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THERMAL ANALYSIS OF THE IMPROVED HUMMERS' SYNTHESIS OF GRAPHENE OXIDE

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Abstract

The improved Hummers' synthesis of graphene oxide (GO) from graphite is investigated to monitor how the functional groups form during the synthesis steps. To achieve these, samples are taken after every preparation step, and analyzed with TG-DTA/MS, FTIR, XRD and SEM-EDX techniques. It was found that the main characteristic mass loss step of GO was around 200 °C, where at first the carboxyl and lactone groups were released, and the evolution of sulphonyl groups followed them right away in a partially overlapping step. It became clear that in the as-prepared acidic GO sample the presence of H₂SO₄ originating from the reaction solution was still dominant. The functional groups were formed only after washing the as-prepared GO with HCl. The consecutive washing step with distilled water did not alter the functional groups or the thermal properties significantly; however, it made the GO structure more ordered. The reduction of the GO structure back to reduced GO (rGO) resulted in the loss of the functional groups and a graphitic material was obtained back.

Keywords

Improved Hummers' method, graphene oxide, carbon nanostructure, functional groups, TG/DTA-MS

1. Introduction

Graphene and its derivatives like graphene oxide (GO) have attracted significant attention due to their beneficial chemical and physical properties as e.g. polymer fillers, composite and catalyst substrates, and the attempts to prepare them on a large scale has increased exponentially [1-3]. GO can be understood as covalently functionalized graphene and the presence of polar groups on graphene surface can improve the compatibility with polymer materials or oxide coatings but reduces its thermal and electrical conductivity [4-7]. The versatility of the material is enhanced by that with the reductive removal of functional groups reduced graphene oxide (ideally graphene) can be obtained.

The widespread approach to yield GO is the graphite exfoliation by using strong, oxidizing agents [8-10]. The most commonly used method to synthesize GO was reported in 1958 by Hummers, where graphite was oxidized by treatment with KMnO_4 and NaNO_3 in concentrated H_2SO_4 [11]. In 2010 Marcano et al. found that excluding the NaNO_3 , increasing the amount of KMnO_4 , and performing the reaction in a 9:1 mixture of $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ improved the efficiency of the oxidation process. This improved Hummers' method provides a greater amount of hydrophilic oxidized graphene material, and it does not generate toxic gases [1].

Carbon materials, including GO, can have various functional groups e.g. carboxyl, lactone, phenol, carbonyl, anhydride, ether, quinone [12-15]. Sulphur containing functional groups were also reported for GO; however, it is disputed whether the sulphur content is an impurity from the H_2SO_4 or part of the structure of GO, because it can strongly influence the properties of the material, e.g. the presence of incompletely hydrolyzed covalent sulfates might contribute to the acidic properties of GO, and they can also effect the electric properties [16-19]. However, the sulphur content present in GO prepared by Hummers' method has only been addressed by a few authors so far. It was reported that hydrolysis of sulphur species took place and that stable sulphonyl groups were present in graphite oxide [17]. In another manuscript, in contrast to earlier reports, sulphate species were identified that were covalently bonded to GO and they were still present after extensive aqueous workup [16].

Hence, in our research we investigate the improved Hummers' method to see monitor the functional groups are formed during the synthesis. We also pay attention to the amount and nature of the sulphur content in the GO. To achieve these, samples are taken from every preparation step, and analyzed with TG-DTA/MS, FTIR, XRD and SEM-EDX techniques. As reference, a chemically reduced GO sample is examined as well.

2. Materials and Methods

2.1. Graphene oxide (GO) synthesis

Graphene oxide (GO) was obtained by the improved Hummers' method from natural graphite (Madagascar) [1]. The as-prepared GO suspension was purified and mildly exfoliated by centrifuging 5 times (7000g) with 1 M HCl and 6–9 times (15100g) with doubly distilled water, in order to remove unreacted graphite, possibly as-formed amorphous carbon and inorganic salts. After the final washing and centrifugation step a light brown suspension with a GO nanoparticle content of 1 w/w% was obtained.

2.2. Chemical Reduction of GO

A 2 mg/mL diluted GO suspension was reduced with ascorbic acid (vitamin C). In the mixture the concentration of ascorbic acid was 20 mM and 1 mL of cc. NH₃ was added to 15 mL reaction mixture to set basic pH and to avoid the precipitation of the reduced GO (rGO). The mixture was stirred and refluxed at 95 °C for 1 hour. Afterwards it was repeatedly washed with pure water and centrifuged until the pH reached neutral. Finally the rGO was air dried.

2.3. Sample preparation for the characterization

Samples were taken from each synthesis, washing and reducing steps. The samples were air dried at room temperature to obtain solid material for the measurements. The description of the samples and their names are listed in Table 1.

2.4. Characterization

SEM-EDX data were obtained by a JEOL JSM-5500LV scanning electron microscope after sputtering an Au/Pd layer on the samples, but they are not calculated in the EDX results. The average EDX data were calculated from 3 different measured points of each sample.

TG/DTA measurements were conducted on a TA Instruments SDT 2960 simultaneous TG/DTA device in He atmosphere (130 mL/min) using an open platinum crucible and 10

°C/min heating rate. EGA-MS (evolved gas analytical) curves were recorded by a Balzers Instruments ThermoStar GSD 200T quadrupole mass spectrometer (MS) coupled on-line to the TG/DTA instrument. The on-line coupling between the two parts was provided through a heated (T=200 °C), 100% methyl deactivated fused silica capillary tube with inner diameter of 0.15 mm.

FTIR measurements were carried out between 4000 and 400 cm^{-1} on a Biorad Excalibur Series FTS 3000 infrared spectrometer. 300 mg KBr pellets were used, which contained 1.0 mg sample. 64 measurements were accumulated into one spectrum.

Powder XRD patterns were recorded on a PANalytical X'Pert Pro MPD X-ray diffractometer using $\text{Cu K}\alpha$ radiation.

3. Results and Discussion

SEM-EDX was used to determine how effective the oxidation and the washing steps were (Table 2). The detailed EDX data and the SEM pictures can be seen in Table S1 and Fig. S1 in the Electronic Supplementary Material. The pristine graphite had ca. 99 atom% carbon content. After the oxidation step the i-Hummers GO sample contained 27 atom% C, 57 atom% O and elements from the oxidizing agents such as Mn, K, P and S. HCl washing changed the C:O ratio to 2:1 and the P, Mn and K content decreased dramatically, almost reaching zero. The Cl appeared, indicating that the HCl washing was successful. Consecutively, the Cl content was eliminated with the H_2O washing step. However, considerable amount of S was still detected after the applied HCl and H_2O washing steps, meaning that it was present in the form of covalently bonded functional groups. The chemical reduction of the functional groups was effective, since in the rGO the O and S content decreased and a composition close to graphite was reached.

Although, thermal analysis of GO was published earlier, to the best of our knowledge, there is no detailed systematic study investigating the steps of the improved Hummers' method by TG/DTA-MS technique. Besides recording the TG and DTA curves, in EGA-MS measurements we followed the H_2O (18^+), CO (28^+), CO_2 (44^+) fragments for carboxyl and lactone groups, and the SO_2 (64^+) for the S containing functional groups.

The pristine graphite material, as expected, was thermally stable and had only 1.6 % mass loss until 900 °C in He atmosphere (Fig. 1a). The as-prepared i-Hummers GO sample began to lose its mass already under 100 °C, resulting from the evaporation of adsorbed water (Fig. 1b). This stage was followed by a dramatic mass loss around 200 °C accompanied by an

endothermic DTA peak. During this abrupt change in mass, H₂O and SO₂ were evolving, without any sign of CO₂ or CO release. The SO₂ evolution continued throughout the entire heating process, indicating that the sample withheld H₂SO₄ from the reaction solution. After the major mass loss step the material had only 27.8 % of its original mass. The carbon structure started to degrade only around 700 °C [8,16,20-23], and the final residue had a mass of 6.7 %.

The endothermic mass loss of the HCl washed GO sample (Fig. 1c) was obviously lower than that of i-Hummers GO sample, indicating that this washing step successfully removed most of the H₂SO₄. Until 300 °C the sample lost only 52.6% of its mass, and not 72.2 %, as previously. After the major mass loss step, the sample decomposed slowly and the residual mass was 32.6%.

The H₂O washed GO sample behaved similarly (Fig. 1d); however, in its case the endothermic mass loss data were even lower. This sample lost only 40.3 % after the main mass loss step, and the residual mass at 900 °C was 44.9 %.

A common feature in the case of the HCl and H₂O washed GO samples was that around in the major mass loss reaction at first the evolution of CO₂, CO and H₂O was detected between 100-250 °C, suggesting the release of carboxyl groups. Then between 250-300 C in an overlapping step the release of CO₂ continued, which was not accompanied by H₂O or CO; this refers to the release of lactone groups. The removal of carboxyl and lactone functionalities was followed by the evolution of SO₂. This means that these samples first lost their carboxyl and lactone groups, and right after them in a partially overlapping step their sulphonyl groups were released, as seen in Figure 1c-d.

To sum up the thermoanalytical results, the functional groups were formed on GO only during the washing steps. No CO₂ and CO evolution was detected by EGA-MS during the thermal degradation of the i-Hummers GO sample.

Figure 1e shows the curves of the chemically reduced rGO sample. Based on the thermal analysis the chemical reduction of GO with ascorbic acid was successful. The mass of the sample decreased continuously, and the residual mass was as high as 76.5 % at 900 °C. There was no major mass loss step around 200 °C as previously. The slight evolution of CO₂ and SO₂ indicated the release of the few remaining functional groups.

The FTIR results confirmed the thermal analysis data. In Figure 2 of the peaks at 1725 cm⁻¹ (-C=O) and 1050 cm⁻¹ (-C-O) suggested the presence of carbonyl and carboxyl groups, while the band at 1250 cm⁻¹ (-C-O-C) was assigned to the epoxy mode of the lactone group. The peaks of the OH in carboxyl group were at 3400 cm⁻¹ (-OH stretching) and 1400 cm⁻¹ (-OH

deformation). The bands belonging to the carbon core were located at 3030 cm^{-1} (aromatic –CH), 3080 cm^{-1} (=CH), 1650 cm^{-1} (C=C), 1400 cm^{-1} (=C-H) and 900 cm^{-1} (-CH deformation). The peaks of the sulphonyl group and the sulphate from the H_2SO_4 could be seen at 1250 cm^{-1} (SO_2 asymmetric), 1100 cm^{-1} (SO_2 symmetric) and 600 cm^{-1} (C-S) [1,13,24-26].

The spectrum of the graphite (Fig. 2a) had less intensive bands, compared to the other samples. Most of the peaks belonged to the carbon structure [27]. The spectrum of the i-Hummers GO sample was dominated by the H_2SO_4 content (Fig. 2b), while the bands associated with the carboxyl and lactone groups at 1725 , 1250 and 1050 cm^{-1} still could not be seen [27]. The presence of C-S stretching band in the IR (this band belongs to sulphonate group and would not be present if only sulfuric acid existed in the graphene oxide) means, that not only free sulfuric acid but some amount of sulphonate containing material is also present in the i-Hummers GO phase. Based on the S-content of the i-Hummers and the HCl washed sample, c.a. 10 % of the S is in sulfonate and 90 % in sulfuric acid form. In agreement with the thermal data, after the HCl washing (Fig. 1c) the bands of the sulphonyl group and the sulphate signal reduced to large extent due to the removal of the H_2SO_4 content, while new peaks appeared, confirming the presence of carboxyl and lactone functionalities. Also, corroborating the result of the thermal analysis, the H_2O washing (Fig. 1d) did not result in significant difference in the type and amount functional groups, as the spectra of the HCl washed and the H_2O washed GO samples looked very similar. In their spectra both the bands of the carbon structure and all the functional groups were visible. Finally, the reduction of GO (Fig. 1e) resulted in the loss of the functional groups, supporting the thermoanalytical results.

FTIR results also give information about how sulfonyl groups possibly formed. The bands below between 900 and 850 cm^{-1} (a doublet) might belong to the permanganyl group, because these bands disappeared after HCl washing (due to decomposition of permanganyl group). The sulfonyl and permanganyl groups could be built into the graphene substrate via addition or substitution (condensation) reactions from certain species, which were present in the $\text{KMnO}_4/\text{H}_2\text{SO}_4$ system, namely Mn_2O_7 , permanganyl sulphate or H_2SO_4 . The possible MnO_3 -containing species could decompose in water due to acidic environment during HCl washing [28-30].

The powder XRD method also revealed the structural changes throughout the oxidation process as shown in Figure 3. The graphite (Fig. 3a) had an intensive, narrow peak at $2\theta = 26.4^\circ$ (002) and a smaller, wider peak at $2\theta = 56^\circ$ (004) in the diffractograms A. This sample was identified with the ICDD 40-1487 card [31]. In the i-Hummers GO sample (Fig. 3b) the $2\theta = 26.4^\circ$ graphite peak disappeared, and the material became amorphous due to the

exfoliation. In the XRD pattern of the HCl washed GO sample (Fig. 3c) signs of the successful oxidation are visible: even though the baseline shows amorphous characteristics, the $2\Theta = 10.9$ (001) GO peak appeared and there were also less intensive peaks at $2\Theta = 44^\circ$ and at $2\Theta = 34^\circ$ (100) [31-33]. The H₂O washed GO sample (Fig. 3d) differed from the HCl washed GO. The $2\Theta = 10.9^\circ$ peak was more intensive, a smaller peak at $2\Theta = 22^\circ$ appeared, and the baseline was smoother, indicating that the structure of the H₂O washed GO sample became more ordered. The results of reducing GO to rGO can be seen in the E curve of Figure 3. The $2\Theta = 10.9^\circ$ peak almost disappeared, the graphitic $2\Theta = 26.4^\circ$ peak was recognizable again and there was a new peak at $2\Theta = 44^\circ$. The region between $2\Theta = 20-30^\circ$ suggested a partially amorphous structure in the case of the rGO sample [26,31,24].

4. Conclusions

In this research the preparation steps of the improved Hummers' method to obtain graphene oxide were investigated with TG/DTA-MS, SEM-EDX, FTIR and XRD techniques. Beside the carboxyl and lactone groups on the surface of GO, the presence of sulphonyl groups were also proven. It was also possible to explore the formation and thermal stability of these functional groups. It was found that the main characteristic mass loss step of GO was around 200 °C, where at first the carboxyl and lactone groups were released in two overlapping steps. The evolution of sulphonyl groups followed them right away in a partially overlapping process. Based on both the EGA curves and the FTIR spectra it became clear that in the as-prepared acidic i-Hummers GO sample the presence of H₂SO₄ originating from the reaction solution was still dominant. The functional groups were formed only after washing the i-Hummers GO suspension with HCl. The consecutive washing step with distilled water did not alter the functional groups or the thermal properties significantly; however, it made the GO structure more ordered. The reduction of the GO structure to rGO resulted in the loss of the functional groups and a graphitic material was regained.

7. Acknowledgement

I. M. Szilágyi thanks for a János Bolyai Research Fellowship of the Hungarian Academy of Sciences, an ÚNKP-17-4-IV-BME-188 and an OTKA PD-109129 grant. Financial support from the National Scientific Research Fund (OTKA) through NN110209 and K109558 is acknowledged. K. László extends her thanks to K. Katsumi for the graphite material. The help

of Virág Bérczes (Budapest University of Technology and Economics, Department of Physical Chemistry and Materials Science) in the synthesis steps is acknowledged.

Electronic supplementary material

The online version of this article contains supplementary material (detailed EDX data and the SEM images of the preparation steps)

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Figures

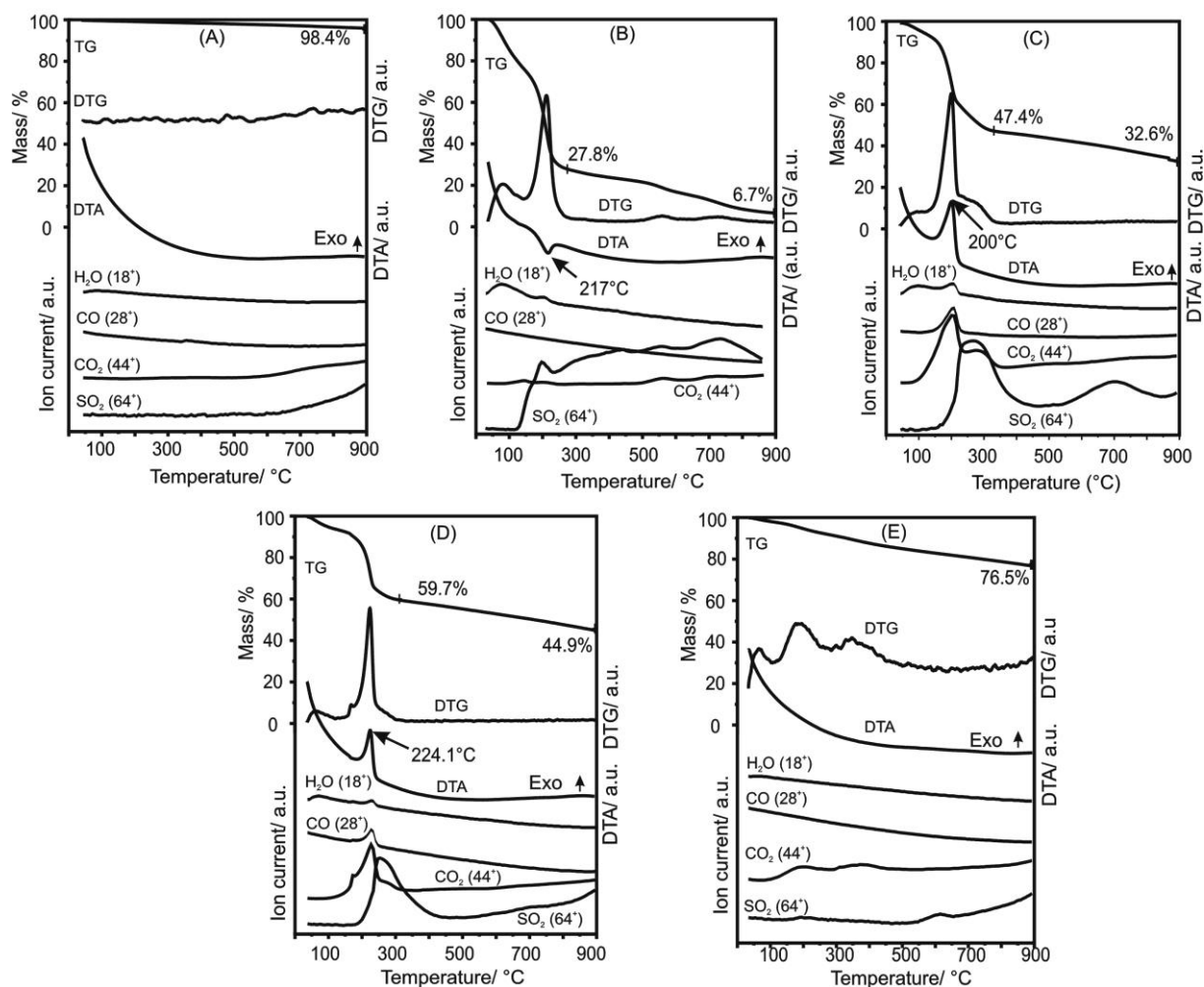


Figure 1. TG/DTA-MS results of (A) Graphite, (B) i-Hummers GO, (C) HCl washed GO, (D) H₂O washed GO and (E) rGO samples in He atmosphere

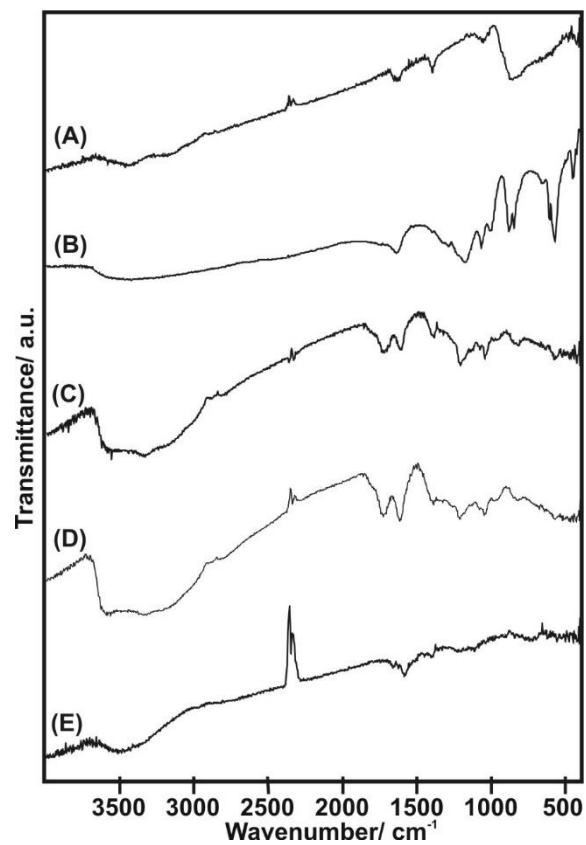


Figure 2. FTIR spectra of (A) Graphite, (B) i-Hummers GO, (C) HCl washed GO, (D) H₂O washed GO and (E) rGO samples

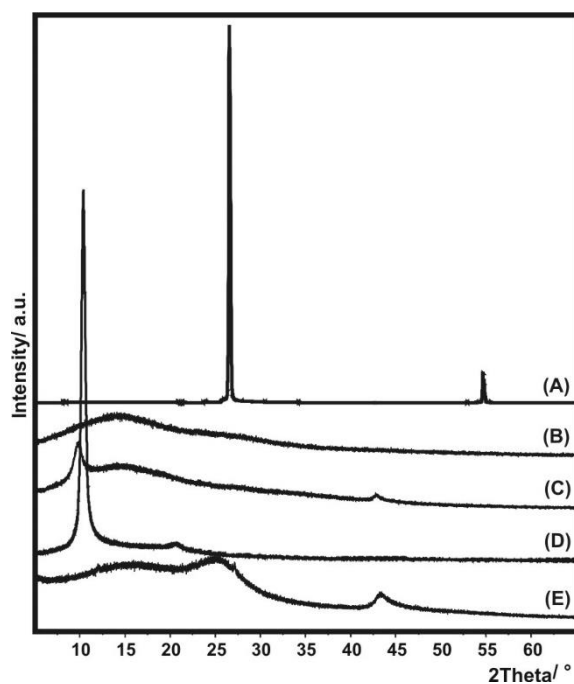


Figure 3. XRD diffractograms of (A) Graphite, (B) i-Hummers GO, (C) HCl washed GO, (D) H₂O washed GO and (E) rGO samples

Tables

| | Sample description | Sample name |
|----|--|----------------------------|
| 1. | Graphite flakes from Madagascar | Graphite |
| 2. | As-prepared graphene oxide suspension by the improved Hummers' method, dried | i-Hummers GO |
| 3. | HCl washed graphene oxide suspension, dried | HCl washed GO |
| 4. | H ₂ O washed graphene oxide suspension, dried | H ₂ O washed GO |
| 5. | Chemically reduced graphene oxide, dried | rGO |

Table 1. The description and name of the samples

| | Element/ atom% | | | | | | |
|------------------------------|-----------------------|----------|----------|----------|-----------|----------|-----------|
| | C | O | P | S | Mn | K | Cl |
| Graphite | 99.10 | 0.89 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 |
| i-Hummers | 27.07 | 57.40 | 0.92 | 11.59 | 2.23 | 0.78 | 0.00 |
| HCl washed | 66.66 | 34.51 | 0.03 | 1.14 | 0.02 | 0.01 | 0.31 |
| H₂O washed | 67.93 | 30.66 | 0.05 | 0.73 | 0.02 | 0.02 | 0.02 |
| rGO | 89.78 | 9.93 | 0.01 | 0.02 | 0.03 | 0.03 | 0.02 |

Table 2. Average EDX data of Graphite, i-Hummers GO, HCl washed GO, H₂O washed GO and rGO samples