SYNTHESIS OF GRAPHENE OXIDE AND REDUCED GRAPHENE OXIDE FROM INDUSTRIAL GRAPHITE FOIL WASTES

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Powdered graphite foil wastes (pGFW) were successfully used for the synthesis of graphene oxide (GO) and reduced graphene oxide (rGO). The remaining graphite foil pieces (wastes) are expanded graphites and their chemical oxidation to GO or to obtain graphene can be conducted using known methods. A fraction with a particle size of <140 µm was obtained by wet and dry grinding. The EDX analysis showed that the powder consists of carbon and oxygen only. The paper presents results obtained in pGF oxidation using low-temperature (~0°C; $KMnO_4$–$NaNO_3$–H_2SO_4) and relatively high-temperature (~50°C; $KMnO_4$–H_2SO_4) modes. In case of low-temperature mode oxidation of pGFW the C/O ratio (at.%) is 61:38. In case of their reduction with ascorbic acid the C/O ratio is 81:19. The method of synthesis of GO and its separation from the reaction mixture were partially corrected. Sulfuric acid and ions (K^+, Na^+, and Mn^{+2}) can be removed using 5-fold decanting (2 times H_2O, 3 times 5% HCl solution). A 5 % solution of HCl precipitates GO-flakes in 7–10 min and, thus, the process of removing the main impurities is accelerated. From decanted solutions, GO was reduced to the rGO with ascorbic acid at 80°C. By the high-temperature treatment of rGO received from graphite foil wastes graphene is obtained with a defective structure.

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Introduction

Due to their unique physical-chemical properties, use of compounds with carbon 2D and 3D structures are great importance and perspective. The graphene oxide (GO) and the reduced graphene oxide (rGO) are graphite graphene-monolayer oxidation products that have organic functional groups; therefore their future functionalization or joining (immobilization) in organic or inorganic precursors may be performed. There are many organic–organic, organic-inorganic, inorganic–inorganic composites containing graphene structures and they have a wide area of application. Both, natural and synthetic graphite can be used to prepare these materials, but the natural graphite is cheaper, therefore the natural flake graphite powders with a particle size of less than 400 µm are mostly used in industry or laboratory practice. Purification of the natural graphite from impurities is carried out by separation or flotation, chemical processing. For example, by the enrichment of raw ore containing 68% C graphite is obtained after enrichment with 97.68% C graphite content, which can be sued in the synthesis of GO and rGO.[1] Thorough cleaning of graphite is necessary, because the impurities in it could be found in targeted products.[2]

In general, GO and rGO structural-morphological properties depend on the used graphite nature, powder particles size, oxidation and reduction methods, thermal treatment conditions, etc. Accordingly, GO and rGO physical-mechanical properties or chemical composition changes within a wide range. The use of different precursors of graphite for GO synthesis is discussed in many scientific sources.[3] Dependence of oxidation degree, hydrophilicity and microstructure of GO prepared on nature of graphite precursors were studied with using flake expendable and microcrystalline graphite precursors. It is estimated that the GO prepared on the basis of expandable graphite is characterized by a higher degree of oxidation than in case of microcrystalline graphite.[4]

GO could be obtained by a modified Hummers method from synthetic graphite powders. The graphite powder SP-1 was washed with NaCl solution, then oxidized with $KMnO_4$–H_2SO_4 at low temperatures (<20 °C).[5] For the synthesis of GO it was successfully used expanded graphite. The process of synthesis was done below <20 °C in $KMnO_4$–H_2SO_4 system [6]. In contrast to other works, GO could also be extracted from low-grade coal and wood charcoal. Extraction was conducted with the dilute nitric acid and by the neutralization of extract with sodium hydroxide. Obtained GO is used in Alzheimer drug encapsulation.[7]

One of the interesting methods for GO synthesis is the improved Hummers method, where flake graphite oxidation is performed with $KMnO_4$–H_2SO_4–H_3PO_4 mixture at 50 °C and at a ratio of $H_2SO_4/H_3PO_{4=}$ 9:1[8], and the optimized conditions led to GO in 3 h.

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GO and rGO could also be obtained from commercial expanded graphite with grain size D_{50} ~ 15 µm. GO was obtained by a new modified Hummers method. At the initial stage the powder of graphite and potassium permanganate is mixed, cooled and then 98 % sulfuric acid is added.[10] The synthesis ends in a relatively short period of time since the particles of the graphite powder used were small.

Expanded graphite was also used in 10–30 µm size.[1] The synthesis was conducted using ultrasonic cleaner used after the reaction is terminated with water (90 °C, 10 min). Thus, for obtaining of the GO and rGO, natural and synthetic graphites, graphite intercalated with different compounds and expanded graphite can also be used. It is established that the reduction of the GO obtained from the samples of the different types of graphite are formed graphenes, in which the number of layers was very different (1–10 layers or more).[12–16]

Flexible graphite foils in various thickness and width are used in modern technologies (chemical, petrochemical, metallurgical processes, for the production of ceramic composites).[17] The remaining graphite foil pieces (wastes) are expanded graphites, and their chemical oxidation to GO or to obtain graphene can be conducted using known methods with some adjustments.[18] The purpose of the present work is studying on the usability of wastes of the graphite foils as the precursors for GO and rGO synthesis.

Experiments

Flake graphite, $KMnO_4$, $NaNO_3$, H_2SO_4 (98 %), HCl (37 %), HI (57 %) and ascorbic acid were purchased from Sigma Aldrich. The morphology of the samples was studied by optical and scanning electron microscopes (Nikon ECLIPSE LV 150, LEITZ WETZLAR and JEOL JSM–6510 LV-SEM). Samples X-ray diffraction (XRD) patterns were obtained with a DRON–3M diffractometer (Cu–K_α, Ni filter, 2°/min). After purification, graphite foil powders were analyzed using EDS.

Obtaining of powdered graphite foil wastes (pGFW)

The initial powders were obtained by grinding of flake wastes in water (blender). After drying the powder, that was still dry ground using a laboratory mill. Removal of impurities from the powders was carried out with chemical reagents and their subsequent sifting fractions with particles <140 µm were collected. From these powders, the graphene oxide was obtained with different oxidation systems ($KMnO_4$–$NaNO_3$–H_2SO_4 and $KMnO_4$–H_2SO_4).

Graphene oxide synthesis with Hummers method

In details, 0.75g $NaNO_3$ and 80ml of 98% sulfuric acid were added to 1 g of pGFW. The reaction mixture was cooled up to -2 – +1 °C and stirred for 30 min. Over the next 50 min, 6 g of $KMnO_4$ was added. The temperature was left to raise until room temperature (3 h) during stirring, and the mixture was further stirred for half an hour at 35–40 °C. The reaction mixture was diluted with 100 ml of cold water, keeping the temperature below 90°C, and then stirred at this temperature for 30 min. The mixture was diluted to 300 ml. Residual amount of potassium permanganate was removed by 3 % hydrogen peroxide solution. A yellowish suspension of graphite oxide was obtained, its color gradually changed to dark brown.

The resulting suspension was left to stand for 20 min, then the precipitate was removed by decantation. This operation was repeated twice. For the rapid precipitation of graphene oxide from the suspension, a 5 % solution of hydrochloric acid (300 ml) was added. Decantation was repeated 3 times in 10 min intervals. An aqueous gel-like mass was obtained by centrifuging and washing the sediment, the pH was between 5 and 6. The sediment was washed with acetone 3 times and is dried in vacuum at 70 °C for 4 h. The decanted solutions contained 12–17 wt.% of GO. Its reduction to the rGO was conducted with ascorbic acid. For this purpose, the decanted solutions were mixed with 1 g of ascorbic acid and heated until 80 °C. The brown solution darkens rapidly due to the formation of reduced graphene oxide. rGO precipitation occurred when the reaction mixture was cooled (10 min). The precipitate was filtered, washed with sodium bicarbonate solution, then with water until reaching pH = 6, acetone (x3) and dried in vacuum at 70 °C.

Oxidation of pGFW with $KMnO_4$–H_2SO_4 system

For oxidation of pGFW, we used a simplified oxidation system of $KMnO_4$–H_2SO_4.[9] In more details, 40 ml of 98 % sulfuric acid is added to 1 g pGFW (<140 µm) in a glass reactor The mixture was stirred at 35–40 °C for half an hour and 3 g of potassium permanganate was added at 40–45 °C under 1 h (the temperature can reach 50°C). The mixture was stirred for 3 h. A gray viscous mass was obtained, which was cooled to 10°C and 100 ml of ice-water was added to the glass reactor. A sharp change in the temperature of the reaction mixture was not observed while adding the water. After adding 3–4 drops of hydrogen peroxide (30 %), the reaction mixture becomes sharp yellow. Isolation of graphene oxide from the suspension and receiving of rGO from decanted solutions was carried out using the way mentioned above.

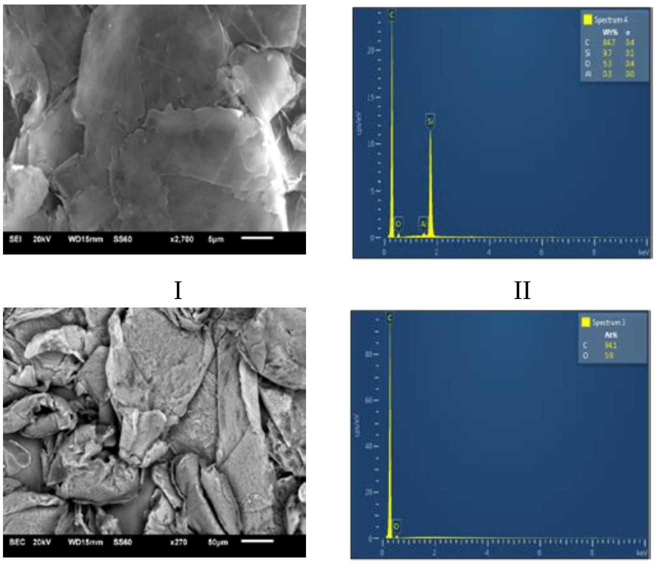
Results and discussion

Graphite foil wastes from various technological processes are contaminated with various types of organic and inorganic compounds which can be removed with various methods after grinding the waste. The graphite foil wastes used in our experiments contained about 6% oxygen and some other elements as well (Figure 1). After their wet grinding, a powder with a particle size of <1 mm was obtained, and the amount of fine fraction (<50 µm) does not exceed 6–8 %. In the case of dry grinding of these powders, a fraction with a particle size of <140 µm could be obtained, which was treated with various reagents to remove the impurities. As the EDX analysis showed, the powder produced consisted of carbon and oxygen (Figure 2).

The SEM image shows that each particle of the powder is composed of layers rolled on each other and had different forms. The thickness of the sheets were found to be ~0.5 µm (Figures 1 and 2).

I II

Figure 1. Graphite foil wastes (I) and pGFW (II).



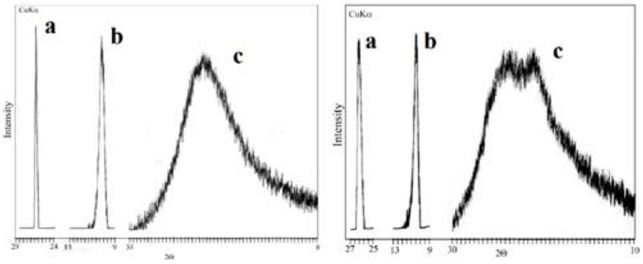
I II

III IV

Figure 2. SEM image (I and III) and EDX spectrum (II and IV) of pGFW and purified (chemically) pGFW

Oxidizing reagents can easily penetrate the layers and intercalation or functionalization-oxidation processes can be occurred resulting in graphite oxide. Using of pGFW with a particle size of 200–500 µm to prepare of GO and the rGO may also possible.

The GO synthesis from pGFW was conducted using the same methods as in case of other types of graphite precursors. The $KMnO_4$–H_2SO_4 and $KMnO_4$–$NaNO_3$–H_2SO_4 systems were tested in the pGFW oxidation using low-temperature (~0 °C; $KMnO_4$–$NaNO_3$–H_2SO_4) and relatively high-temperature (~50 °C; $KMnO_4$–H_2SO_4) modes. The characteristic XRD peak of pGFW at 2Θ=26.45–26.50° completely disappears during the oxidation process (Fig.3) due to complete oxidation of pGFW into graphite oxide. XRD analysis also confirmed that both oxidation methods led to the GO-phases characterized with the peaks located at 2Θ = 10.90 and 10.60°, respectively (Fig. 3). The obtained results correspond to the available data of processes used flake graphite or expanded graphite as a precursor.[4,13,14] In case of low-temperature mode oxidation of pGFW, the C/O ratio (at.%) was found to be 61:38. During its reduction with ascorbic acid, the C/O ratio was modified to be 81:19. The peak of GO at 2Θ = 10.90° completely disappeared during the reduction process and appeared a broad diffraction maximum for rGO at 2Θ=23.80°.

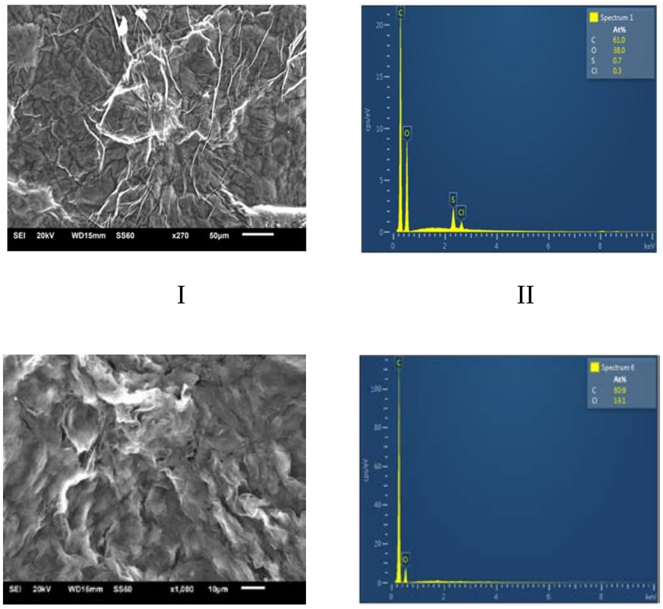


I II

Figure 3. XRD patterns of graphite foil (Ia), GO (Ib), rGO (Ic), and pGFW (IIa), GO (IIb), rGO (IIc). GO was obtained by oxidation of pGFW with $KMnO_4$–$NaNO_3$–H_2SO_4 (Ib) and with $KMnO_4$–H_2SO_4 (IIb).

When the pGFW was oxidized in a high temperature mode (~50 °C, $KMnO_4$–H_2SO_4), the C/O ratio (at.%) was found to be 64:35. In case of its reduction with ascorbic acid, rGO is obtained and the C/O ratio (at.%) was changed to 80:20. The diffraction peak at 2Θ = 10.6° disappeared and two peaks of rGO appeared at 2Θ = 21.2 and 23.7° (the sample was dried in vacuum at 150 °C in 2 h).

During the reduction of GO to rGO by the different methods, the diffraction peak maximums appeared at different values of 2Θ between 20.0 and 26.6°.[4,13,14] The location of the peaks depended on the rGO drying temperature and shifted to higher values with increasing that. Using the hydroiodic acid solution (57 %) to reduce GO obtained by us, this diffraction maximum could be detected at 2Θ=23.7°. Natural flake graphite pGFW oxidation required 8–15 % more sulfuric acid because the viscosity of the reaction medium, but it confirmed that the powder oxidation process effectively passed using 93–95 % sulfuric acid as well because it is cheaper and easier available than the concentrated H_2SO_4 (98 %).



I II

III IV

Figure 4. SEM image (I and III) and EDX spectrum (II and IV) of GO platelets and rGO sheets, respectively.

The method of synthesis of GO and its separation from the reaction mixture was partially corrected in a way that the experiments would finish after 8–10 h only. Sulfuric acid and metal ions (K^+, Na^+, and Mn^{+2}) were removed with decanting (2 times with H_2O, 3 times with 5% HCl solution). A 5 % solution of HCl precipitates GO-flakes in 7–10 min, thus, the process to remove the main impurities could be accelerated. Subsequent GO purification was carried out using traditional centrifuging and washing methods.

It is confirmed that the received GO (Figure 4) contains sulfur and chlorine as impurities, S:Cl atomic ratio (at.%) was found to be 0.7:0.3. A similar result was obtained using flake graphite (0.7–2.8):(0.6–0.8).[8,9] These impurities can be removed during the reduction process of GO. The decanted solutions contained 12–17 wt.% GO, but the large volume of the solutions complicated the separation.

It is easier to remove the GO from these acidic solutions in its reduced form. In strong acidic solutions, GO can be reduced to rGO using various chemical reagents.[12,13] We selected ascorbic acid to reduce GO in solutions to rGO (Figure 4) at 80°C. The EDX analysis confirmed the completeness of reduction and elimination of the chlorine and sulfur-containing contaminants.

Using a high-temperature (1000–1500°C) thermal treatment, the reduced graphene oxide can be transformed into graphene with a defect structure.

Conclusions

Grinding of waste industrial graphite foils resulted in graphite powders (pGFW) with a particle size of <140 µm, which oxidation to obtain GO was carried out with $KMnO_4$–$NaNO_3$–H_2SO_4 oxidation system (Hummer method). The C/O ratio in GO and its ascorbic acid reduced from (rGO) were found to be 61:38 and 81:19, respectively. It was confirmed that GO could also be obtained from pGFW using $KMnO_4$–H_2SO_4 system as well at 50 °C. Industrial wastes of graphite foils were found to be appropriate precursors for an eco-friendly synthesis of GO and rGO, which can be transformed into graphene by thermal treatment at high temperature.

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