Large-scale production of graphene by microwave synthesis and rapid cooling[†]

Zhanwei Xu, Hejun Li,* Wei Li, Gaoxiang Cao, Qinglin Zhang, Kezhi Li, Qiangang Fu and Jie Wang

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Graphene was prepared *via* carbonization of microwave synthesized metal phthalocyanine, followed by a rapid cooling process. The morphology and structure of the obtained graphene were controlled by the coolants.

Graphene, as a two-dimensional sheet of sp²-hybridized carbon, has been regarded as a promising material used in the fields of nanoscale devices, sensors and catalysts for its unique electronic properties.¹⁻⁴ Chemical vapour deposition, micromechanical cleavage of graphite, reduction of graphite oxide and the graphite intercalation technique are the main methods employed to prepare graphene.^{5–12} Recently, a few novel methods have been reported. Kosynkin et al. have demonstrated a method involving longitudinal unzipping of carbon nanotubes to form graphene nanoribbons.¹³ Choucair et al. have shown a method to prepare graphene based on hydrothermal synthesis and sonication.¹⁴ However, generally, the methods above-mentioned need a very long time. In most cases, they are carried out in a solution of strong acid or oxidant. All these constitute an obstacle for scale-producing graphene.

The microwave synthesis method has several advantages, such as higher reaction rates, selectivities, and realizing reactions in a very short time, and has attracted much interest for several decades.^{15–17} However, to the best of our knowledge, only a few studies related to the preparation of graphene by using the microwave synthesis method have been reported.¹⁸⁻²⁰ Here, we propose an easy, time-saving and scalable approach to prepare graphene. The graphite is prepared via carbonization of microwave-synthesized metal phthalocyanine at high temperature followed by a rapid cooling process. Fresh graphite surfaces are generated through the neighbor carbon atomic layers cleavage to release the thermal stress caused by rapid cooling from high temperature, and the graphene forms. The obtained graphenes have ~ 8 , ~ 4 , 1 to 2 layers of graphite by using water, a mixture of water and ice, and liquid nitrogen as coolants. The overall procedure takes less than 0.5 h.

Metal phthalocyanine (MPc) compounds are widely used as precursors to synthesize carbon-based nanosized materials.^{21–26} In an attempt to carbonize the MPc, the reaction time is

prolonged and the power of the microwave reactor is improved accordingly based on the work on microwavesynthesis of MPc compounds.²⁷ Subsequently sufficient coolants, such as water, a mixture of water and ice, and liquid nitrogen, are added to the reaction system, then fresh surfaces between the layers of graphite are produced *via* the effect of thermal stress (as shown in Fig. 1, details are shown in ESI). In addition, NH₄Cl is used as the protective material because it can be decomposed into NH₃ and HCl gases at high temperature. These gases can protect the graphite from oxidation at high temperature.

$$NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$$
 (1)

UV-vis spectra of the obtained products provide evidence for the formation of graphite materials rather than CoPc (shown in ESI Fig. S1). X-ray photoelectron spectroscopy (XPS) is used to detect the chemical composition of the products. The XPS spectra indicate that the initial crude carbon products obtained consist of carbon, oxygen and a small number of heteroatoms N, Co, and Mo. The obtained graphene S1 produced using water consists of 77.19% C, 22.15% O, 0.30% N, 0.12% Co and 0.24% Mo by atomic composition. The graphene S2 produced using a mixture of water and ice is composed of 76.21% C, 23.06% O, 0.35% N, 0.17% Co and 0.21% Mo. The graphene S3 produced using liquid nitrogen as coolant is composed of 75.31% C, 23.84% O, 0.45% N, 0.20% Co and 0.20% Mo. The impurities came from $(NH_4)_2Mo_2O_7$ and metal catalyst Co. After purification, the impurities were removed completely. The residual graphene S1 consists of 86.21% C, 13.79% O, S2 consists of 85.89% C, 14.11% O, and S3 consists of 84.54% C, 15.46% O by atomic composition.



Fig. 1 Diagram of synthesis of graphene from the starting materials of CoPc. CoPc is synthesized and carbonized by microwave synthesis. Subsequently sufficient coolant is used to exfoliate the obtained graphite, and then fresh surfaces between the layers of graphite are produced.

C/C Composites Research Center, State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an 710072, P. R. China. E-mail: lihejun@nwpu.edu.cn

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C 1s XPS spectra of S1, S2 and S3 peak at around 284.1 eV, showing a typical graphite spectrum (as shown in Fig. S2). The strong oxygen signal was attributed to the adsorbed substances on the sample surface, such as water,^{14,28} which was supported by thermo-gravimetric analysis (TGA). The weight losses of the samples S1, S2 and S3 are 7.3%, 7.9% and 8.0% at around 100 °C (as shown in Fig. S3). Yields of S1, S2 and S3 are 1.42, 1.35 and 1.30 g, respectively.

Graphite with high crystallinity was obtained when the reactants were microwave-heated to 450 °C. This process was completed within 20 min, suggesting that the microwave synthesis method is an efficient way to synthesize graphite materials from the starting materials of MPc compound (SEM, TEM and Raman spectra of the synthesized graphite are shown in ESI Fig. S4, S5 and S6). After adding water, a mixture of water and ice, and liquid nitrogen to the synthesis system, the temperature reached 28, 4, and -105 °C, respectively (the ambient temperature was 20 °C). The obtained graphene S1 produced using water as coolant shows a folding silk-like morphology with transparent feature (as shown in Fig. 2c and b) consisting of ~8 layers of graphite (as shown in Fig. 2c and d). When a mixture of water and ice was used as coolant, the morphology and structure of the

Fig. 2 SEM and TEM images of the obtained graphene S1, S2 and S3. (a) SEM image and (b) TEM image of S1, showing folding silk-like structure. (c, d) HRTEM images of S1, showing the graphene obtained by using water as coolant consists of \sim 8 layers of graphite. (e) SEM image and (f) TEM image of S2, showing folding silk-like structure. (g, h) HRTEM images of S2, showing the graphene obtained by using a mixture of water and ice as coolant consists of \sim 4 layers of graphite. (i) SEM image and (j) TEM image of S3, showing a foam-like structure. (k, l) HRTEM images of S3, showing the graphene obtained by using liquid nitrogen as coolant consists of 1 to 2 layers of graphite.

obtained graphene were similar to those of the products obtained by using water as coolant (as shown in Fig. 2e and f). However, the obtained graphene S2 consists of ~ 4 layers of graphite (as shown in Fig. 2g and h), which contains half of the graphitic layers of that using water as coolant. When liquid nitrogen was used as coolant, the obtained graphene S3 showed a foam-like morphology (as shown in Fig. 2i). The structure of the graphene exhibits a transparent state (as shown in Fig. 2j), consisting of 1 to 2 layers of graphite (as shown in Fig. 2k and l). The morphology, shape and thickness of the obtained graphene strongly depend on the coolants, which was attributed to the thermal stress and the unique structure of graphite. Graphite is a highly anisotropic crystal with strong covalent bonds among neighbour carbon atoms in the same layer but weak van der Waals bonds between adjacent layers. As the graphite under high temperature is rapidly cooled, the weak van der Waals bonds are easily broken, and fresh surfaces are generated to release the thermal stress caused by the rapid cooling. The faster the cooling process is, the higher the thermal stress formed. As a result, more fresh surfaces are created and graphene with decreased thickness is produced.

Raman spectroscopy is a powerful tool to characterize graphene-based materials, and can provide facile structural information on the obtained products.^{6,29,30} Raman shifts of the reference graphite show a typical graphite spectrum, where the D band is around 1349 cm^{-1} , the G band is around 1581 cm^{-1} and the 2D band is around 2704 cm^{-1} . The ratio of D and G band intensity is correlated to the in-plane crystal domain size, which is often used to estimate the degree of disorder in the graphite. The intensity ratio I_D/I_G of the reference graphite is 0.38, showing higher crystallinity. Raman shifts of the obtained graphene samples reveal the typical graphene material spectrum, 6,29,30 where the G band is around 1585 cm⁻¹ and the 2D band is in the range $2690-2698 \text{ cm}^{-1}$ (Fig. 3). The secondorder Raman 2D band is sensitive to the number of layers of graphene.^{5,29,30} A typical sharp 2D band of the single layer graphene can be clearly observed in the sample S3,²⁹



Fig. 3 Raman shifts of the obtained graphenes S1, S2, S3 and the reference, performed utilizing a 514.5 nm Ar laser.





Fig. 4 CVs for O_2 reduction in 0.1 M KOH. The solution was O_2 saturated. Scan rate: 50 mV s⁻¹. GCE, black line; GCE modified by graphene S1, pink line; GCE modified by graphene S2, blue line; GCE modified by graphene S3, red line.

distinguished from samples S1 and S2 and the reference graphite. As sample S1 possesses about 8 layers of graphite, the Raman spectrum becomes hardly distinguishable from that of bulk graphite.²⁹ In addition, in comparison with the peak of the 2D band of the reference graphite at 2704 cm⁻¹, the 2D bands of samples S1, S2 and S3 shift to the low-position. The shifts of the 2D band of samples S1, S2 and S3 are 6, 11, 14 cm⁻¹, agreeing well with the results which have been reported.²⁹ Typical atomic force microscopy (AFM) images with the corresponding height profiles, and layer distribution provide further evidence to support the results (as shown in ESI).

To show their potential applications in the field of electrocatalysts, the obtained graphenes were used to make electrodes and their electrochemical properties were compared by cyclic voltammogram (CV) measurements. CVs of the GCE modified by samples S1, S2 and S3 in a 0.1 M KOH solution saturated by O_2 show oxygen reduction peaks at about -0.30 V with strong background currents (Fig. 4). These currents are 15 to 20 times higher than that of GCE unmodified. The area under the CVs for the graphene S3 is the largest among them, showing that the graphene S3 exhibits the highest electrocatalytic activity. This is possibly due to the more active sites resulting from the higher specific surface area of the graphene S3. The area under the CVs for the graphene S1 is the smallest among the three tested graphene samples, suggesting the graphene S1 has relatively low electrocatalytic activity.

In summary, we have shown for the first time that graphene with several graphite layers could be produced through microwave synthesis, carbonization of MPc followed by a rapid cooling process. A fracture surface between the layers of graphite forms via the effect of thermal stress. The overall procedure was carried out within ~ 0.5 h. The obtained graphenes have ~ 8 , ~ 4 , 1 to 2 layers of graphite by using water, a mixture of water and ice, and liquid nitrogen as coolants. The results show the thickness of the graphene can be controlled by using different coolants. This method provides a convenient way to prepare graphene with controllable structure, and can be used for large-scale production. The obtained graphenes exhibit high catalytic activity to oxygen reduction and can be used as promising catalysts in fuel-cell and other applications. The graphene S3 obtained using liquid nitrogen as coolant, consisting of 1 to 2 layers of graphite, exhibits the highest electrocatalytic activity among them.

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