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Mass production of graphene oxide from expanded graphite

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Abstract

In a deviation from the conventional Hummers method, a spontaneous expansion approach was introduced with expanded graphite as the precursors. The intercalating agent (H_2SO_4) was able to penetrate into the expanded graphite; this had further expanded the graphite and as a result, a foam-like intermediate was produced. The foam-like graphite was more easily oxidized in reaction with the oxidant (KMnO_4) to form graphene oxide (GO). Fully exfoliated GO was obtained with expanded graphite having the median diameter $\sim 15 \mu\text{m}$ as the precursors. This procedure was much safer and productive in scalable applications than the conventional Hummers methods.

Keywords

Expanded graphite, graphene oxide, spontaneous expansion, mass production

1. Introduction

Graphene oxide (GO) is of great interest due to its low cost, easy access, and widespread ability to convert to graphene.[1-5] Scalability is also a much desired feature. At present, a conventionally-modified Hummers method is the primary method for preparing GO. Graphite is commonly chosen as the starting material due to its availability and low cost. Proportional amounts of oxidants, such as potassium permanganate, sodium nitrate, and concentrated sulfuric acid, are mixed in order with the graphite. Subsequently, a three-phase procedure is conducted with low, mid, and high temperature reactions, each occurring separately at scheduled times. GO, the oxidized graphene sheet, acquires multiple defects, of which the degree is subject to the additive amount of oxidant and the oxidizing time.[6, 7]

In regard to the oxidants, some research groups, including that of James M. Tour, excluded sodium nitrate as an additive due to its negligible role in graphite oxidation[8]. A mixture of $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ (9:1 volume ratio) instead of only H_2SO_4 resulted in increased hydrophilic and oxidized GO without the emission of toxic gas, which differs from the traditional Hummers method.[8] Of these typical processes, the throughput normally benefits from the preparation with a prolonged stirring over time (over 12 h or even 2

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d).[3, 8] In addition, proper preparation requires that particular attention be paid to some key steps, for example, the addition of water for high temperature hydrolysis. Unintentionally, the mixed highly explosive oxidants can decompose in an exothermic process or as a large explosion; therefore, off-the-rack methods starting with graphite are still flawed.

Expanded graphite has long been commercially available and its sizes have been optionally chosen. In this paper we report on synthesizing GO with increased safety and productivity from commercial expanded graphite, of which the sizes in a moderate range (the median diameter D50 ~ 15 μm) as a raw material and with a newly modified hummers method. Therein we introduced a spontaneous-expansion-step modification, which resulted in a preparation that strongly contributes to safety, efficiency, and productivity. Comparisons were also conducted among three raw materials with different sizes. This promising method has applications to the scalable industrialization of graphene.

2. Experimental

2.1 Materials and reagent

Commercial expanded graphite (EC300 with D50 ~ 50 μm , EC1000 with D50~ 15 μm as manufactured) was purchased from Ito Kokuen Co., Ltd, Mieken, Japan. Highly oriented pyrolytic graphite (HOPG) was acquired from Bay Carbon, Inc., Michigan, USA. Other chemicals unless specifically noted were from Wako Pure Chemical Industries, Ltd., or Sigma-Aldrich Inc., Japan.

2.2 Preparation of GO

Some modifications were made to the Hummers method[9] and applied to the preparation of GO from industrially expanded graphite. In a typical reaction, potassium permanganate (15 g) and expanded graphite (5 g) were initially stirred until homogeneous. Then, in a bottom-round flask (500 mL) with ice-water bath, concentrated sulfuric acid (98 %, 100 mL) was added to the mixture with continuously stirring until a uniform liquid paste was formed. Then the water bath was removed. The stirring continued until a foam-like intermediate spontaneously formed (around 30 min) at room temperature with a large volumetric expansion. Deionized water (400 mL) was added, and rapid stirring was restarted to prevent effervescing. Next, the flask was placed in a 90 °C water bath, and after 1 hour a homogeneous suspension was obtained that was dark yellow in color. The suspension was then filtered and was subjected to repeated washing and centrifugation (10000 rpm, 2 h per cycle) to remove impurities.

2.3 Characterization

The samples were characterized using various analytical methods such as atomic force microscopy (AFM, Agilent series 5500 AFM instrument using the tapping mode at a scanning rate of 0.5 Hz), scanning electron microscopy (SEM, JSM-6300, JOEL, with acceleration voltage of 30 kV), X-ray photoelectron

spectroscopy (XPS, JPC-9010MC, JOEL, using Mg K α , 1×10^{-7} Torr), and X-ray diffraction (XRD) using RINT 2000 (Rigaku Denki, Ltd, X-ray $\lambda_{\text{Cu } k\alpha} = 0.154$ nm) . Fourier transform infrared spectroscopy (FTIR, FT/IR-6100 FT-IR Spectrometer, JASCO), and thermogravimetric analysis (TGA, TG/DTA 6200, SII Exstar6000, with a heating rate of 5°C per minute), Hitachi HD-2000 Scanning Transmission Electron Microscope (STEM, accelerating voltage 200 KV) equipped with an Energy Dispersive X-ray (EDX) detector.

3. Results and discussion

Intercalation of graphite (Fig. 1) is required for subsequent exfoliation when preparing GO. H₂SO₄ is the most common intercalating agent. Under identical conditions, graphite with relatively small lateral sizes would help save considerable time because of a lower resistance than in the case of large graphite ($t_1 > t_2$). Further, if such graphite is pre-expanded with the inter-layer space being larger, the intercalation would then complete even sooner ($t_2 > t_3$). Meanwhile the intercalation emits heat as well as produces water. With these points of view, expanded graphite was used as the starting material. A spontaneous full intercalation along with the evaporation of water at room temperature would prepare a foam-like graphite-intercalating intermediate.

The universal Hummers method has drawbacks with respect to throughput and safety. For small graphite crystals with a large specific surface area, such as expanded graphite (D50~15 μm), an unpredictably fast exothermic process could be induced by the addition of water, and as it produces heavy purple smoke, it implies a large loss of oxidants. Consequently, the conversion efficiency is significantly reduced; furthermore, this process is both terrifying and dangerous.

This difficulty, in this study, was overcome by developing the above mentioned spontaneous expansion approach. In contrast to the conventional preparation, features of the proposed approach included: (1) a full mixing of graphite and potassium permanganate in advance to the addition of H₂SO₄ to ensure homogeneity and completeness of the subsequent reaction, excluding sodium nitrate; (2) a mid-temperature reaction performed once the above mixture has reached to a uniform paste in an ice bath; (3) the mid-temperature reaction, free from homothermal measurements at room ambient, terminated by a spontaneous volumetric expansion so that the stirring was stopped—this is referred to as “spontaneous-expansion-step”; (4) the ratio of sulfuric acid to graphite is reduced to about 20:1 (v/w), which differs from 23:1 reported in other literature[10, 11]; and finally, (5) a high-temperature hydrolysis under a lower temperature (90 °C) as compared with before.

The as-mentioned “spontaneous-expansion-step” (Fig. 2b) reached soon after the mid-temperature reaction started (less than 30 min). Benefitting from the “foam-like intermediate”, water addition was free

from security and oxidization failures. With a high-temperature hydrolysis, the “foam-like intermediate” was finally transformed into a suspension with both color and volume distinctly changed. Notably, before achieving the “cake” (Fig. 2c), a homogeneous solution with no particles settling down at the bottom indicated a full conversion of graphite. Importantly, this procedure was highly repeatable. The removal of impurities rendered the solution dark brown (Fig. 2d). A concentrated GO solution was obtained with colloid-like stability over 10 months. The resultant GO sheet (Fig. 3) had thickness of about 1 nm which was identical to conventionally prepared single GO sheets (0.7 ~ 1.2 nm) [8, 12-14], indicating of full exfoliation of graphite.

Two types of expanded graphite, namely, EC1000 and EC300 were used to indicate the importance of graphite size (Fig. S1). As the manufacturer denoted, both EC1000 and EC300 were made of graphite having pre-expansion and sifting. EC1000 was in smaller size; this results in more reactive sites to attack for the oxidant. On the contrary, EC300 was in the size similar to that of HOPG, thereby having fewer reactive sites. In fact, the “GO cakes” with EC300 and HOPG as the precursors contained many coarse particles, indicative of an insufficient exfoliation/oxidation of graphite (Fig. S1).

C1s XPS was performed to acquire the detailed information regarding the functional groups (Fig. S2). The peak at the binding energy (B.E.) around 284.5 eV was assigned to CC/CH; 286.1, 288, and 290 eV were attributed to C-O, C=O, and O=C-O, respectively. Note that for EC1000, the peak at 291.5 eV was assignable to the $\pi \rightarrow \pi^*$ transition of the aromatic C-C bonds. Changes of ratios for these key functional groups for the precursor (EC1000) and GO were summarized in Table S1. The overall ratio of the oxygen-containing groups, namely, C-O, C=O, and O=C-O, was found to be 90.6% for GO, which was comparable or even higher than that of the ratio for GO reported in other works [8, 15].

Further with a reduction, as-produced GO was demonstrated potentially available for the production of graphene since the C/O ratio changed from 2.5 (GO) to 4.7 (RGO) with large removal of functional groups (see Fig. S2 and S3), increased thermal stability (Fig. S4) and significant decrease of electric resistivity (from insulating to $1.8 \times 10^2 \Omega \text{ cm}^{-2}$). Moreover the GO by this proposed method also indicated extremely low impurities as analyzed from the annealing (Fig. S5) and EDX element mapping (Fig. S6).

4. Conclusions

We have demonstrated experimentally that starting with suitable resources (expanded graphite, D50 ~ 15 μm), the traditional Hummers method once being modified with a spontaneous expansion process enabled it to become facile and practical for scalable GO production. This method was safe, productive, and most importantly, offers a solid performance. This method introduced in this paper should be applicable for the mass production of GO.

Acknowledgments

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Fig.s and tables

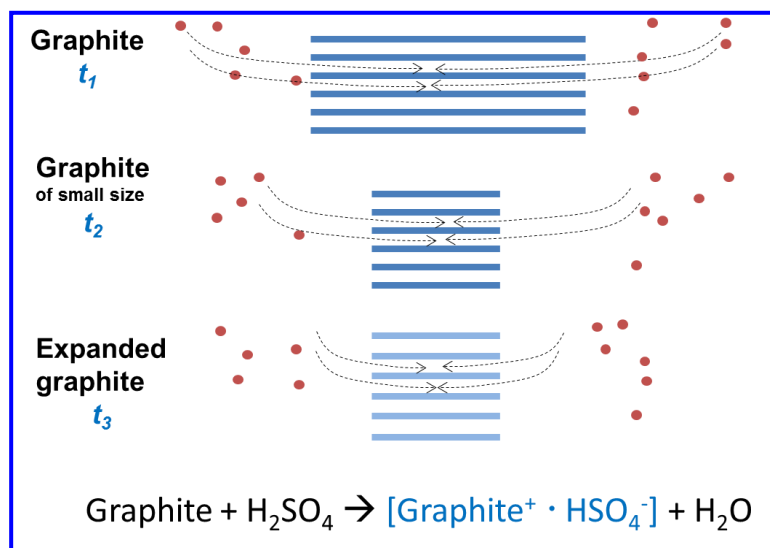


Fig. 1. The schematic regarding the intercalation of graphite by H_2SO_4

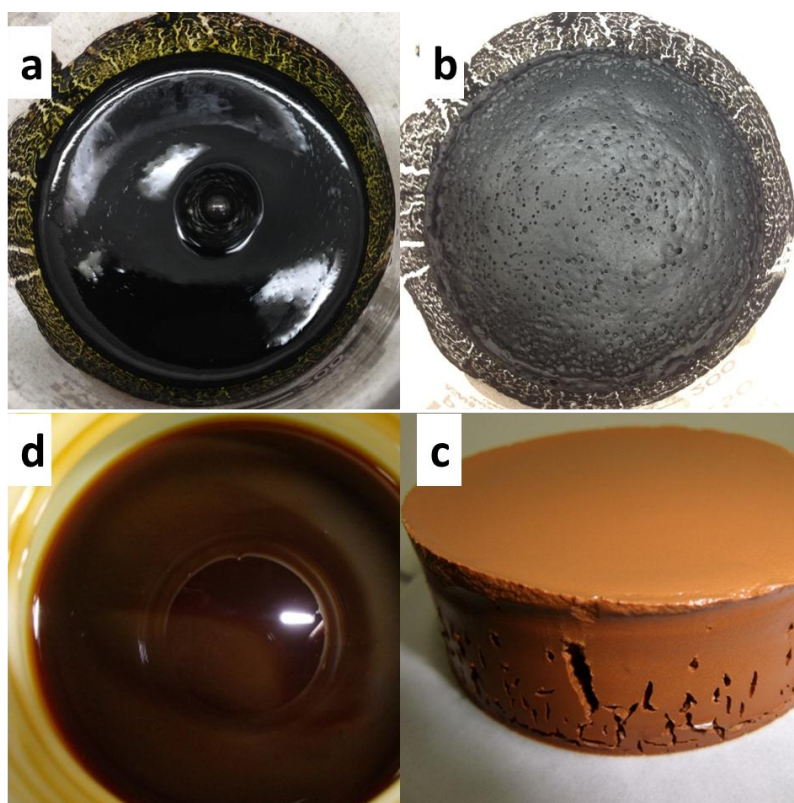


Fig. 2. Photos of preparation of GO from EC1000 with the proposed method. (a) A mixing of raw materials, (b) the scene at the moment of spontaneous-expansion: foam-like volumetrically expanded graphite intermediate, (c) the product of high-temperature hydrolysis: a homogeneous light-brown GO “cake”, (d) concentrated GO solution in dark brown after purification.

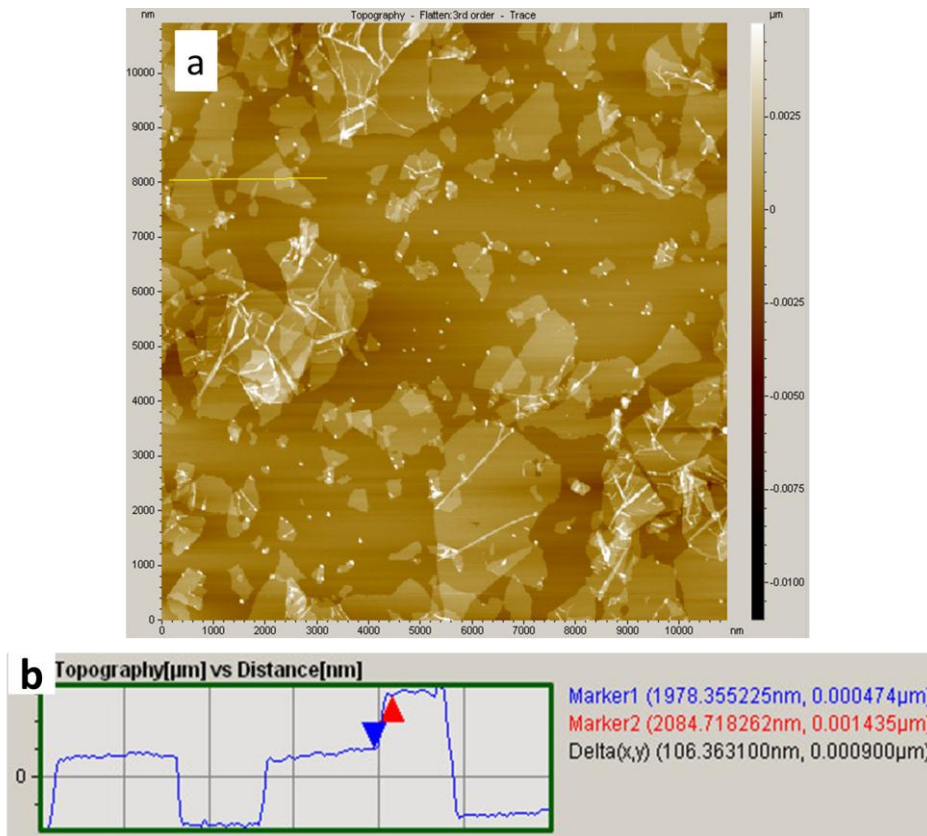


Fig. 3. Fully exfoliated GO sheets on freshly mica (a) and a topographic image of sheets (b).

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Materials and methods

Preparation of RGO

For RGO, the as-obtained GO at a specified volume was filtered through a polycarbonate membrane filter (pore size 0.4 μm , diameter 47 mm, Toyo Roshi Kaisha, Ltd). Then the filter film was dried in an oven (80 $^{\circ}\text{C}$) for several hours. The dried film was processed in a 70 $^{\circ}\text{C}$ $\text{Na}_2\text{S}_2\text{O}_4$ solution (100 mg mL^{-1}) as a reducing environment for 10 min. The film color rapidly changed to a deep metallic gray. The reduced GO film was washed several times using deionized water and dried again in the oven (80 $^{\circ}\text{C}$) prior to further characterization.

Results and discussion

The IR spectra of EC1000 and the RGO were of a similar shape (Fig. S3), specifically in the relatively sharp peak around 3340 cm^{-1} , interpreted as the vibration of C-OH. In contrast, for GO, a very broad peak (3200~3400 cm^{-1}) was generated from the stretching vibrations of -OH from COOH, C-OH, and H_2O ; an adjacent sharp peak at 3618 cm^{-1} was also assigned to the vibration of C-OH. In addition, GO exhibited a very strong C=O peak about 1736 cm^{-1} , compared with EC1000 and the chemically reduced GO.[1] Fig.S4 shows the TGA data obtained under nitrogen conditions; for GO, a typical two-step weight loss appeared against the temperature, including the liberation of hydrate water and the decomposition of the functional groups. The RGO (1000 $^{\circ}\text{C}$, ~22% loss) showed much higher stability with less weight loss than the GO (1000 $^{\circ}\text{C}$, ~53% loss), while the EC1000 remained unchanged.

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A further annealing analysis of air-dried GO in air were presented to determine the residual impurities. Graphene oxide comprises of 2D carbon skeleton and those implanted oxygen-containing functional groups. Its complete annealing products are gaseous water and carbon dioxide, and there should be no residual. As shown in Fig. S5, a temperature-dependent weight changes stepwise, like that in N₂. Temperature being over 472 °C, a large weight loss occurred due to the drastic burning of the residual carbon. At 1000 °C the residual became around 0.3%, the ash from the oxidization of the GO-contained impurity. Meanwhile in the typical STEM image (Fig. S6), GO with wrinkles was clearly observed. Element mapping indicated that the carbon and oxygen atoms widely well distributed over the surface. As calculated, the total proportion of only Carbon and Oxygen counted over 99.9 Atom%. Therefore the samples we prepared were of high purity.

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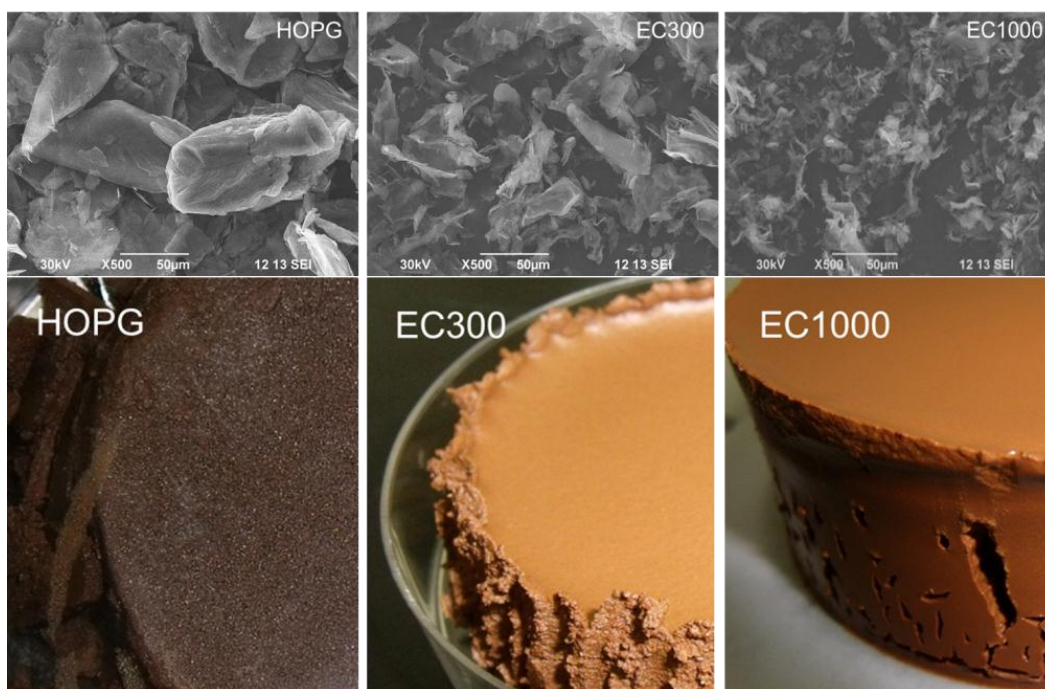


Fig. S1. SEM images of graphite sources as well as corresponding GO “cakes”.

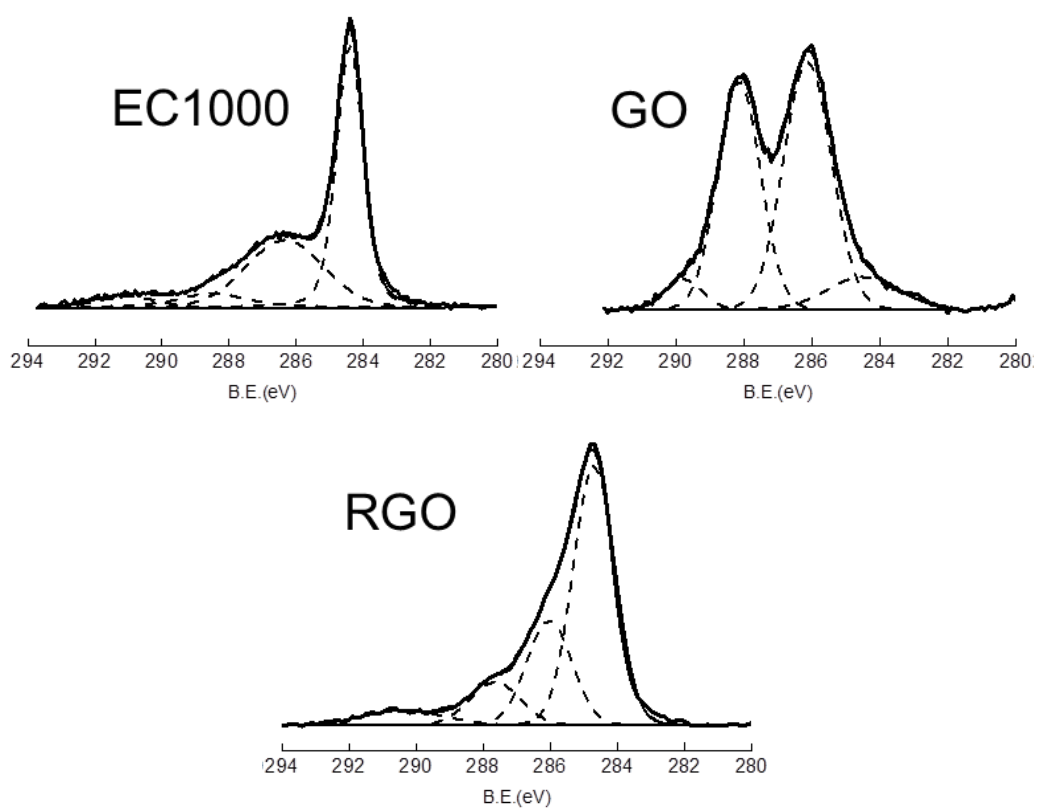


Fig. S2. XPS spectra of EC1000 and GO. Dashed lines represent fitting components constituting the respective spectra.

Tab. S1. Proportions of the typical components.

Components	B.E. (eV)	EC1000	GO	RGO
CC/CH (%)	284.5	49.8	9.4	57.8
C-O (%)	286.1	33.9	47.2	24.7
C=O (%)	288	11.7	39.3	11.3
COO (%)	290	-	4.1	6.2
$\pi \rightarrow \pi^*$ (%)	291.5	4.6	-	-

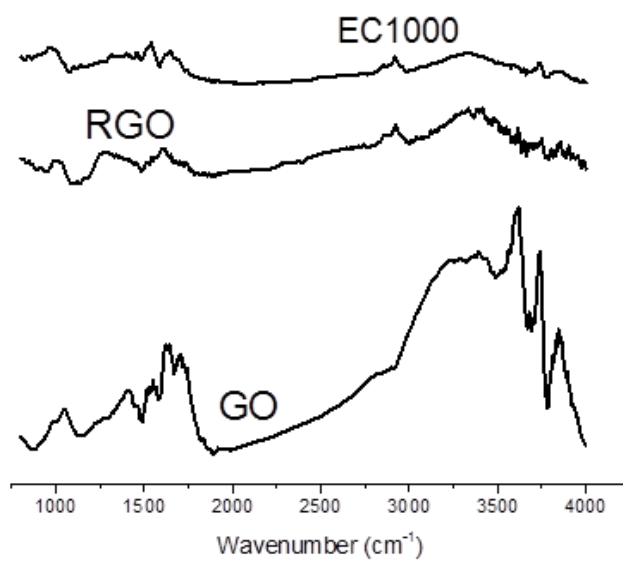


Fig. S3. FTIR spectra of EC1000 (powder), GO film, and the chemically reduced GO (RGO) film.

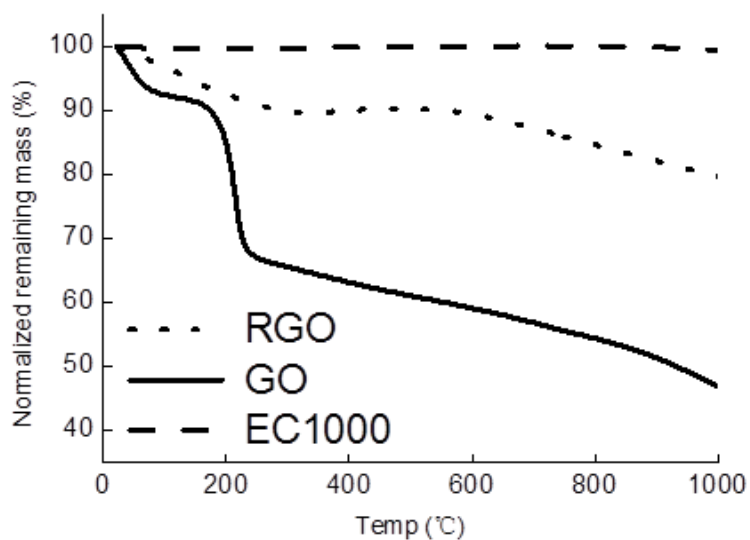


Fig. S4. TGA analysis on EC1000 (powder), GO film, and RGO film under N₂.

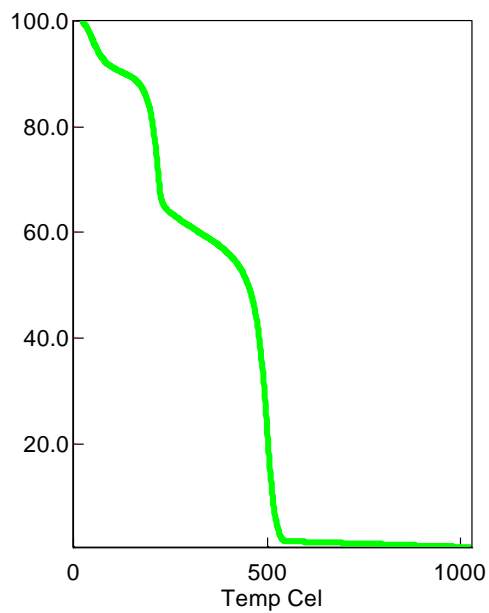


Fig. S5. The annealing of GO in air.

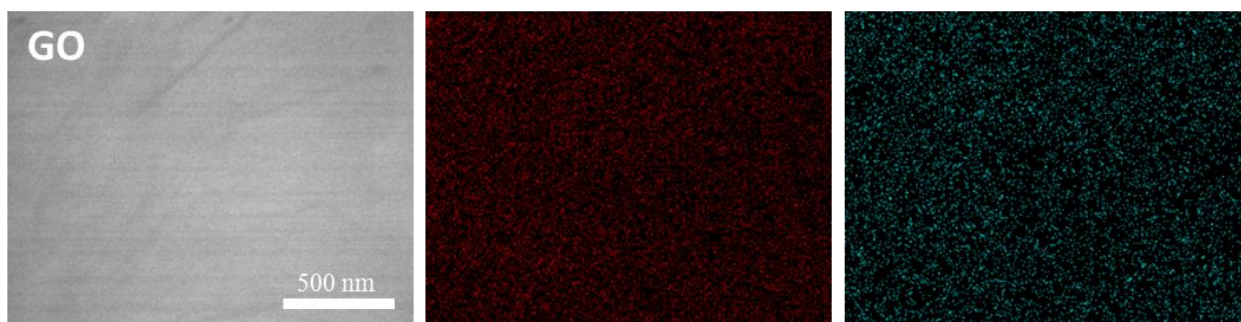


Fig. S6. Transmission electron microscopic image of GO ($\times 70000$) and its element mapping images (Red: Carbon; Blue: Oxygen).