Supplementary Information

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, Jie Wang
C/C Composites Research Center, State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an 710072, P.R.China
*Corresponding author. Tel: +86 29 88495004; Fax: +86 29 88492642.
E-mail: lihejun@nwpu.edu.cn.

1. Preparation and purification of the graphenes and reference graphite

The synthesis and carbonizition of CoPc were done in a microwave oven (Galanz G80F23CSL-A9(S0), Shunde Galanz Co. Ltd.). The procedure of preparation of the product is: a mixture of 3.60 g (24.32 mmol) O-phthalic anhydride acid, 6.00 g (100.00 mmol) urea, 3.00 g (11.40 mmol) $CoCl_2.6H_2O$, 6.00 g (112.20 mmol) NH_4Cl and 0.20 g (0.59 mmol) $(NH_4)_2Mo_2O_7$ in a 150 ml crucible was microwave-heated to 140 ^oC at a power setting of 600W (it took about 10 min), then to 450 ^oC at a power setting of 800 W (it took about 10 min). Next, the crucible was taken out of the oven. About 60 ml of water (or mixture of water and ice, or liquid nitrogen) was added to the crucible rapidly. After being cooled to room temperature, the products were washed by water, ethanol and acetone orderly for several times. After being vacuum dried, the purification of the as-products was done by using 100ml 2 $molL^{-1}$ hydrochloric acid to remove metal particles, then using hot water for several times to remove the residue $(NH4)_2Mo_2O_7$. Subsequently, the products were washed by ethanol three times. The precipitate was dried under vacuum at 70 ºC overnight. Yields of the obtained products: S1 (as water was used as coolant), 1.42 g, S2 (as a mixture of water and ice was used as coolant), 1.35 g, and S3 (as liquid nitrogen was used as coolant), 1.30 g.

The graphite as reference was prepared by using similar method but without adding any coolant to the synthesis system. Yield: 1.64 g.

2. Characterization

The scanning electron microscopy (SEM) image of the obtained samples was obtained by ZEISS-SUPRA55. The transmission electron microscopy (TEM) of the samples was conducted by field emission transmission electron microscopy Tecnai $F30G^2$. UV-vis spectra of the products were measured using Perkin-Elmer Lambda 40 UV-visible spectrometer. The X-ray photoelectron spectroscopy (XPS) spectra were recorded by a Kratos AXILS ULTRA spectrometer with Al (Mono) Kα X-ray source (1486.6 eV). The base pressure of the analysis chamber was below 10^{-9} mbar. The differential thermal analysis (DTA) was performed on METTLER TOLEDO STAR TGA/SDTA851 thermal analysis with Al_2O_3 crucible under the atmosphere of N_2 and recorded at the heating rate of 10 ^{o}C min^{-1}. The initial sample masses were about 10 mg. Powder Al_2O_3 was used as a reference. AFM measurements were performed using a PicoPlus AFM system (Molecular Imaging (MI) Corporation (AZ, USA) operating in contact mode under air ambient conditions. The samples were prepared by dropping ethanol solution of graphene on the freshly cleaved mica surface and then air dried. Raman shift of the samples was performed with a Renishan InVia system utilizing a 514.5 nm Ar laser, resulting in an approximately 2 μm diameter sampling cross section. The intensity of laser decreases to 1/10 to avoid damaging the samples.

3. Electrochemistry

Prior to modification, the glassy carbon electrode (GCE, 3 mm in diameter) was polished with ~ 0.5 μm alumina slurry, sequentially, washed ultrasonically in distilled water for 3 min and in acetone for 3 min. The cleaned GCE was dried in air. 10 μL of a 2 mg mL^{-1} obtained samples (ethanol) suspension was pipetted onto the GCE. After evaporation of ethanol, 10 μL of a diluted Nafion solution (5 wt% in ethanol) was put on top of the product suspension, and then dried in air to hold the product to the electrode surface. The thin-film electrode was put in an electrochemical cell and immersed in 0.1 M KOH solution for electrochemical measurement. Electrochemical experiments were performed with a CorrTest electrochemical work station (CS310 Wuhan CorrTest Instrument Co. Ltd.) in a conventional three-electrode cell using the modified GCE (3 mm diameter) as the working electrode, platinum foil as the auxiliary electrode, and Ag/AgCl as reference electrode. Before the measurements, the electrode was repeatedly potentiodynamic swept from 0.2 to -1.2 V in an oxygen-protected 0.1 M KOH until a steady voltammogram curve was obtained. All the experiments were done at room temperature.

4. UV–vis spectra of the obtained graphenes and CoPc

The UV–vis spectra of the obtained graphene S1, S2, S3 and CoPc are shown in Fig. S1.The UV–vis spectra of sample S1, S2, S3 show the strongest band in the wavelength region of 280-350 nm due to the backbone of graphene.[1] To CoPc, the strongest band in the wavelength region of 580–710 nm ascribed to the π –π transition centered on the macrocycle of CoPc molecules, is the Q band. Another band in the wavelength region of 280–360nm due to the backbone of the phthalocyanine ring, is the B band.[2]

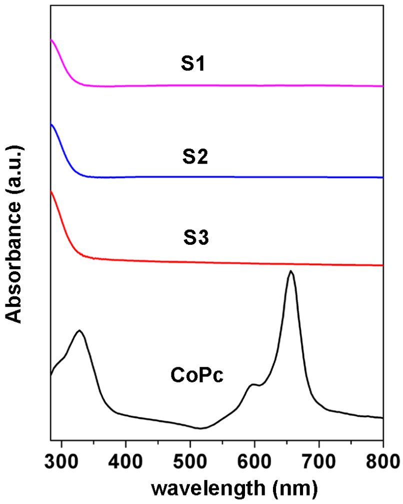

Fig. S1. UV–vis spectra of the obtained graphene sample S1, S2 S3 and CoPc.

5. XPS data and spectra of the obtained graphenes

XPS data and spectra of the obtained graphenes show that the initial crude carbon product obtained consist of carbon, oxygen and a small number of heteroatoms N, Co, and Mo. After purification, the graphenes contain no impurity (as shown in Fig. S2, Table S1 and S2).

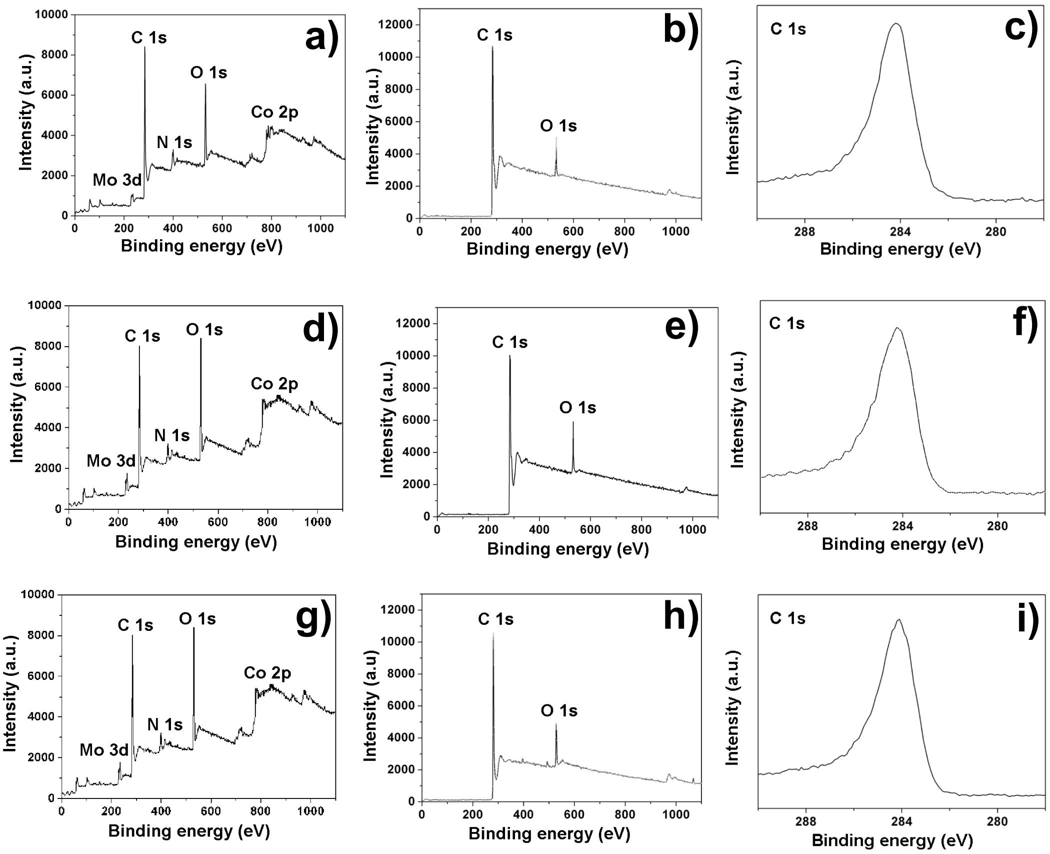

Fig. S2. XPS spectra of graphene sample S1 before purification (a), after purification (b) and C 1s XPS spectrum of S1(c). XPS spectra of S2 before purification (d), after purification (e) and C 1s XPS spectrum of S2(f). XPS spectra of S3 before purification (g), after purification (h) and C 1s XPS spectrum of S3(i).

Table S1. XPS data of the samples before purification

Material	Atomic %				
	C	O	N	Co	Mo
Graphene S1	77.19	22.15	0.30	0.12	0.24
Graphene S2	76.21	23.06	0.35	0.17	0.21
Graphene S3	75.31	23.84	0.45	0.20	0.20

Table S2. XPS data of the samples after purification

Material	Atomic %				
	C	O	N	Co	Mo
Graphene S1	86.21	13.79	-	-	-
Graphene S2	85.89	14.11	-	-	-
Graphene S3	84.54	15.46	-	-	-

6. Thermal analysis data

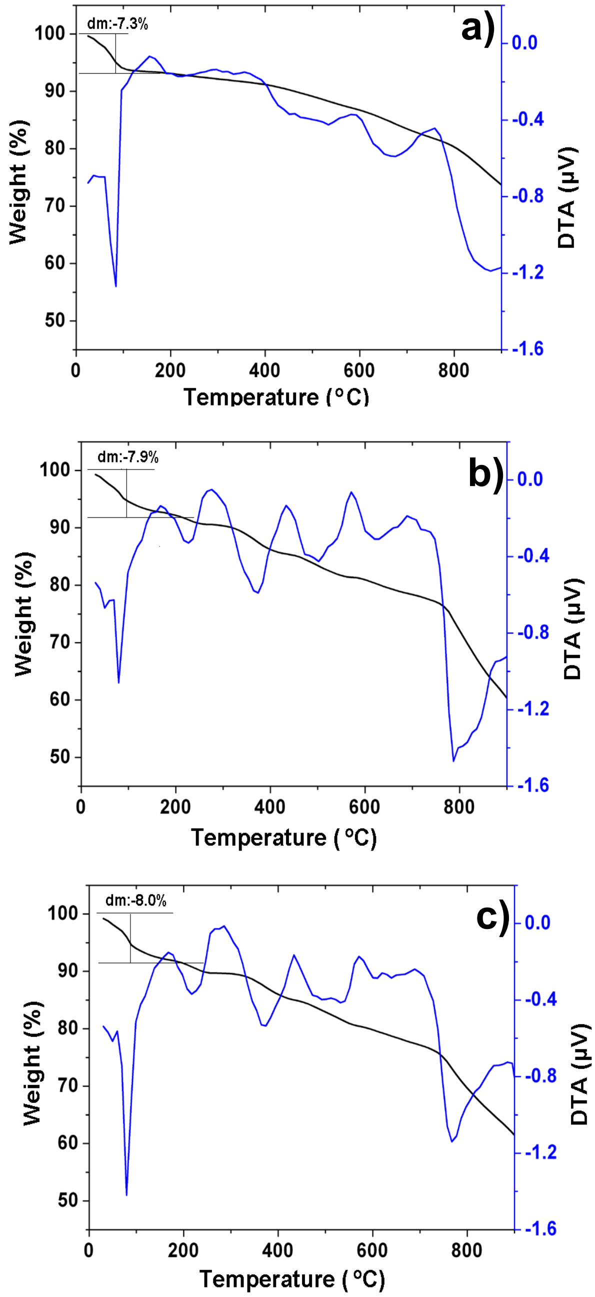

Fig. S3. TG (black) and DTA (blue) data of the obtained graphene S1(a), S2(b) and S3(c).

TG and DTA data of the obtained graphenes show that the initial mass loss of the Sample S1, S2 and S3 are ~7.3% , 7.9% and 8.0% at about 100 ^{o}C, indicating the loss of water using as solvent. And the biggest mass loss with a big endothermal peak of S1, S2, and S3 occur at 780, 760 and 730 ^{o}C, indicating the samples undergo the pyrolysis, suggesting as the stability of the obtained graphenes decreases as the thickness of them decreases (Fig. S3).

7. Characterization of the reference graphite

SEM image of the obtained microwave synthesized graphite is shown in Fig. S5. TEM image shows the obtained graphite exhibits high crystallinity (as shown in Fig. S6). Raman spectrum shows D band is around 1349 cm^{-1}, G band is around 1581 cm^{-1} (as shown Fig. S7). The ratio of D and G band intensity is correlate to the in-plane crystal domain size, which is often used to estimate the degree of disorder in the graphite and the extend of edge plane graphite. The intensity ratio I_D/I_G of the reference graphite is 0.38, provide further evidence for the obtained graphite with high crystallinity.

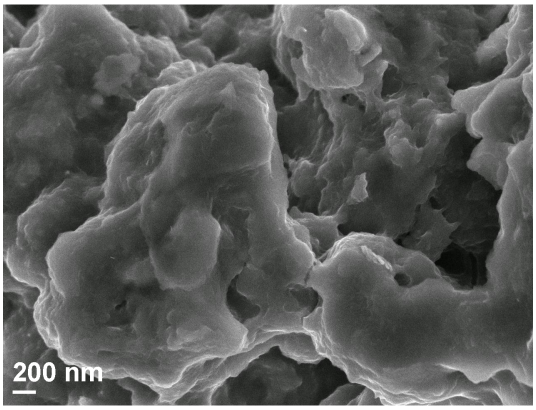

Fig. S4. SEM image of the reference graphite, measured using scanning electron microscope (JEOL, JSM-6700F).

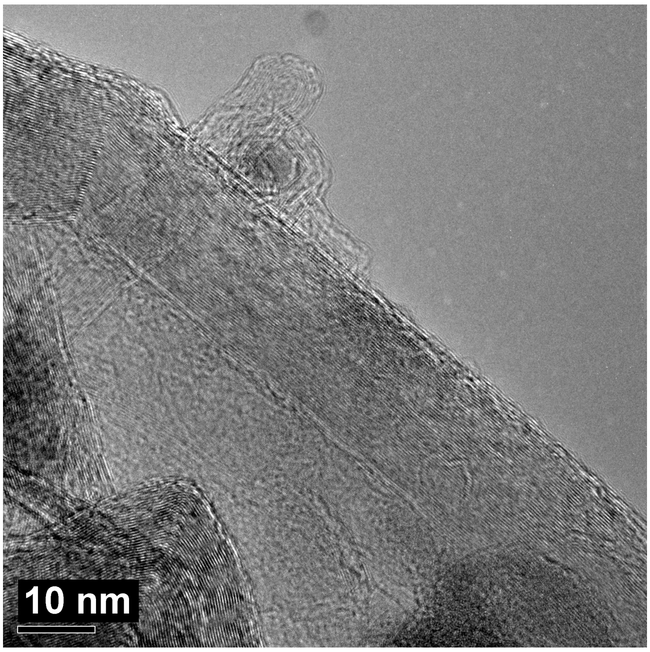

Fig. S5. TEM images of the reference graphite.

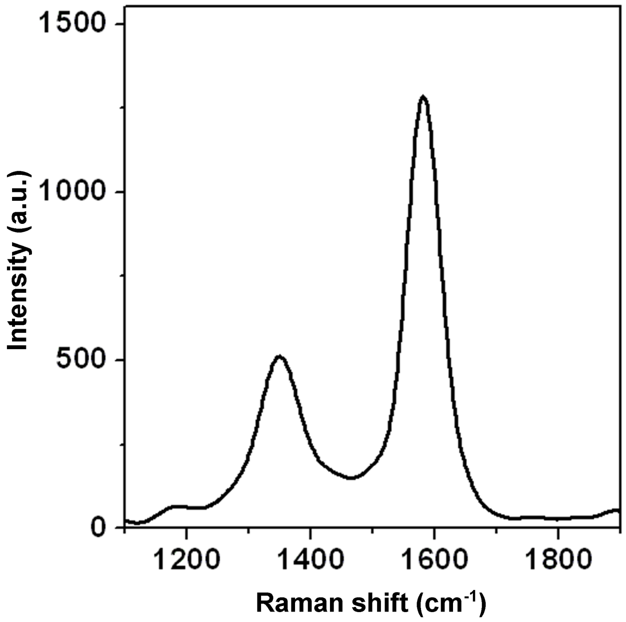

Fig. S6. Raman spectrum of the reference graphite.

8. AFM images and Layer distribution of the obtained graphene samples

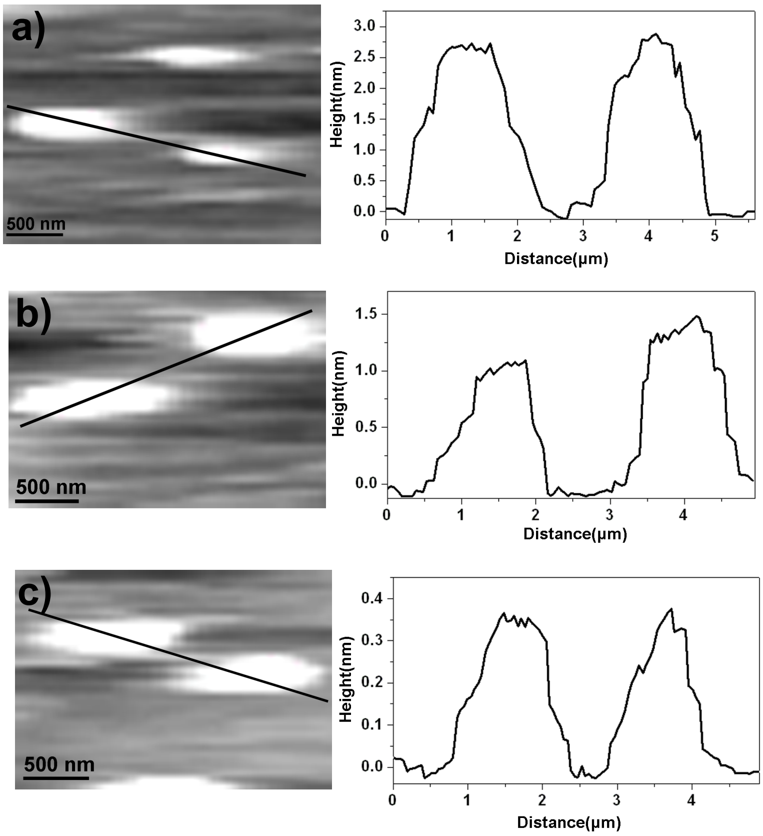

Fig. S7. Typical AFM images and corresponding height profile of: (a) sample S1, (b) S2 and (c) S3.

Typical AFM images with the corresponding height profiles show the thickness of the obtained graphene sample S1, S2 and S3 to be 2.76, 1.39 and 0.35 nm, corresponding to 8, 4 and 1 layer(s) (as shown in Fig. S7). Very narrow graphene layer distributions are observed for the obtained three samples. The bar charts show that the majority of the obtained sample S1 possesses 8 layers, with occasional presence of 7 and 9 layers (as shown in Fig. S8a). Sample S2 possesses 4 layers, with occasional presence of 3 and 5 layers (Fig. S8b). Sample S3 possesses only 1 layer, with occasional presence of 2 layers (Fig. S8c).

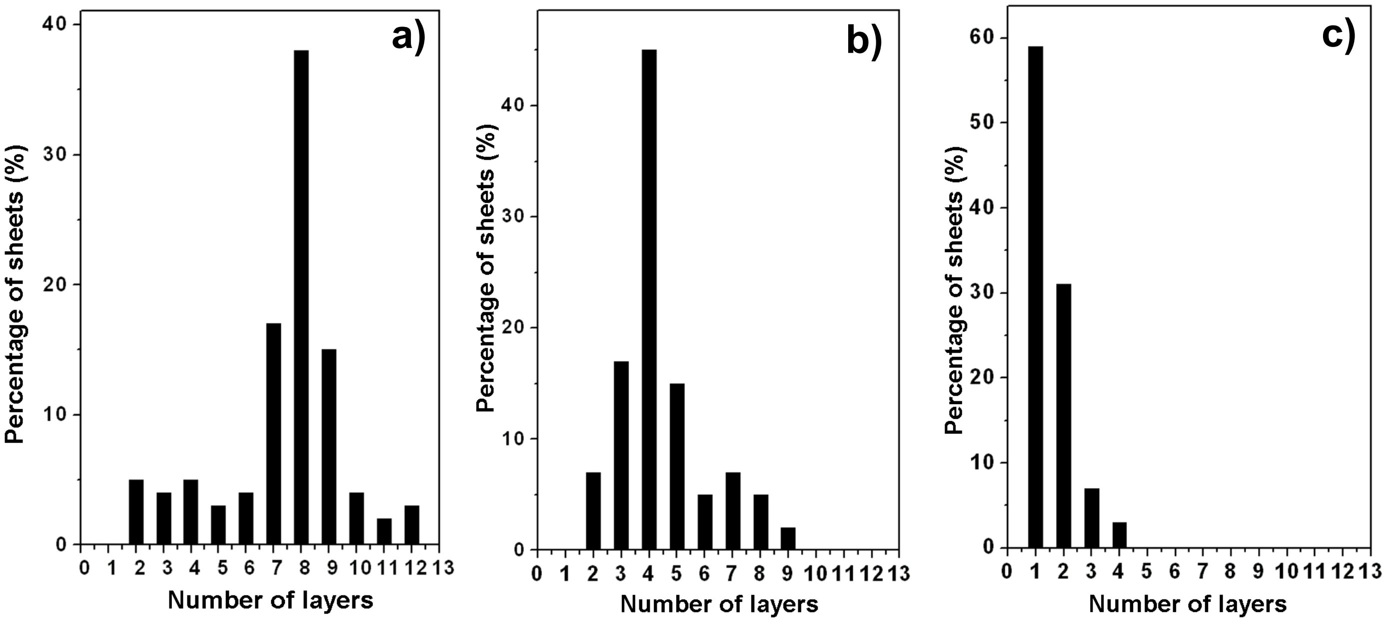

Fig. S8. Layer distribution of the obtained graphene S1(a), S2(b) and S3(c)

References

1 J. F. Shen, Y. Z. Hu, C. Li, C. Qin, M. Shi and M. X. Ye, *Langmuir* 2009, **25(11),** 6122– 6128.

2 Z. W. Xu, G. X. Zhang , Z. Y. Cao, J. S. Zhao and H. J. Li, *J. Mol. Catal. A* 2010, ***318,*** 101–105.