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A green method of graphene preparation in an alkaline environment

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ABSTRACT

We present a new, simple, quick and ecologically friendly method of exfoliating graphite to produce graphene. The method is based on the intercalation of a permanganate M_2MnO_4 ($M = K$, Na, Li), which is formed by the reaction of a manganate $MMnO_4$ with an alkali metal hydroxide MOH. The quality of exfoliation and the morphology were determined using X-ray photoelectron spectroscopy, X-ray diffraction and microscopic techniques, including transmission electron microscopy and atomic force microscopy. We observed that a stable graphene suspension could be prepared under strongly alkaline conditions in the presence of permanganate and ultrasound assistance. The use of only an alkaline environment for the direct preparation of graphene from graphite structures has not been previously described or applied. It was found that such a method of preparation leads to surprisingly high yields and a stable product for hydrophilic graphene applications.

1. Introduction

The "extremely thin lamellae of carbon" [1], later called graphene, was prepared in 1962 by chemist Hanns-Peter Boehm [2] using a procedure based on the oxidation of graphite to graphite oxide, which was published in 1859 [3] and modified by Hummers in 1957 [4].

Edwards and Coleman [5] highlighted the different methods available for the synthesis of graphene and discussed the viability and practicality of using the materials produced via these methods for different graphene-based applications. The aim of that review [6] article was to provide a comprehensive overview of the scientific progress of graphene to date and evaluate its future prospects. Wu et al. [7] summarized the state-of-the-art self-assembly strategies that have been established to construct chemically modified graphene-based nanomaterials. The versatility of graphene-based devices goes beyond conventional transistor circuits and includes flexible and transparent electronics, optoelectronics, sensors, electromechanical systems, and energy technologies [8]. Machado and Serp [9] presented the most relevant synthetic routes to obtain graphene and focused attention on the properties and characterization techniques of graphene that are of relevance to catalysis, with emphasis on adsorption.

Micromechanical exfoliation, called the "Scotch tape method" [10], was the first method for preparing single-layer graphene from natural graphite. The oxidative pathway to graphene preparation starts with the oxidation of graphene to graphite oxide or graphene oxide using strong oxidants in strong concentrated acids. Graphite oxide (graphitic oxide or graphitic acid) was first prepared by Brodie [3] in 1859 by the reaction of graphite with a mixture of potassium chlorate ($KClO_3$) and fuming nitric acid (HNO_3). In 1898, Staudenmaier [11] improved this method by using concentrated sulfuric acid as well as fuming nitric acid and adding the chlorate in multiple aliquots over the course of the reaction. Hofmann [12] used concentrated nitric acid, concentrated sulfuric acid and $KClO_3$. The best-known Hummers method [4] uses a mixture of sulfuric acid, sodium nitrate ($NaNO_3$) and potassium permanganate ($KMnO_4$). The exact composition of the graphene oxide is defined by the various functional groups attached to the graphene planes; most important are the hydroxyl ether and carbonyl groups. They are eliminated by strong reducing agents, such as hydrazine hydrate ($NH_2NH_2{\cdot}H_2O$) [13], sodium borohydride ($NaBH_4$) [14], hydroxylamine (NH_2OH) [15], thiourea ($SC(NH_2)_2$) [16] or the industrial reducing agent thiourea dioxide (formamidinesulfinic acid) ($NH_2C({=}NH)SO_2H$) [17], which converts the graphene oxide to more or less reduced graphene oxide.

Chemical exfoliation is based on the intercalation of graphite by various ions or molecules, such as tetrabutylammonium cations [18], 1-pyrene carboxylic acid [19] or alkali metals in tetrahydrofuran (THF). Potassium forms ternary potassium salts, $\mathrm{K(THF)}x\mathrm{C}_{24}$

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($x = 1–3$), in N-methyl pyrrolidone (NMP) readily and spontaneously exfoliates the intercalated graphite and yields air-sensitive solutions of reduced graphene sheets [20].

Liquid exfoliation uses the effect of low-intensity ultrasound and suitable solvents. The layered materials are sonicated for tens of hours in solvents in ultrasonic baths, and individual nano-sheets are separated by centrifugation. The most commonly used solvents are N-methyl pyrrolidone [21], water–alcohol mixtures [22], 1-hexyl-3methyl-imidazolium hexafluorophosphate [23], benzylamine, N,N-dimethylacetamide, cyclohexanone, benzylbenzoate [24] and perfluorinated aromatic solvents such as fluorobenzene (C_6F_6), octafluorotoluene ($C_6F_5CF_3$), fluorobenzonitrile (C_6F_5CN) and pentafluoropyridine (C_5F_5N) [25]. An alkaline environment has thus far been used to subsequently prepare graphene from GO. Fan et al. [26] described the preparation of graphene from the oxidation of exfoliated graphite oxide in a strongly alkaline medium at temperatures of 50–90 °C without the use of reducing agents.

The use of only an alkaline environment for the direct preparation of graphene from graphite structures has not yet been described or applied. It was found that such a method of preparation in an alkaline environment leads to surprisingly high yields and a stable product, as described in this report. Alkaline graphite intercalation compounds were prepared from flake graphite, potassium dichromate, concentrated sulfuric acid and sodium hydroxide under low-intensity ultrasound irradiation [27]. High-intensity ultrasound can be used to induce chemical reactions that do not normally take place. The intense ultrasonic waves permeate the fluid to create a small cavity that becomes larger and implodes, thereby creating tremendous heat; these extreme conditions provide an unusual chemical environment. High-intensity ultrasound was found to achieve significant changes in both physical and chemical processes, such as solvent degassing, formation of emulsions from two immiscible liquids, acceleration of reaction rates, use of less hazardous reagents, and milder conditions.

The exfoliation of graphite using ultrasound in strongly polar aprotic solvents in a pressurized batch reactor is based on the origin of the stationary ultrasound waves. These waves are able to vibrate lamellar particles, which are gradually peeled off to reveal individual sheets. Herein, we report a new method of graphite exfoliation inspired by the idea of graphite oxidation in mellitic acid (benzene hexacarboxylic acid, $C_6(COOH)_6$) in an alkaline environment, based on the idea of one of the most famous Czech chemists, Votoček [28]. We have developed a new and facile method of graphite exfoliation to graphene in an alkaline environment. According to the available literature, an alkaline manganate solution has not been previously used for the preparation of graphene [29].

2. Experimental

2.1. Preparation of graphene

All used chemicals, potassium permanganate ($KMnO_4$), sodium permanganate ($NaMnO_4$), barium permanganate ($Ba(MnO_4)_2$), potassium hydroxide (KOH), sodium hydroxide (NaOH), lithium hydroxide (LiOH), lithium sulfate (Li_2SO_4) and hydrochloric acid (HCl) were obtained from Sigma–Aldrich. Natural graphite was obtained from Koh-i-noor Grafite, Ltd., the Czech Republic. Lithium permanganate was prepared by reacting $Ba(MnO_4)_2$ and Li_2SO_4.

The graphene was prepared using high-intensity ultrasound in a solution of $KMnO_4$ in an alkaline environment. 1 g graphite was added to a 100 ml aqueous solution containing 1.5 g $KMnO_4$ and 24 g KOH in a batch-pressurized ultrasonic reactor. The reactor was sealed and pressurized to 6 bar, and then the reaction mixture was irradiated with high-intensity ultrasound (UIP2000hd, 20 kHz, 2000 W, Hielscher Ultrasonics, GmbH) for 10 min. After irradiation, a suspension of exfoliated graphite and MnO2 in a dark green solution of potassium manganate K_2MnO_4 was obtained. The suspension was neutralized to pH = 7–8 by adding HCl to convert all higher-valent (III, IV, VI) manganese species to soluble Mn(II) species. The final reaction product was purified by dialysis using a Spectra/Por 3 dialysis membrane. The same reaction with 1 g graphite was performed using equal amounts (1.5 + 24 g) of $NaMnO_4$ + NaOH and $LiMnO_4$ + LiOH, respectively.

2.2. Characterization methods

Diffraction patterns were collected using a PANalytical X'Pert PRO diffractometer equipped with a conventional X-ray tube (CuKα 40 kV, 30 mA, line focus) in transmission mode. An elliptic focusing mirror, a divergence slit of 0.5°, an anti-scatter slit of 0.5° and a Soller slit of 0.02 rad were used in the primary beam. A fast linear position sensitive detector PIXcel with an anti-scatter shield and a Soller slit of 0.02 rad were used in the diffracted beam. All patterns were collected in the range of 1–85° 2θ with a step size of 0.013° and 500 s/step; the total scanning time was ca. 3.5 h. A qualitative analysis was performed with the DiffracPlus Eva software package (Bruker AXS, Germany) using the JCPDS PDF-2 database [30]. An aqueous suspension of the sample material was placed onto a sample holder for the transmission experiments and covered with a mylar foil (6 μm thick). The sample was then covered with a second mylar foil to avoid losses. Finally, the sample holder was completed with a sample holder ring, and then it was ready for transmission XRD measurements. The next samples were dropped onto a silicon sample holder, which was dried to form a thin layer. Diffraction patterns of these samples were collected with diffractometer Bruker D2 equipped with conventional X-ray tube (Cu Kα radiation, 30 kV, 10 mA). The primary divergence slit module width 0.6 mm, Soler Module 2.5, Air scatter screen module 2 mm, Ni Kbeta-filter 0.5 mm, step 0.00405° and time per step 3 s and the LYNXEYE 1-dimensional detector were used. The crystallite size, interlayer spacing and number of C atom layers were calculated using the Debye–Scherrer equations [31,32].

The XPS high-vacuum chamber was equipped with a SPECS X-ray XR50 (Al cathode 1486.6 eV) and a SPECS PHOIBOS 100 Hemispheric Analyzer with a 5-channels detector. The background pressure in XPS was under 4109 mbar. The XPS survey-scan spectra were recorded at a pass energy of 40 eV; the energy resolution was set to 0.5 eV. The individual high-resolution spectra were taken at a pass energy of 10 eV with 0.05 eV energy steps. CasaXPS software was used to fit the high-resolution multi-components peaks. The atom concentration of the compounds was calculated with RSF defined in the standard table of CasaXPS.

The surface areas of the samples were determined from nitrogen adsorption–desorption isotherms at liquid nitrogen temperature using a Coulter SA3100 instrument with 15 min outgas at 150 °C. The Brunauer–Emmett–Teller (BET) method was used for the surface area calculations [33]. The morphology of the exfoliated graphite samples was inspected by transmission electron microscopy (TEM) using a 300 kV TEM microscope JEOL 3010F. As a specimen support for the TEM investigations, a microscopic copper grid covered by a thin transparent carbon film was used.

AFM images were obtained using a Bruker Dimension FastScan microscope. The samples for AFM measurement were prepared using a spin-coating method. Exfoliated graphite in an aqueous suspension was pipetted onto an atomically smooth synthetic mica support. The solution was spread over the substrate at 6000 RPM for 1 min. A silicon tip on a nitride lever was used in ScanAsyst – air contact mode at resonance frequencies ranging from 50 to 90 kHz.