Utilization of multiple graphene nanosheets in fuel cells: 2. The effect of oxidation process on the characteristics of graphene nanosheets

Burcu Saner, Fatma Dinç, Yuda Yürüm *

Faculty of Engineering and Natural Sciences, Sabanci University, Orhanlı, Tuzla, İstanbul 34956, Turkey

Abstract

Structural properties of graphene nanosheets that will be used as electrode material in fuel cells were investigated at different oxidation times. As the oxidation time was increased, the strong bonding between graphene layers in graphite was reduced and graphene layers started to exfoliate forming clusters with a few number of graphene layers. The variations in interplanar spacings, layer number and percent crystallinity indicated how stepwise chemical procedure influenced the morphology of graphite. It was possible to produce relatively flat graphene clusters with definite number of layers by controlling the oxidation time. Graphene nanosheets were characterized in detail by scanning electron microscopy, atomic force microscopy, X-ray diffraction, Raman spectroscopy, and thermal gravimetric analyzer.

1. Introduction

With the appropriate surface treatments, single graphene sheets can be separated from the graphite material and the layer-to-layer distance can be extended [1,2]. There are numerous old methods for the graphite modifications to reduce the number of graphene layers in graphitic structure. One of the applicable methods is the graphite oxidation in order to reduce the strong bonding between sheets in graphite and to receive monolayer graphene sheet. All the methods used for this purpose are presented by Saner et al. [2].

After the oxidation process, GO still preserves a layered structure, yet is much lighter in color than graphite owing to the loss of electronic conjugation. GO is composed of graphene oxide sheets, hydrophilic oxygenated graphene sheets, having carboxyl and carbonyl functional groups at the edges of the sheets, hydroxyl and epoxide groups on the basal planes [3]. The structure of GO is similar to that of graphite but only distinction is that the sp² hybridization in carbon atoms which reveals that the individual layers are noticeably bent [4].

GO is naturally an insulating material, and it requires chemical modifications to be used in electronic applications. Furthermore, GO is thermally unstable material which can be pyrolyzed at high temperatures due to the existence of the oxygen functional groups [2,5]. After heat treatment, the crystal lattice planes of graphite flakes are extended, and this leads to the formation of expanded graphite called as “worm-like” or accordion structure. The expanded graphite is a loose and porous material and its pore sizes range from 10 nm to 10 mm [6].

GO nanoplatelets having exceptional in-plane mechanical, structural, thermal, and electrical properties as graphite have been recently used as cheap fillers in polymer nanocomposites [7]. Cost reduction and improvements are significant tasks for large-production for polymer electrode membrane (PEM) fuel cells. In addition, the incorporation of graphene and its derivatives into polymer matrix can enlarge the surface area by π–π stacking with polymer hosts [8] and provide high conductivity [9]. Therefore, the combination of characteristic properties makes graphene sheets a promising candidate for the fabrication of advanced type of electrode materials to be utilized in fuel cell applications. Novel geometric structure of graphene can control the transport directions of gases, water, protons and electrons in PEM fuel cells [10].

In this paper, there are three main objectives which are (i) to tailor the characteristic properties of graphene nanosheets via various oxidation times, (ii) to optimize reactant ratios during graphite oxidation, and (iii) to decrease the number of graphene layers in graphitic structure to be used as fuel cell electrodes.

2. Experimental procedure

2.1. Materials

The following materials were used in this experiment: graphite flake (Sigma Aldrich); acetic anhydride (Merck, extra pure); sulfuric acid (Fluka, 95–97%); potassium dichromate (Chempur,
99.9%); hydroquinone (Acros, 99%); sodium hydroxide (Merck, 97%).

2.2. Graphite oxidation and Graphene oxide sheets preparation

GO was obtained regarding the technique used by Saner et al. [2] using potassium dichromate and sulfuric acid as oxidant and acetic anhydride as intercalating agent. Potassium dichromate and sulfuric acid were mixed in a flask in two different weight ratios as 2.0:9.3 and 2.1:55. In each condition, 1.5 ml distilled water was also added to prepare chromic acid. Then, graphite flake (1.0 g) was added into flask and the mixture was stirred gently. Afterward, acetic anhydride (1.0 g) was slowly dropped into the solution. Experimental conditions for graphite oxidation are summarized in Table 1. The reaction temperature was adjusted as 45 °C and the solution was stirred at different reaction times as 50 min, 6 h, 12 h, 24 h, 48 h, 72 h and 120 h. In order to observe the change in surface morphology, graphite flakes were exposed to longer oxidation. Neutralization and filtration were performed with 0.1 M NaOH and distilled water. All GO samples were dried in a vacuum oven at 60 °C overnight.

Each GO sample was exfoliated into dispersed GO sheets in distilled water for 1 h at room temperature via ultrasonic vibration.

2.3. Thermal exfoliation

All sonicated GO samples were exfoliated by rapid heating to 1000 °C rapidly in a tube furnace and kept for 1 min at this temperature under an argon atmosphere. Expanded samples were then exfoliated through ultrasonication for 1 h in distilled water and dried in a vacuum oven at 60 °C overnight.

2.4. Fabrication of graphene nanosheets

Both sonicated expanded GO and sonicated GO samples were reduced by refluxing in hydroquinone and distilled water under N2 atmosphere for 1 day. Then, the products were washed with distilled water and dried in a vacuum oven at 60 °C overnight. General experimental procedure for the production of graphene nanosheets was shown schematically in Fig. 1 [2].

2.5. Characterization

All the products obtained at different oxidation times were investigated by a Leo Supra 35VP Field Emission Scanning Electron Microscope (SEM). The surface and thickness of the samples were analyzed by Ambient Atomic Force Microscope (AFM) LAMF02-007, NanoMagnetics Instruments.

X-ray diffraction (XRD) measurements were taken with a Bruker AXS advance powder diffractometer fitted with a Siemens X-ray gun, using Cu Kα radiation (λ = 1.5406 Å). The samples were rotated at 10 rpm and swept from 2θ = 10° through to 90° using default parameters of the program of the diffractometer that was equipped with Bruker AXS Diffrac PLiS software. The X-ray generator was set to 40 kV at 40 mA.

Structural changes were examined by Renishaw InVia Reflex Raman Microscopy System using (Renishaw Plc., New Mills, Wotton-under-Edge Gloucestershire, UK) using a 514 nm argon ion laser in the range of 100–3200 cm⁻¹.

Thermal behaviors of the samples were investigated by Thermal Gravimetric Analyzer (TGA). TGA was used to measure the weight loss of the sample as a function of temperature under both air and N2 atmospheres. The heating rate was 5 K/min to a final temperature of 1000 °C.

3. Result and discussion

3.1. Morphology analysis by SEM

SEM image of pristine graphite flake consists of rigid and condensed layers in Fig. 2. The influence of sulfuric acid concentration on graphite oxidation was examined by SEM characterization. During oxidation process, sulfuric acid was used as an inserting agent which caused swelling of the graphite oxide layers. When the acid amount was insufficient, complete oxidation could not be achieved. Two kinds of experiment were carried out in order to understand the acid effect on oxidation, Table 1. Fig. 3a shows the graphite layers after the oxidation process conducted using low amount of sulfuric acid (9.3 g sulfuric acid/g of graphite) and the expansion of layers was not enough due to the low oxidation. However, when the acid concentration was increased (55 g sulfuric acid/g of graphite), a more loose structure formation and much more enhancement between the layers were observed, Fig. 3b.

GO sheets started to exfoliate at longer reaction times. After 6 h of oxidation process, graphite started to crumble forming randomly stacked irregular structures, Fig. 4a. A period of 120 h of oxidation caused GO sheets to separate from graphitic layers that were separated in the early steps of the process, Fig. 4b.

Both GO and expanded GO samples as explained in the scheme in Fig. 1, were chemically reduced through refluxing with hydroquinone in water to produce graphene nanosheets. SEM images of the samples obtained using either of the two routes in the
scheme in Fig. 1, indicated that graphene nanosheets could be obtained after the reduction process, Fig. 5a and b. The wrinkled appearance of sheets was due to the rapid heating of GO because its expansion and delamination brought about rapid evaporation of intercalants (acetic anhydride and sulfuric acid) into CO$_2$ and H$_2$O vapor produced by thermal pyrolysis of the oxygen-containing functional groups [11]. Graphene nanosheets could also be separated using a method without the thermal expansion step in the chemical reduction of GO samples, which were obtained after 120 h oxidation in Fig. 6. Graphene sheets made of a few graphene layers could be clearly seen in Fig. 6b. Consequently, both the reaction procedures with thermal expansion and without thermal expansion led to the formation of graphene nanosheets. Therefore the process time could be reduced by using the steps of graphite oxidation, ultrasonic treatment and chemical reduction of GO samples.

### 3.2. AFM characterization

AFM was used for the measurement of sheet thickness and the surface morphology. All AFM experiments were carried out in tapping mode using a silicon cantilever probe. Three-dimensional views of samples produced evidence for the reactions that occurred in each step of the process (Fig. 7). Three-dimensional surface topography of pristine graphite flakes indicated smooth and flat morphology, Fig. 7a. However, after oxidation process, intercalating compounds diffused between the graphene layers caused wavy and swelled structure as it was observed in Fig. 7b. Also, the functional groups (epoxide, carbonyl, quinone, ketone, and hydroxyl) on the basal plane of GO caused corrugation or local “puckering” of the carbon skeleton [12]. After direct reduction of GO sheets, surface topography of the sheet became rigid and flat in Fig. 7c.

On the other hand, after heat treatment the layers appeared as a loose worm-like material, Fig. 7d. The formation of this appearance

---

**Fig. 2.** SEM image of pristine graphite flake via secondary electron detector.

**Fig. 3.** SEM images of GO (a) in low acid amount (oxidation process about 50 min using first experimental conditions in Table 1) (b) in higher acid amount (oxidation process about 50 min using second experimental conditions in Table 1) via secondary electron detector.

**Fig. 4.** SEM images via secondary electron detector of GO (a) after 6 h oxidation process and (b) after 120 h oxidation process.
was stemmed from the gas evolution between layers during thermal shock. Reduction of expanded GO induced the flattening of the sheets, Fig. 7e but still the thickness was not identical because oxidation process was not uniform throughout the sample. AFM measurements showed that layers were flattened and the height difference on the surface decreased after chemical reduction. AFM measurements supported the SEM results of the samples obtained after ultrasonic vibration and chemical reduction, and bulk GO could be exfoliated into graphene nanosheets without thermal shock.

3.3. Raman spectroscopy characterization

Raman spectroscopy is an efficient technique to establish the number of graphene layers and the change of crystal structure of carbon materials. Raman spectrum of graphite has four principal peaks: the G band around 1580 cm\(^{-1}\), the G’ band around 3248 cm\(^{-1}\), the D band around 1360 cm\(^{-1}\) and the D’ band around 2700 cm\(^{-1}\). The intensity of D band relies on any kind of disorder of defects in sample, and G band intensity increases almost linearly as the flake thickness increases [13]. In Fig. 8a, a strong G band at 1580 cm\(^{-1}\), a weak D band at 1360 cm\(^{-1}\) and a broad D’ band at 2724 cm\(^{-1}\) were observed in the Raman spectrum of raw graphite. After 6 h oxidation process, G band of GO sample was broadened and the intensity of D band was increased due to the significant reduction in size of the in-plane sp\(^2\) domains, Fig. 8b. During oxidation reactions, diffusing oxygen species randomly attached through the layers and thus graphite lattice was destroyed. After thermal shock, the strong G band with a weak D band and broad D’ band was detected in Fig. 8c. The broad D’ multi-band peaks observed at ~2700 cm\(^{-1}\) are compatible with multi-layer aspect of bulk graphite [14]. Then, thermally exfoliated GO was subjected to a chemical reduction, D band around 1350 cm\(^{-1}\) disappeared due to the defect-free graphene nanosheet formation, Fig. 8d. Additionally, direct reduction of GO sheets led to a decrease in the G band intensity (lowering from 2002 a.u. to 815 a.u.) which indicated a reduction in the number of layers when compared with GO, Fig. 8e.

The structural change from graphite to graphene nanosheets could be observed by the intensity ratio of the D and G bands, I(D)/I(G). This ratio varied inversely with the size of the crystalline grains or interdefect distance and this was also used to estimate the amount of defects [15]. In Fig. 9a, I(D)/I(G) values decreased via an increase in oxidation time and this indicates an increase in order in structure. D band intensity decreased with increasing layer numbers. D’ band became more prominent than G band if only the number of graphene layers were smaller than 5 [16]. Subsequently, layer number could be determined regarding the intensity of G band. Fig. 9b exhibited that the ratio between the intensity of G and D’ peak, I(G)/I(D’), raised with increasing oxidation time. The gradual increase in the values of I(G)/I(D’) ratio indicated increases in the number of layers.

Raman spectroscopy characterization was also used for the reduced GO and reduced expanded GO samples. After the chemical
Fig. 7. Three-dimensional AFM images by tapping mode of (a) pristine graphite flake (b) GO sheet obtained after 72 h oxidation (c) graphene nanosheets after direct reduction of GO (d) expanded GO (e) graphene nanosheets after heat treatment and reduction.
reduction of both GO and expanded GO sheets, $I(G)/I(D)$ decreased by increasing oxidation time, which denoted reduction in the number of graphene layers as shown in Fig. 10a and b. Therefore, stacking height of graphene sheets decreased as oxidation degree increased.

### 3.4. Thermal analysis by TGA

The thermal behavior of pristine graphite flakes, GO obtained after 6 h of oxidation, and graphene nanosheets obtained after direct reduction were analyzed by TGA in both dry air and $N_2$ atmospheres. Pristine graphite flake started to lose weight around 750 °C due to the carbon dioxide evolution, Fig. 11a. The thermal decomposition of GO sheets under dry air occurred in two steps around 300 °C and 550 °C due to the removal of oxygen functional groups and carbon oxidation [17]. Graphene nanosheets exhibited a weight loss at about 240 °C. Thermal analysis under dry air indicated that graphene nanosheets decomposed thermally at lower temperatures when compared with pristine graphite flakes.

Fig. 11b also supported thermally unstable behavior of GO samples under a nitrogen atmosphere. Graphene nanosheet samples seemed to decompose considerably at higher temperatures when compared with GO samples. Furthermore, the percentage of weight loss of GO sample was about 40% after thermal treatment under a nitrogen atmosphere, while no weight loss was observed in graphite and graphene nanosheets samples.
3.5. Calculation of the average number of graphene layers

For the calculation of the average number of graphene layers in treated graphite samples, two methods were proposed. The first way is the application of Debye–Scherrer equations [18]:

\[
L_a = 0.89 \lambda / \beta_{002} \cos \theta_{002}
\]

\[
n = L_a / d_{002}
\]

where \(L_a\) (stacking height), \(\beta\) (full width half maxima–FWHM), \(n\) (number of graphene layers), \(d_{002}\) (interlayer spacing) were obtained by using the data from XRD patterns.

In the second method, for the determination of the stacking height AFM micrographs of the samples were used. The average stacking height, \(L_s\), determined from AFM measurements obtained from different zones of the surface of the sample was divided into interplanar spacing, \(d_{002}\), obtained from XRD patterns and thus the number of the graphene layers was calculated. Stacking height and lateral size of the crystallites computed by Debye–Scherrer equation were approximate values due to wavy structure of graphene sheets.

Comparison of these two methods was exhibited in Table 2. The average number of layers for pristine graphite flake, GO, expanded GO, reduced expanded GO (graphene nanosheets) and reduced GO (graphene nanosheets) were calculated as 86, 17, 30, 37, and 9 via XRD characterization [2], and 89, 17, 25, 17, and 11 via AFM characterization, respectively. When looking the layer number results obtained either by XRD or by AFM characterization techniques, there were small deviations. This proved that both two techniques supported each other to calculate average number of layers, and the average number of graphene layers decreased steadily from pristine graphite flake to graphene nanosheets samples by applying proposed chemical routes. The variations in interplanar spacings also clarified how stepwise chemical procedure influenced the morphology of graphite. Intercalation of acetic anhydride into the crystal structure of graphite during oxidation increased the interplanar spacing of graphite from 3.37 Å to 3.61 Å. Expansion process initiated the formation of “worm-like” or accordion structure. However, this structure is flexible and can be cut into different shapes and compressed [19]. Therefore, the interplanar spacing of expanded GO is lower than that of GO because graphite layers can also be easily restacked during characterization. Increase in the average number of graphene layers after thermal expansion

![Fig. 10. I(G)/I(D') as a function of oxidation time of (a) reduced GO (graphene nanosheets) and (b) reduced expanded GO (graphene nanosheets).](image)

![Fig. 11. TGA curves for pristine graphite flake, graphene nanosheets and graphite oxide-6 h (a) under a dry air atmosphere and (b) under nitrogen atmosphere.](image)

<table>
<thead>
<tr>
<th>Samples</th>
<th>(d) (Å)</th>
<th>Average number of layers (XRD)</th>
<th>Average number of layers (AFM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite flake</td>
<td>3.37</td>
<td>86</td>
<td>89</td>
</tr>
<tr>
<td>GO-50 min</td>
<td>3.61</td>
<td>17</td>
<td>17</td>
</tr>
<tr>
<td>Expanded GO</td>
<td>3.36</td>
<td>30</td>
<td>25</td>
</tr>
<tr>
<td>Reduced expanded GO (graphene nanosheets)</td>
<td>3.38</td>
<td>37</td>
<td>17</td>
</tr>
<tr>
<td>Reduced GO (graphene nanosheets)</td>
<td>3.62</td>
<td>9</td>
<td>11</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Intensity of (0 0 2) peak (counts)</th>
<th>FWHM (°)</th>
<th>Area (experimental)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>169,814</td>
<td>0.327</td>
<td>50,944</td>
<td>100</td>
</tr>
<tr>
<td>GO-50 min</td>
<td>761</td>
<td>1.294</td>
<td>647</td>
<td>2.5</td>
</tr>
<tr>
<td>GO-6 h</td>
<td>574</td>
<td>1.151</td>
<td>603</td>
<td>3.2</td>
</tr>
<tr>
<td>GO-12 h</td>
<td>378</td>
<td>1.501</td>
<td>397</td>
<td>1.9</td>
</tr>
<tr>
<td>GO-24 h</td>
<td>780</td>
<td>1.631</td>
<td>1082</td>
<td>9.3</td>
</tr>
<tr>
<td>GO-48 h</td>
<td>556</td>
<td>1.876</td>
<td>584</td>
<td>5.9</td>
</tr>
<tr>
<td>GO-72 h</td>
<td>431</td>
<td>1.664</td>
<td>410</td>
<td>4.2</td>
</tr>
</tbody>
</table>

![Table 3. XRD data analysis for the calculation of percent crystallinity of GO samples.](image)
was thus also explained by Raman spectroscopy characterization results which revealed a return to the graphitic structure with the thermal treatment.

### 3.6. Crystallinity analysis via XRD

XRD data were employed to characterize the percent crystallinities of modified graphitic structures at different oxidation times. The area of (0 0 2) peak of 1 g pristine graphite was accepted as reference data. The area of the same peak in diffractograms of the samples will give the amount of the graphite present in the samples. The ratio of the area of (0 0 2) peak in the treated samples to the area of the (0 0 2) peak of 1 g pristine graphite gave the ratio of the graphite (crystallinity) present in the sample.

Table 3 shows the XRD data analysis for the calculation of percent crystallinity. As seen in Table 3, FWHM values of the (0 0 2) XRD peak are considerably larger for GO samples than that for pristine graphite [12].

Assume that the graphite flake is nearly 100% crystalline, chemical process induced the change in the structure from crystalline to amorphous. GO samples became amorphous and the percent crystallinity decreased down to nearly 2%. However, there was no gradual decrease in percent crystallinity regarding oxidation times, Fig. 12. This disorder in percent crystallinity values stemmed from the change of stacking order between graphene layers and the random destruction of graphitic structure after oxidation process. Furthermore, turbostratic random ordering of GO structure obtained after the acid exposure at different hours may affect the crystallinity [12].

### 4. Conclusions

In the present study, we have developed a chemical synthesis procedure to tailor the structural properties of graphene nanosheets. This procedure was repeated at different oxidation times until the desired monolayer graphene sheets were obtained. GO sheets started to exfoliate at longer reaction times. Surface modification with oxidants lead to distortions in graphitic structure and Raman spectroscopy showed that the regular layered structure of graphite or GO was destroyed. Turbostratic random ordering of GO structure was also supported by XRD analysis. Both the reaction procedures with thermal expansion and without thermal expansion led to the formation of graphene nanosheets. As the degree of oxidation increased, stacking height of graphene sheets decreased and thus the number of graphene layers decreased. Both SEM and 3D AFM images showed that graphene layers became flattened after each reaction step. It was possible to produce relatively flat graphene clusters with definite number of layers by controlling the oxidation time. Moreover, TGA results showed that graphene nanosheets were thermally more stable than GO sheets. Functionalyzed graphene sheets could potentially lead to a more stable, efficient, and lower-cost fuel cell. Therefore, graphene-based nano-composites as fuel cell electrodes have a dramatic effect on fuel cell performance. We suggested that incorporation of few-layer graphene in composites as a catalyst support might enhance the surface area to volume ratio and increase the catalytic activity and reduce rare metal usage. In future work, the effect of surface oxygen functional groups on catalyst dispersion in graphene nanosheet-based nanocomposites will be investigated in detail and the exfoliated graphene nanosheets will be used as electrode material for fuel cells and the performance of the electrode will be determined while they are used in a fuel cell equipment that we have in our laboratories.

### References