Tailoring the characteristics of graphite oxides by different oxidation times

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Abstract
Graphite oxide was synthesized using various oxidation times and characterized by its physical and chemical properties. The degree of oxidation of the graphite oxide was systematically controlled via oxidation time up to 24 h. Three phases of interlayer distances were identified by x-ray diffraction: pristine graphite (3.4 Å), intermediate (4 Å) and fully expanded graphite oxide (6 Å) phases. These phases were distinguished by an atomic ratio of O/C, which occurred from the different compositions of epoxide, carboxyl and hydroxyl groups. The band gap of the graphite oxides was also tuned via the oxidation time, resulting in direct band gap engineering from 1.7 to 2.4 eV and strong correlation with the atomic ratio of O/C.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Graphene has stimulated interest in alternative and fast electronics instead of conventional silicon electronics because of its excellent transport properties with a high mobility of 200 000 cm² V⁻¹ s⁻¹ [1, 2]. In practice, however, large area graphene is required in many applications such as the integration of high-speed nanotransistors and transparent conducting films. The direct synthesis of large area graphene on a desired substrate is not yet available. One alternative to preparing graphene is to use a detour route, i.e. graphite oxide. Unlike graphene, graphite oxide is soluble in water, and can be exfoliated to a single layer, graphene oxide, which can be deposited on a desired substrate by a spin-coating or a spray method. Graphene oxide can be converted to graphene layers with reasonable sheet resistance through thermal and/or chemical reduction treatment [3–11]. The amount of oxygen-related functional groups in the reduced graphene oxide is related to the degree of reduction. This raises a question for the possibility of defining a new class of graphite oxide in terms of oxygen content.

It is worth designing a new approach other than the reduction methods to synthesize graphite oxide with different oxygen levels. One synthesis strategy is to control the oxygen level in an oxidation stage by varying the oxidation time, which nullifies the use of the reduction process in controlling the oxygen level. Many experiments were performed using different oxidation treatment times [12–16]. However, in all previous studies, the oxidation treatment time varied from 24 h to longer. Since the graphite oxide obtained after 24 h or more of oxidation is fully insulated with light brown colours, it is not scientifically interesting for electronic device applications. A more intriguing oxidation time is less than 24 h, in which graphite oxide can be tuned from an insulator to a semiconductor with different band gaps. Recent graphene/graphene oxide devices showed the presence of Schottky barriers, raising further investigations of tuning the band gap by changing the degree of oxidation [17].

The purpose of this paper is twofold: (i) to control the oxidation level of graphite oxide during synthetic oxidation for less than 24 h and (ii) to understand the effects of the oxidation level on the physical and chemical properties such as the interlayer distance, composition, functional groups and band gap of graphite oxide. Graphite oxides were synthesized with various oxidation times, from 5 min up to 24 h, and analysed by x-ray diffraction (XRD), elemental analysis (EA), thermogravimetric analysis (TGA), UV–visible diffuse reflection spectroscopy and Fourier-transformed infrared
We found that the band gap of the graphite oxides can be tailored and had a strong correlation with an atomic ratio of O/C.

2. Experimental methods

Graphite oxides were synthesized as described elsewhere [15, 16]. One gram of graphite (99.999% purity, -200 mesh, Alfar Aesar), 6.5 g of sodium chloride oxide and 20 ml of fuming nitric acid were mixed at room temperature for a specified oxidation time followed by neutralization and filtration with deionized water. The oxidation times were 5, 10, 20, 30, 40 and 60 min and 6, 12 and 24 h. The interlayer distances of the samples were investigated by powder x-ray diffraction (XRD, Rigaku Rotaflex D/MAX system, Rigaku, Japan). Compositional information of the percentage weights of carbon, hydrogen, nitrogen and heteroatoms (halogens, sulfur) in the compound was obtained by elemental analyses (EA: C, O, H, N, S; EA1110, CE Instrument, Italy) through a dynamic flash combustion method [18]. TGA (TGA Q500) was performed to determine the weight change as a function of temperature. The heating rate was 5 °C min⁻¹ to a final temperature of 1000 °C under ambient conditions. Functional groups were identified using FTIR (Bruker IFS-66/S). The samples were mixed with KBr and then finely ground to produce a pellet for the FTIR experiment. The band gap of the graphite oxides was extracted from the UV–visible diffuse reflection spectroscopy (UV-3600, SHIMADZU, Japan) at room temperature. The graphite oxide powder for the UV–visible diffuse reflection spectroscopy was pressed into a very flat, smooth pellet with a diameter and thickness of 2 cm and 2 mm, respectively.

3. Results and discussion

Figure 1 shows the XRD data of the graphite oxides (GOs) and pristine graphite (PG). The (0 0 2) peak of the PG near 26° was very sharp and indicates an interlayer distance of 3.34 ± 0.005 Å. The intensity of the (0 0 2) peak (PG phase) decreased as the oxidation proceeded, while the intensity of a new peak near 15° (GO phase) increased gradually. Detailed peak analysis in figure 2 shows the spectrum deconvoluted into five peaks with Gaussian–Lorentzian fitting: water-like (12° ± 0.3°), GO-related (15.1° ± 0.3°), intermediate (23.3° ± 0.6°), PG (26.6° ± 0.5°) and (1 0 0) in-plane (42.5° ± 0.4°) phases. The intermediate peak near 23°, which is located between the GO and the PG phases, appeared at an oxidation time of 5 min and smeared out after 24 h of oxidation. It is noted that all the graphite oxide samples showed the (1 0 0) in-plane phase at 42.5°, indicating a lattice constant of 1.4 Å in the plane. Therefore, the graphite oxides retained a lattice constant similar to that of the PG, and thus the graphitic structure of the graphite oxides may not be completely distorted through the oxidation process which was observed in other experiments [19, 20]. If the samples were dried sufficiently, the peak at 12° ± 0.3° disappeared, and had been aptly named elsewhere as the water peak [21].

Three main peaks (GO-related, intermediate and PG) are summarized in figure 3, in which the peak area and its corresponding interlayer distance are displayed as a function of oxidation time on a log scale. The corresponding interlayer distances were calculated with Bragg’s law (λ = 1.54 Å), and the full width at half maximum of each peak was indicated by error bars in figure 3(b). The peak area of the PG phase at 26.6° decreased, whereas the peak area of the graphite oxide (GO) phase at 15.1° increased reversely with oxidation. The intermediate peak at 23.3° persisted for up to 12 h of oxidation, but then disappeared after 24 h of oxidation. As shown in figure 3(b), the corresponding interlayer distances showed three phases up to 60 min of oxidation, two phases between 6 and 12 h of oxidation and a single phase after 24 h of oxidation.

Figure 4(a) shows the compositional atomic ratios of O/C and H/C in addition to the carbon atomic percentages based on the results of EA. The O/C and H/C atomic ratios increased with oxidation, while the carbon atomic percentage decreased, indicating that the oxygen and the hydrogen atoms are incorporated increasingly with oxidation time. The compositional atomic ratio of O/C (marked by filled squares)
Figure 3. (a) XRD peak area and (b) corresponding interlayer distance as a function of oxidation time.

in figure 4(b) shows a strong coupling with the peak area of the GO phase (marked by open squares) at 15.1° from the XRD. In addition, the atomic percentage of carbon (marked by filled circles) correlates strongly with the peak area of the PG phase (marked by open circles) at 26.6°. Therefore, the peak near 15.1° is an oxygen-related peak (GO phase), which increased the interlayer distance up to approximately 0.6 nm. The oxygen-related peak (GO phase) exists as graphite oxide, with two phases (intermediate and PG) up to 60 min of oxidation, with one intermediate phase between 6 and 12 h of oxidation and itself after 24 h of oxidation. The single GO phase of graphite oxide obtained after 24 h of oxidation indicates a uniform interlayer distance over the graphite oxide samples. The atomic ratio of H/C shown in figure 4(a) exhibits a more complicated relationship with oxidation time, and will be discussed with the FTIR results.

The TGA results provide another indicator for the oxidation level of the graphite oxide. Figure 5(a) shows the TGA and differential TGA scans of a representative graphite oxide sample at an oxidation time of 20 min. Four main peaks in the derivative weight curve were observed near 200, 230, 630 and 720 °C, along with a water-related peak near 100°C. These peaks were labelled peaks 1–5 in figure 5(a). The integrated area underneath the differential TGA curve represents the mass loss percentage in the temperature region as \( \int \frac{dW}{dT} \, dT = W \), where \( W \) and \( T \) represent weight percentage and temperature in Celsius, respectively. The differential TGA peak was integrated between the two temperature points that were the minimum points of the curve, and the integrated area of each peak as a function of oxidation time was summarized in figure 5(c).

The first two dominant peaks (2 and 3) near 200 and 230 °C are ascribed to the burning of functional groups and the second two dominant peaks (4 and 5) near 630 and 720 °C were ascribed to the burning of carbon backbones. Peak 5 was present in the PG as shown in figure 5(b), but the integrated area decreased with increasing oxidation time and completely disappeared after a long oxidation time. Therefore, peak 5 was ascribed to the sp² carbon backbones. Alternatively, peak 4 was maximized at long oxidation times and was assigned to the sp³ carbon backbones of the fully oxidized material. The areas of peaks 2 and 3 have the opposite tendency. Peak 2 first increased and then later decreased as the oxidation time lengthened. Peak 2 has a burning temperature near 200 °C, which can be assigned to hydroxyl groups [22]. Peak 3 has a higher burning temperature than peak 2, and therefore could have a strong bond that can be attributed to carboxyl groups [23], since the double bond between carbon and oxygen of the carboxyl group should be stronger than the single bond between carbon and oxygen of the hydroxyl group. In addition, peak 2 showed a strong correlation with the intermediate phase in the XRD, as shown in figure 5(d). Therefore, the hydroxyl group is the most commonly generated functional group in the graphite oxide at the initial stage of oxidation, and the hydroxyl
groups were converted to epoxides and/or carboxyl groups with enhanced interlayer distances as well as a sp³ carbon backbone as oxidation continues. This result is consistent with the FTIR data, which revealed a gradual development of epoxide up to an oxidation time of 6 h and decreased upon saturation, as shown in figure 6(c). The carboxyl groups gradually increased and became saturated with longer oxidation times in figure 6(d). The formation of hydroxyl groups witnessed with FTIR also increased during the initial stage of oxidation; however, the intensity of the hydroxyl groups decreased after reaching saturation (figure 6(b)). This trend is consistent with the atomic ratio of H/C in figure 4(a). The hydroxyl group increases the atomic ratio of H/C at the initial stage of oxidation, and then the atomic ratio decreases due to the transformation from hydroxyl to epoxide groups. The atomic ratio of H/C increases again because of the increasing carboxyl group (O=–C–OH). A strong correlation between the XRD and TGA results was very interesting, as the XRD and TGA were used to provide microscopic and macroscopic information regarding atomic arrays and the chemical environment, respectively. It should be noted that the integrated area of peak 1 slowly increased from 0.4 to 3.8, indicating enhanced hydrophilic properties [24, 25] of the graphite oxides with longer oxidation time. The enhanced hydrophilic properties are also consistent with the FTIR result marked W1 in figure 6(a).

The band gap of graphite oxide can be deduced from the UV–visible diffuse reflectance spectra in which the Kubelka–Munk function \(F(R)\) was used to convert the reflectance of the sample \(R_{\text{sample}}\), normalized by the reflectance of the reference \(R_{\text{reference}}\), into an equivalent absorption spectrum with the following equations [26, 27]:

\[
R = \frac{R_{\text{sample}}}{R_{\text{reference}}} ,
\]

\[
F(R) = \frac{(1 - R)^2}{2R} = \frac{\alpha}{S} \quad \text{(absorption coefficient)} ,
\]

\[
\alpha hV \propto (hV - E_0)^n ,
\]

where \(hV\) is the energy of the incident photon and \(E_0\) is the optical absorption edge energy. The exponent, \(n\), depends on the type of optical transition caused by the photon absorption [27]. In this study, \(n\) was chosen for the best fit to 1/2, indicating a direct-allowed optical transition since the LUMO and HOMO meet at the \(K\) point for PG [28, 29]. The bands are expected to slowly separate as the oxidation proceeds at the same \(K\) point in momentum space. The scattering coefficients are weakly dependent on the energy, and thus \(F(R)\) can be assumed to be proportional to the absorption coefficient within the narrow energy range containing the absorption edge features. BaSO₄ was used as the reference sample. Figure 7(a) shows the square of the Kubelka–Munk function multiplied by the photon energy as a function of the photon energy. The abscissa of the linear fit of the absorption edges indicates the band gap of the graphite oxide. The induced band gaps of the graphite oxides are shown in figure 7(b). The direct band gap increases from 1.7 eV for the GO₅ min sample to 2.4 eV for the GO₂₄ h sample. Interestingly, the band gap has a strong correlation with the atomic ratio of O/C, as shown in figure 7(b). To this end, the band gap can be tuned by the oxidation time in the synthesis of the graphite oxide. Tailoring the direct band gap of the graphite oxide presents the possibility of using the new material in many applications.
Figure 6. FTIR of graphite oxides with oxidation time. (a) Full range and (b)–(d) specific ranges are shown. Peaks H1 and H2 originated from the hydroxyl group and peaks W1 and W2 originated from water. Epoxide is marked by E, and alcohol was observed at 1120 cm\(^{-1}\) in the onset of the oxidation of graphite oxide.

Figure 7. (a) Absorption spectra related to the Kubelka–Munk function and (b) induced band gap of the graphite oxides as a function of oxidation time.

4. Conclusions

Graphite oxides with various oxidation levels were synthesized by controlling the oxidation time. Three phases (PG, intermediate and GO) were observed in the XRD analysis of the graphite oxides; however, a single GO phase remained after 24 h of oxidation. The compositional ratio of O to C shows a strong coupling with the GO phase of the (0 0 2) peak area. The atomic percentage of carbon correlated strongly with the PG phase of the (0 0 2) peak area, representing the pristine interlayer distance. The intermediate phase was attributed to hydroxyl groups that were converted to epoxide and carboxyl groups as the oxidation time progressed, enhancing the interlayer distance and switching the carbon backbone to a sp\(^3\) structure. The various oxidation levels of the graphite oxides triggered different direct band gaps between 1.7 and 2.4 eV, expanding the potential applications of graphite oxide as a new material.

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