functionalities at the GO surface which would allow chemically coupling between the components when using this filler as modifier for polyurethanes.

The reduction of GO will reduce the number and types of functional groups. Proportional to the degree of reduction, this is connected with an increase the electrical conductivity and a decrease of the hydrophilic character. Such reduced graphite is suitable for preparation of composite materials [21–23]. Reduction can be carried out by heat [24–26], hydrothermal treatment [27], using reducing agents like hydrazine [21,28], hydroquinone, hydrides, alcohols [29] and natural substances [30,31]. Even though the reduction process results in decreasing oxygen content, which can be proven by elemental analysis, further research is needed to understand the changes happening to the carbon network of the reduced graphite oxide. Following Marcano's improved oxidation method, in the present work we were able to reproduce graphite oxide nanoplatelets with intact graphene oxide sheets sticking together. The diisocyanate modification also results in intact nanoplatelet structures with increased interlayer distance, which proves the presence of oxygen functionalities on both surfaces of the graphene sheets and the possibility for grafting of diisocyanate on the surface. On the other hand, the comparison between thermal and alcohol reduction process of the original GO gives a detailed understanding of the defect repair capability of the alcohol reduction process. Thermal reduction removes the defects in the graphite oxide not only by defect repair but also by decomposition accompanied by overall weight loss, which is disadvantageous for

commercial usage. By utilizing the defect repair capability of the benzyl alcohol reduction process, we studied the possibility for producing an isocyanate modified graphite oxide nanofiller with reduced oxygen content and increased electrical conductivity compared to directly modified GO, suitable as reactive modifier of electrical and mechanical properties e.g. for polyurethanes.

2. Experimental

2.1. Materials

Natural graphite (powder, universal grade, 200 mesh, 99.9995% [metal basis]) was purchased from *Alfa Aesar*, Germany. 4,4'-Methylenebis(phenyl isocyanate) (MDI), crystalline phosphoric acid (H_3PO_4), and benzyl alcohol were purchased from *Aldrich*, Germany. Hydrogen peroxide and N,N-dimethyl formamide were obtained from *MERCK*, Germany. Sulphuric acid from *ACROS Organics* and potassium permanganate ($KMnO_4$) from *FLUKA* analytical, Germany, were used. All the chemicals and solvents were used as received without further purification.

2.2. Synthesis

2.2.1. Oxidation of graphite

Natural graphite (Alfa Aesar, 200 mesh) was oxidized to graphite oxide (GO) through the method described by Marcano et al. [9]. A typical oxidation procedure is as follows: To a dispersion of 10 g graphite in a mixture of 1.2 L of H_2SO_4 and 133 mL (1 M) H_3PO_4 60 g $KMnO_4$ was very slowly added. The acid mixture was precooled to compensate high exothermic heat during the addition of permanganate to the acid. The mixture was set in an oil bath at 50 °C for 16–18 h with magnetic stirring. Dark purple slurry was obtained due to the presence of excess permanganate. Then the mixture was quenched by pouring into cold water and H_2O_2 was added (~6 mL) to destroy the excess permanganate. After all the permanganate was destroyed the mixture became yellow as shown in Fig. 1.

The yellow color is typical for the highly oxidized form of graphite in acidic condition at pH ~1 and can be used as criterion for the degree of oxidation and purity of the graphite oxide [8]. The mixture was concentrated by centrifugation at 14000 rpm for 10 min, the supernatant was thrown away and the concentrate was washed with distilled water and Millipore water. The washing and concentration process continued to remove excess acidic ions and permanganate, if any, until the pH was between 6 and 7. The color of the suspension gradually changed from yellow to brownish and finally black (pH ~ 6) which is caused by the tendency of the graphite oxide to agglomerate at neutral pH. The graphite oxide (GO) was dried in vacuum oven at 80 °C for 15 h. The GO obtained in a yield of 13.8 g was not a fine powder, but contains bulky particles. To breakup these bulky agglomerates we crushed them with mortar and pencil, but this resulted in partial explosive-like decomposition with visible sparks and partial burning. This behavior could be due to the high oxygen concentration and residues of acids intercalated between the carbon layers during the oxidation. During milling, these oxygen functionalities undergo exothermic decomposition which is initiated by frictional heat and thus explosion-like burning occurs [32].

2.2.2. Diisocyanate modification of graphite oxide

The graphite oxide was functionalized with isocyanate groups by conversion with the 4,4'-methylenebis(phenyl isocyanate) (MDI). The GO (1 g) was dispersed in DMF (100 mL) using sonication for 5–10 min (UP400S, power 400 W, *Hielscher Ultrasonics GmbH*, equipped with H7 ultrasonic horn, amplitude 80%, cycle 0.8). The suspension was placed under N_2 atmosphere and MDI

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