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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.

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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 (KClO₃) and fuming nitric acid (HNO₃). 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 KClO₃. The best-known Hummers method [4] uses a mixture of sulfuric acid, sodium nitrate (NaNO₃) and potassium permanganate (KMnO₄). 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 (NH₂NH₂·H₂O) [13], sodium borohydride (NaBH₄) [14], hydroxylamine (NH₂OH) [15], thiourea (SC(NH₂)₂) [16] or the industrial reducing agent thiourea dioxide (formamidinesulfinic acid) (NH₂C(=NH)SO₂H) [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, K(THF)xC₂₄



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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 (KMnO₄), sodium permanganate (NaMnO₄), barium permanganate (Ba(MnO₄)₂), potassium hydroxide (KOH), sodium hydroxide (NaOH), lithium hydroxide (LiOH), lithium sulfate (Li₂SO₄) 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(MnO₄)₂ and Li₂SO₄.

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 K₂MnO₄ 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 NaMnO₄ + NaOH and LiMnO₄ + LiOH, respectively.

2.2. Characterization methods

Diffraction patterns were collected using a PANalytical X'Pert PRO diffractometer equipped with a conventional X-ray tube $(CuK\alpha 40 \text{ kV}, 30 \text{ mA}, \text{ line focus})$ 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 $1-85^{\circ} 2\theta$ 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 μ m 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 Ka 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 Xray 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.

Infrared spectra were recorded using a Nicolet Impact 400D spectrometer over the range of approximately 4000–500 cm⁻¹ with a mirror assemblage for the diffuse reflectance spectra measurements.

Elemental analysis was performed by a Perkin Elmer 2400 system.

2.3. Ultrasonic equipment

For ultrasound treatment procedure was used industrial processor UIP2000hd (20 kHz, 2000 W, Hielscher Ultrasonics, GmbH) with water cooled pressurized stainless-steel reactor (100 ml). The ultrasonic horn consists of titanium booster (amplitude ratio 1:2.2) and sonotrode with tip diameter 34 mm and amplitude ratio 1:1.0. The generator finds the optimal operational frequency of attached transducer–booster–sonotrode configuration automatically. The period time of ultrasound irradiation was 10 min.

3. Results and discussion

This new method of exfoliating graphite in an alkaline environment is based on a process related to the cavitation phenomenon. $KMnO_4$ and KOH react at elevated temperatures to form dark green unstable potassium manganate (K_2MnO_4), which slowly and spontaneously decomposes to MnO_2 according to the following reactions:

$$4KMnO_4 + 4KOH \Rightarrow 4K_2MnO_4 + 2H_2O + O_2 \tag{1}$$

$$2K_2MnO_4 + 2H_2O \Rightarrow 2MnO_2 + 4KOH + O_2$$
⁽²⁾

The energy provided by ultrasonic waves increases the temperature of the reaction mixture and also accelerates the spontaneous decomposition of manganate. The manganate solution intercalates graphite, and the oxygen species formed in these reactions exfoliates graphite. This method exfoliation was successfully used for exfoliation inorganic analogs of graphene, MoS₂, WSB, h-BN and h-BCN [34]. The exfoliation processes based on longitudinal and stationary ultrasonic waves take place simultaneously [35].

The XPS survey spectrum of exfoliated graphite shows the main C 1s, O 1s and Mn 2p peaks observed in Fig. 1a. The presence of potassium was not confirmed due to the rather low RSF factor of approximately 3.97 for K 2p and its partial overlap with C 1s, but the second strong peak of K 2s around 3.77 eV was also not found. Therefore, the potassium content is less than the detection limit of XPS. The calculated composition of the identified compound from the high-resolution spectra is approximately 60 at.% carbon. 30.2 at.% oxygen and 9.8 at.% manganese. The C 1s peak was deconvoluted into individual components observed on Highly Ordered Pyrolytic Graphite (HOPG) layer planes [36]. The identified carbon components in the C 1s spectrum are sp2 (284.5 eV; 79%), sp3 defects (285.4 eV; 7%) and mainly phenols (286 eV; 10%), with negligible traces of other carbon-oxygen bonds (carbonyl, carboxylic), as observed in Fig. 1b. The identified oxygen components in the O 1s spectrum are at approximately 529 and 531.5 eV, which can be identified as O2- in MnO and OH-, respectively [37] (Fig. 1c). The component at a binding energy (BE) of approximately 531.5 eV also has a contribution from C-O bonds, as observed in PET polymer at 532 eV (carbonyl) and 533.5 eV (esters), for example [38]. Another probable contribution is water with a BE around 532 eV [37]. The complexity of the Mn 2p metal photo-peaks arises from





Fig. 2. XRD pattern of raw graphite and exfoliated graphite measured in mylar foil.

the coupling of angular momenta associated with the partially filled core and valence shells containing unpaired electrons. The maximum of the Mn 2p3/2 peak is at 642.4 eV, which can be identified as $MnO_2 (Mn^{4+})$ [37] (Fig. 1d). The other oxidation states have lower BEs, around 461.8 and 641.0 eV for Mn^{3+} and Mn^{2+} , respectively [37]. The BEs reported in the literature are different by about 0.5 eV. The experimental data of Mn 2p3/2 were successfully fit by the Gupta and Sen model for Mn^{4+} [37,39,40].

The elemental analysis showed an overall composition of C 60.73%, H 0.5% and O 29.67% (impurities from natural graphite: SiO₂ 1%, K₂O 3.2%, CaO 0.6%, TiO₂ 1.3%, CuO 1.5%, ZnO 1.5%), confirming the results of the XPS analysis.

The XRD patterns of the raw and exfoliated graphite in the presence of different alkaline metals are presented in Fig. 2. The calculated peak position is 28.5° and d-spacing 3.15 Å, the spacing is smaller than that of graphite (0.335 nm). Banhart et al. observed a similar reduction in the spacing of graphene layers in carbon onions and interpreted the reduction on the basis of compression and the transition of orbitals from sp² to sp³ [41]. In the Fe₃C-encapsulated carbon nanocapsules produced in that study [42], the smaller spacing of the graphene layers is related to the Fe₃C particles. The bonding between the graphene layers and the Fe₃C particle may contribute to the transition of the orbitals from sp² to sp³. In our case, the reduction in the d-spacing could be caused by the compression pressure from the collapse of the cavitation bubbles or turbostratic arrangement of exfoliated graphene nanosheets as measured using mylar foil [43].

The diffraction patterns of exfoliated samples prepared as thin layer on silicon holder is presented in Fig. 3. The XRD pattern shows a strong peak at $2\theta \sim 3^{\circ}$ which correspond to the (001) reflection of the preferred orientation of graphene sheets [44]. Inset is XRD pattern measured in range of $2\theta 26-27^{\circ}$, the calculated d_{002} is listed in Table 1. The crystalline interplanar distance increases, and becomes higher than that of natural graphite (d_{002} = 3.33 Å).

The degree of functionality of the prepared exfoliated graphite sheets was evaluated by infrared spectroscopy. However, using $KMnO_4$ and H_2SO_4 (Hummers method) unavoidably results in contamination of the resulting graphene with different functional groups (CO, COOH, SO₄, etc.), which are very difficult to remove completely [45]. The infrared spectra of the exfoliated graphite and graphene oxide [45] are presented in Fig. 4. The resulting



Fig. 3. XRD pattern of exfoliated graphite measured in thin layer on silicon holder in 20 from 0° to 40°. Inset XRD pattern measured in interval 26–27°.

 Table 1

 Peak position, integral breath, d-spacing, crystallite size, surface area and pore volume of exfoliated samples.

Sample	Peak position (°2 θ)	d-Spacing (Å)	Surface area $(m^2 g^{-1})$	Pore volume $(cm^3 g^{-1})$
Graphite	26.76	3.33	5.2	0.0302
Graphene (K ⁺)	26.54	3.36	176.6	0.4007
Graphene (Na ⁺)	26.63	3.35	122.8	0.3677
Graphene (Li ⁺)	26.52	3.36	6.3	0.0396



Fig. 4. FTIR spectrum of the exfoliated graphene in comparison with that of graphene oxide.

sample of exfoliated graphite exhibits no functional groups compared with graphene oxide, indicating its high purity.

The measured surface area of graphene depends on many factors, but principally on the manner of preparation of a dry sample for surface area measurement [35]. The specific surface area, (see Table 1) as measured using the nitrogen-absorption Brunauer–Emmett–Teller (BET) method, decreases from 176 m² g⁻¹ to ~6 m² g⁻¹ (see Table 1), depending on the alkaline metal used (K > Na > Li). Although the ionic radius of K⁺ is 0.133 nm larger than Li⁺ (0.068 nm), it was found that K⁺ intercalates more readily than Li⁺ into graphite [46]. This may be related to the stronger coordination of Li⁺ with water, as when Li⁺ is intercalated, it is accompanied by a bilayer of water, while K⁺ is only accompanied by a monolayer.

Definite proof of the presence of the exfoliated graphite sheets (graphene) was provided by TEM images, selected area electron diffraction patterns (SAED) and AFM. Fig. 5 shows a TEM image of an exfoliated graphite sheet obtained using ultrasound-assisted exfoliation in an alkaline solution of potassium permanganate. The

large single sheet appears transparent and folded over at the edges, similar to what one observes for micromechanically cleaved graphene. The EDX analyses did not detect any manganese in the exfoliated graphite sample.

By using the Miller-Bravais indices (hk i l) for graphene, each set of diffraction spots was observed to exhibit an inner hexagon that corresponded to the $1\bar{1}\bar{1}0$ indices and an outer hexagon that corresponded to the $1\bar{2}\bar{1}0$ indices. The intensity profiles of the graphene diffraction patterns could be used to determine the number of layers in the graphene sheet. The relative intensities of the diffraction spots in the inner and outer hexagons were shown to be equivalent in single-layer graphene, while the relative intensities of the spots in the outer hexagon were shown to be twice those of the spots in the inner hexagon for bilayer graphene [47]. The SAED of the prepared graphene is presented in Fig. 6 and shows the typical sixfold symmetry expected for graphene. The intensity



Fig. 5. TEM images of the exfoliated graphite using KOH and KMnO₄.



Fig. 6. Selected area electron diffraction (SAED) of the exfoliated graphite using KOH and KMnO₄. Inset: intensity of a line section through the $1\overline{2}\overline{1}0$, $0\overline{1}\overline{1}0$, $\overline{1}\overline{0}10$, and $\overline{2}\overline{1}10$ spots.



Fig. 7. AFM images of the exfoliated graphite using (a) KOH and KMnO₄, (b) NaOH and NaMnO₄ and (c) LiOH and LiMnO₄.

of a line section through the $1\bar{2}\bar{1}0$, $0\bar{1}\bar{1}0$, $1\bar{0}10$, and $\bar{2}\bar{1}10$ spots is shown in the inset figure. The inner $0\bar{1}\bar{1}0$ - and $\bar{1}\bar{0}10$ -type reflections are more intense than the outer $1\bar{2}\bar{1}0$ - and $\bar{2}\bar{1}10$ -type reflections, which is consistent with isolated single-layer graphene.

Measurements using AFM can be used to determine the morphology and texture of exfoliated materials and the exact height or number of layers. By means of AFM, we also observed the effect of the alkali metal on the quality of exfoliation and the morphology of the exfoliated particles. Fig. 7 shows typical tapping-mode AFM images of graphene prepared using a solution of KMnO₄ and KOH and deposited on a mica substrate. Cross-sectional analysis shows that the exfoliated graphite sheet has a thickness of \sim 0.7 nm, and it can also be observed that the sheet has a size of ${\sim}0.5\times1.0\,\mu\text{m}.$ Thus, the observed exfoliated graphite particles are single-layer graphene sheets. This result is consistent with the above TEM observations. The AFM images of the exfoliated graphite using alkaline solutions of NaMnO4 and LiMnO4 are presented in Fig. 7b and c, respectively. The cross-sectional analyses showed a thickness \sim 3–4 nm, which corresponds to 2–3 layers. It is clear that the exfoliation was related to the ionic radius of the alkali metals (K > Na > Li); the Li and Na remain intercalated to form bilayers.

4. Conclusions

For graphite exfoliation to graphene, we used a new, simple, mild and ultrasound-assisted method in an alkaline environment. This new method of preparation of graphene is based on the interaction of potassium manganate in an alkaline environment with natural graphite in the presence of high-intensity ultrasound. This non-oxidative method allows the preparation of high-purity graphene with a minimum content of functional groups and defects. This new method of preparation represents a green synthetic route towards graphene with hydrophilic properties and excellent dispersibility in water. Considering that nontoxic potassium hydroxide is readily available, this study opens possibilities for the production of graphene on an industrial scale. This method could be used for the exfoliation of graphene-analogous compounds, such as the natural minerals molybdenite (MoS₂) and tungstenite (WS₂) or the synthetic materials h-BN and h-BCN.

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