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Thermal Reduction Study of Graphene Oxide Paper

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Abstract. We report the preparation, reduction and characterization of GO paper that obtained by assembly of individual GO sheets. The free standing GO paper was prepared from 4 mg/ml GO dispersed in water, and following by evaporation of water and then detach from the petri dish. In order to obtained graphene-like film, the free-standing GO film then thermally reduced by heating the samples at 250ºC at varied heating time. Characteristic and properties of the thermally reduced GO paper was measured by means of infrared spectroscopy, X-ray diffraction and EDS.

1. Introductions

The unique electronic property of graphene provides potential applications such as electromechanical resonator, protective layers, chemical filters, components of electrical batteries or supercapacitors [1]. Some those applications require a free-standing paper-like or foil-like materials. It is reported that graphene oxide (GO) and reduced graphene oxide (RGO) papers have been investigated as an electrode for actuator [2], sensor [3], and flexible supercapasitor [4]. Also, it has previously been reported a preparation of graphene oxide paper [5] and reduced graphene oxide paper [6] using vacuum filtration technique. It is our main concern to justify if the GO and RGO thin film properties will remain if the films become thicker and forming a paper.

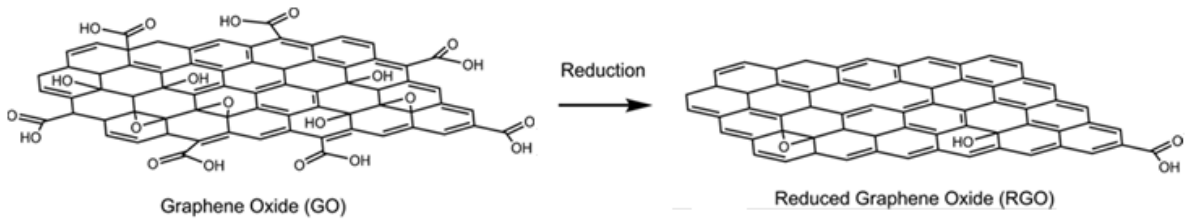

Figure 1. Schematic illustration of the reduction of graphene oxide (GO) to reduced graphene oxide (RGO) [7]

In this paper, we report a preparation of GO paper and its reduction process by means of thermal heating at 250 °C, as well as its characterization results. Reducing GO to produce RGO is a vital process since it will be effect a quality of the produced RGO. The reduction process will remove oxygen functional group of GO as described in Figure 1 [7]. We have previously studied a thermal reduction of GO thin film using optic characterization [8]. We found that in the form of thin film, the absorption of RGO is increased significantly after thermal reduction process. It is related to a recovery of conjugation bonds after thermal reduced process that has removed oxygen functional groups. It is interesting to find out if the RGO properties will remain if the thin films become a paper.

2. Experiment

We synthesize graphite oxide from natural graphite using modified Hummers by added graphite powder into a solution mixture of concentrated sulfuric acid (H_2SO_4, 95 – 97 %, MERCK) and sodium nitrate ((NaNO3, 30 %, AnalaR) that placed in the ice bath. Then the potassium permanganate (KMnO4, MERCK) was slowly added to the reaction mixture and then stirred at room temperature for several days. The peroxide acid solution (1 % H_2O_2 in water) was added to the dark brown paste, then the mixture was filtered and washed with chloric acid and water. The resulting black solid material was then further washed with excessive water to remove residual salts and acids. The brown suspension was dispersed in water. In order to obtained graphene oxide (GO), exfoliation was carried out by sonicating of 0.4 mg/mL graphite oxide dispersion under ambient condition for 30 minutes.

The free-standing GO paper was prepared in petri dish from 4 mg/ml GO dispersed in water, and following by evaporation of water in atmospheric and room until it is almost dried. It was further dried at 50ºC the vacuum oven overnight and then detached from the petri dish. In order to obtain graphene-like film, the free-standing GO film then thermally reduced by heating the samples at 250 ºC inside the pyrex tube that flow with Argon gas with various heating time.

We performed Energy Dispersive Spectroscopy (EDS) measurement using Hitachi Tabletop Microscope TM3000 to probe ratio of C/O of the prepared samples. Fourier transform infrared (FTIR) spectroscopy was carried out in absorption mode to measure structure of prepared samples using Prestige 21 Shimadzu. X-ray diffraction experiments were performed using SmartLab (Rigaku) diffractometer (Cu Kα radiation, X-ray wavelength $K\alpha1 = 1.54056$ Å, $K\alpha2 = 1.5444$ Å, ratio = 0.5 operating at 40 keV, cathode current of 40 mA) under normal laboratory conditions in the range of $2\theta = 5^o$ to $2\theta = 40^o$ and with step size of 0.02.

3. Results

The prepared GO paper can be easily detached from the petri dish and its shape was a circle with a diameter of 10 cm, that the same as the petri dish. The GO samples were cut in size of 1.5 cm x 3 cm for further characterizations. The EDS measurements show that before reduction the amount of percentage atomic of carbon and oxygen of GO paper is 62.3 % and 36.7 %, respectively. After reduction for 1 hour, the atomic percentages of carbon and oxygen of RGO are changed to 78 % and 21 %. The ratio of C/O is increased from 1.69 to 3.73 after thermal reduction of GO paper that was done by heating at 250 °C for 1 hour. Notably, the longer reduction time can significantly increase the C/O ratio. This result shows that the thermal reduction had reduced its oxygen functional groups from the GO paper.

Figure 2 shows FT-IR spectra of GO and RGO that thermally reduced for 30 minutes and 1 hour. These spectra of GO paper show a present of the broad and intense peak of O–H groups that centered at 3400 cm^{-1}, strong C=O peak at 1735 cm^{-1}, the O–H deformation peak at 1400 cm^{-1}, the C–OH stretching peak at 1200 cm^{-1}, and the C–O stretching peak at 1000 cm^{-1}. When it was thermally reduced and becomes RGO, the intensity of hydroxyl O-H group at 3400 cm^{-1} are almost completely removed after heating for 1 hour. Figure 2 shows a magnification spectra of samples between wavenumbers of 2000 and 900 cm^{-1}. It is obvious that the intensity at 1400 cm^{-1} that related to carboxyl are significantly reduced and intensity of C=C (aromatics) at 1600 cm^{-1} are increased. The increasing of C=C vibration intensity indicates a recovery of conjugated bonds in the RGO film.

However, several carboxyl and carbonyl of C=O groups at 1735 cm^{-1}, epoxy C-O at 1200 cm^{-1}, alkoxy C-O at 1000 cm^{-1} are still remained on the RGO films. This results confirm a formation of RGO by thermal reduction of GO paper, although the reduction process need to be improved in order to further reduce the oxygen contain.

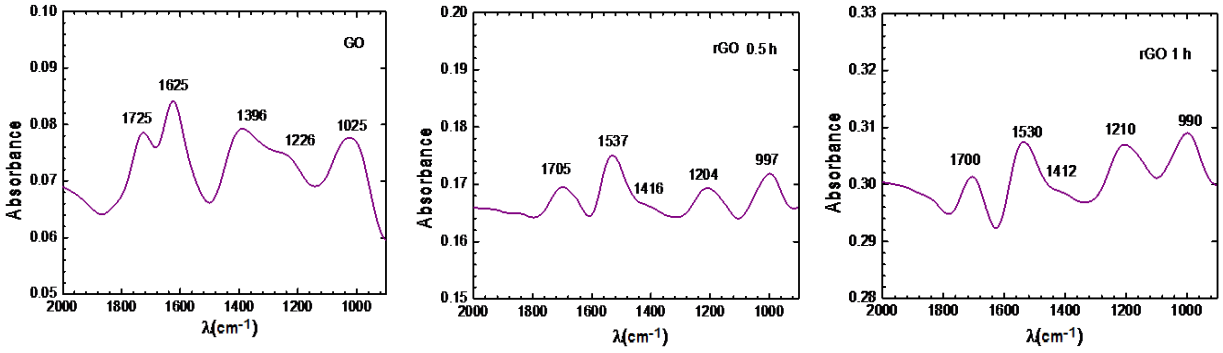

Figure 2 FTIR spectra of GO paper (a), RGO reduced for 0.5 hour (b), RGO reduced for 1 hour (c)

Figure 3 shows XRD patterns of GO paper and RGO papers that thermally reduced for 30 minutes and 1 hour. The X-ray pattern of GO has a peak centered at 2θ = 11.4°, corresponding to the (002) inter-planar spacing. After reducing for 30 minutes the peak value that centered at 2θ = 11.4° reduced significantly and then appeared two new peaks at 2θ=19° and 23.8°. When the reduction time was increased to 1 hour, the two peaks emerge and becomes one broad peak with the centre 2θ at 23.5°. Since the peak is corresponding to the layer-to-layer distance (*d*-spacing) [9], shifting of X-ray peaks of RGO to higher angle result in a decreasing *d*-spacing, it shows that reduction process decreases the inter-planar spacing. Sharp peak on the right-hand side at 2θ = 28° is artefact and should be disregarded. This results imply a removing of oxygen were taken part during reduction process, that are in-line with characterization results using EDS and FTIR spectroscopy.

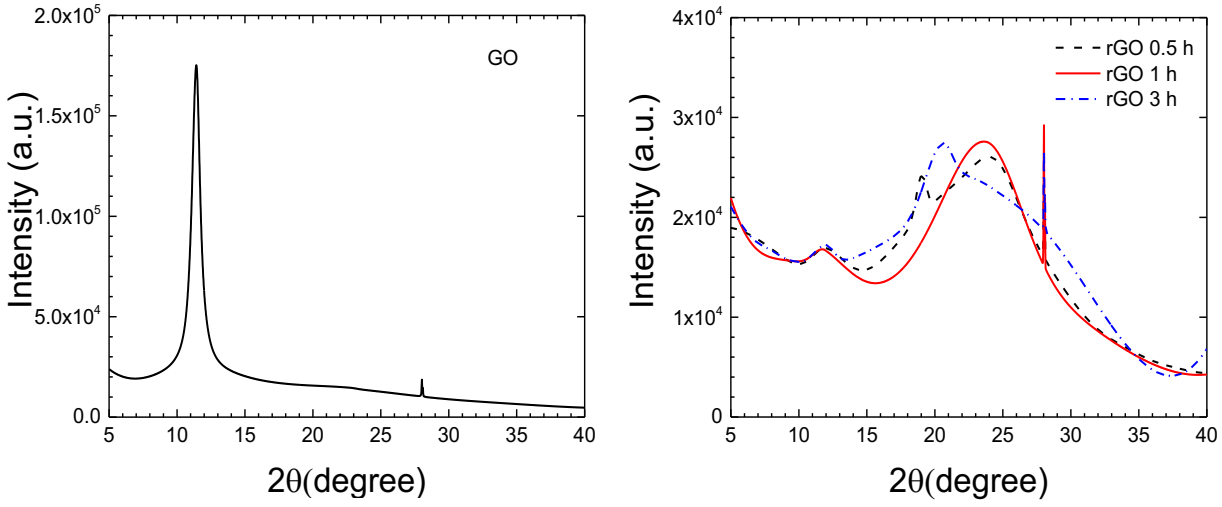

Figure 3 XRD patterns of GO paper (a) and RGO reduced at varied heating time (b)

4. Conclusions

We have successfully prepared GO paper by using solution casting technique. The GO paper can be converted into RGO paper by means of reduction thermal at 250 °C in argon atmosphere. The EDS measurement confirmed removing of oxygen functional groups by increasing of C/O ratio after thermal reduction process. The FTIR spectra show a recovery of C-O and O-H bond to C=C bond, and XRD measurement show a decreasing of interlayer spacing of RGO layer that also confirmed removing of oxygen group. This show that we still can use thermal reduction process to obtain RGO paper from GO.

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