

Growth of silver nanocrystals on graphene by simultaneous reduction of graphene oxide and silver ions with a rapid and efficient one-step approach

Xiu-Zhi Tang,^a Zongwei Cao,^b Hao-Bin Zhang,^a Jing Liu^a and Zhong-Zhen Yu^{*a}

^a Beijing Key Laboratory on Preparation and Processing of Novel Polymeric Materials, Department of Polymer Engineering, College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China

^b State Key Laboratory for Biology of Plant Diseases and Insect Pests, Institute of Plant Protection, Chinese Academy of Agricultural Sciences, Beijing 100193, China

Support Information

Supporting Information Available: Details of the syntheses and characterizations of FAG and PAG are included.

Raw materials

Silver nitrate (A.R. >99.8 %) and ammonia (A.R. 25 wt%) were purchased from Beijing Chemical Factory. Poly(N-vinyl-2-pyrrolidone) (PVP) with an average molecular weight of 29,000 g/mol and a trade name of K30 was provided by Beijing Yili Fine chemical Co. Formaldehyde (A.R. 37%) was commercially obtained from Fuchen Chemical Reagents (Tianjin, China). Natural graphite flakes with an average diameter of 48 μm were supplied from Huadong Graphite Factory (Pingdu, China). All chemicals were used as received.

Preparation of graphene oxide

Graphene oxide (GO) was prepared using the Staudenmaier methodology: Briefly, 5 g natural graphite powder was added into a mixture of 87.5 ml concentrated sulfuric acid and 45 ml concentrated nitric acid, the suspension was stirred for 15 mins in an ice-water

bath and then 55 g KClO_3 was added with 11 portions. The oxidizing reaction was maintained at room temperature for 96 hours and the product was centrifuged and washed with plenty of deionized water until $\text{PH} \approx 7$.

Synthesis of graphene oxide/silver nanocomposite with PVP (PAG)

PVP (2.5 g) was dissolved in 8.0 ml deionized water in a glass vial and the solution was heated to 60 °C in a water bath with magnetic stirring. With ultrasonication, graphene oxide solution (0.05 wt%) was rapidly added into the vial and the magnetic stirring continued for 0.5 h. Then, 3 ml aqueous solution of AgNO_3 (188 mM) was added into the vial that was located in the water bath. After the reaction lasted for another 7 hrs, the sample was taken from the vial using a glass pipette, centrifuged, and washed with water for three times and then with ethanol for three times to remove the excess PVP. Note that the samples without the centrifuging and washing were used for UV-Vis absorption measurement.

Synthesis of graphene/silver nanocomposite with formaldehyde (FAG)

Silver-ammonia solution was firstly prepared: Ammonia (2 wt%) was dropped into 10 ml silver nitrate solution (2 wt%) until the precipitation just disappeared. To exfoliate the GO nanosheets, 5 ml aqueous solution of GO (0.05 wt%) was treated by a Y99-2 DN ultrasonicator (Ningbo, China) for 20 mins and then mixed with 5 ml aqueous solution of PVP (4 mg/ml). After the mud was ultrasonicated for 30 mins, 1 ml of newly made silver-ammonia solution was added. Finally, 3 drops of formaldehyde were added and the mixture was stirred for seven mins. The resulting suspension was centrifuged at 130,000

rpm and washed repeatedly with deionized water and ethanol. The final product was stored in ethanol solution for characterizations.

Characterizations

The resulting products were characterized with a Nexus670 Fourier transform infrared spectroscopy (FT-IR). The morphologies of GO, FAG and PAG were observed with a JEOL TEM-3010 HRTEM after drop-drying the samples from their diluted ethanol solution onto copper grids coated with holy carbon. The scanning electron microscope (SEM) observation was conducted using Hitachi S-4700 and JEOL 6701 Field Emission microscopes. XRD measurements were carried out using a Rigaku D/Max 2500 VB2t/PC X-ray diffractometer with CuK α radiation ($\lambda = 0.15418$ nm) at a generator voltage of 40 kV and a current of 50 mA. The samples for SEM observation were prepared by placing drops of their ethanol solution onto glass slides and then dried. High resolution X-ray photoelectron spectroscopy (XPS, Thermo V G Scientific ESCALab 220i2XL) was used to characterize the surface compositions of PAG and FAG. Optical absorption of PAG aqueous solution was measured at different times on a SP752-PC UV-VIS spectrophotometer over the wavelength range from 300 to 800 nm.

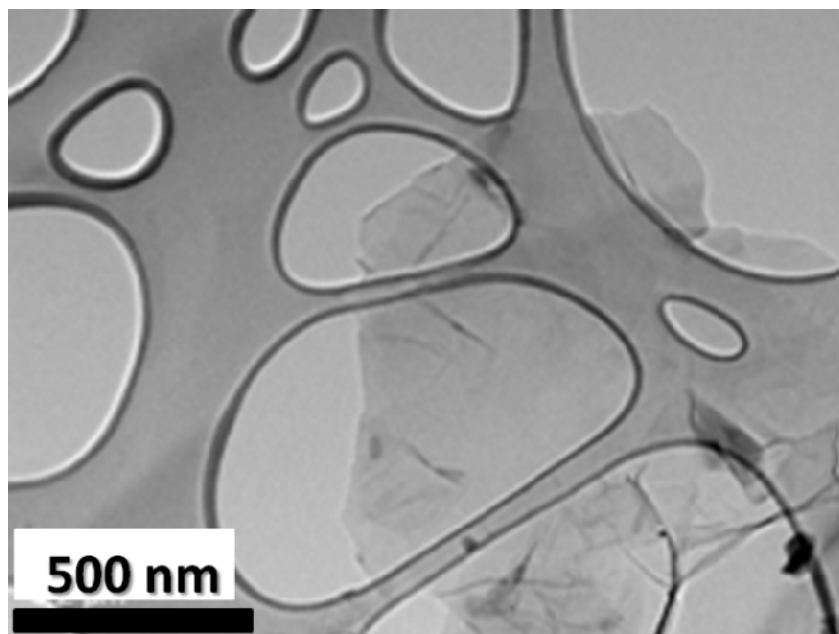
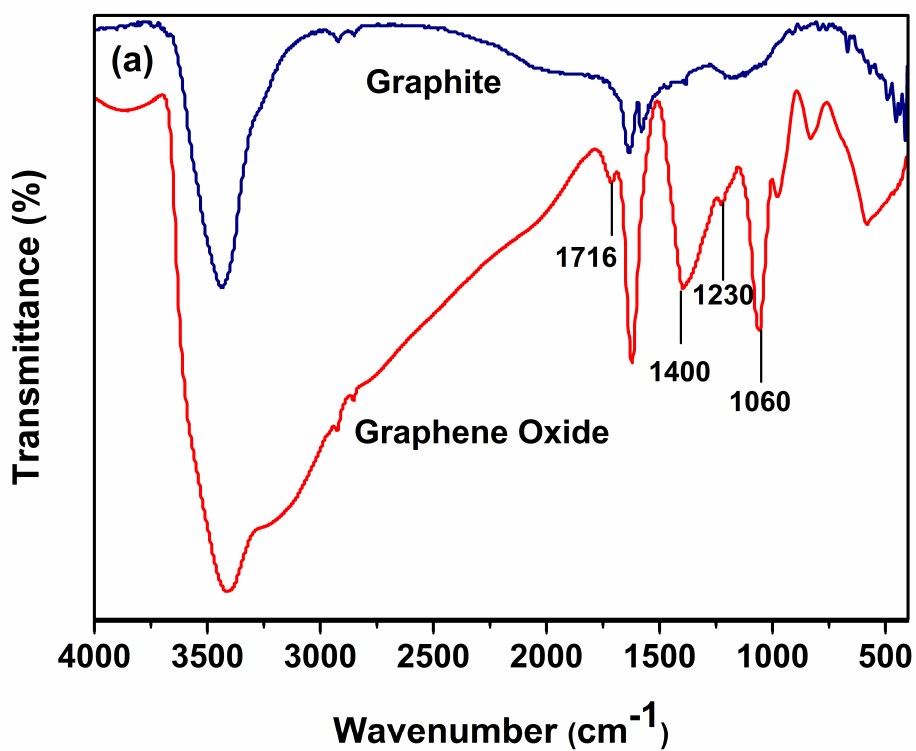


Fig. S1. TEM image of graphene oxide.



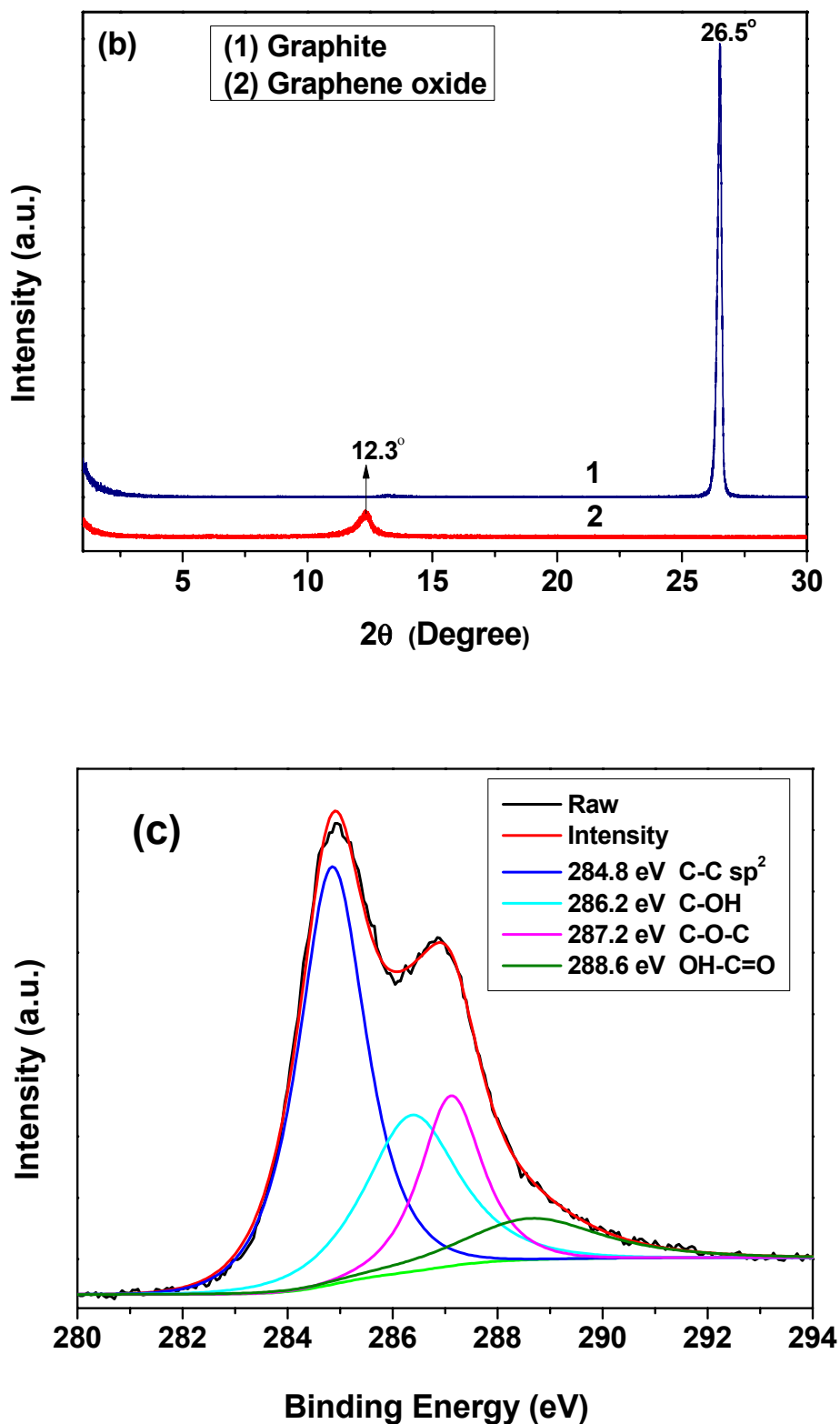


Fig. S2. (a) FT-IR spectra of natural graphite and graphene oxide; (b) XRD spectra of natural graphite and graphene oxide; (c) C1s XPS spectrum of graphene oxide.

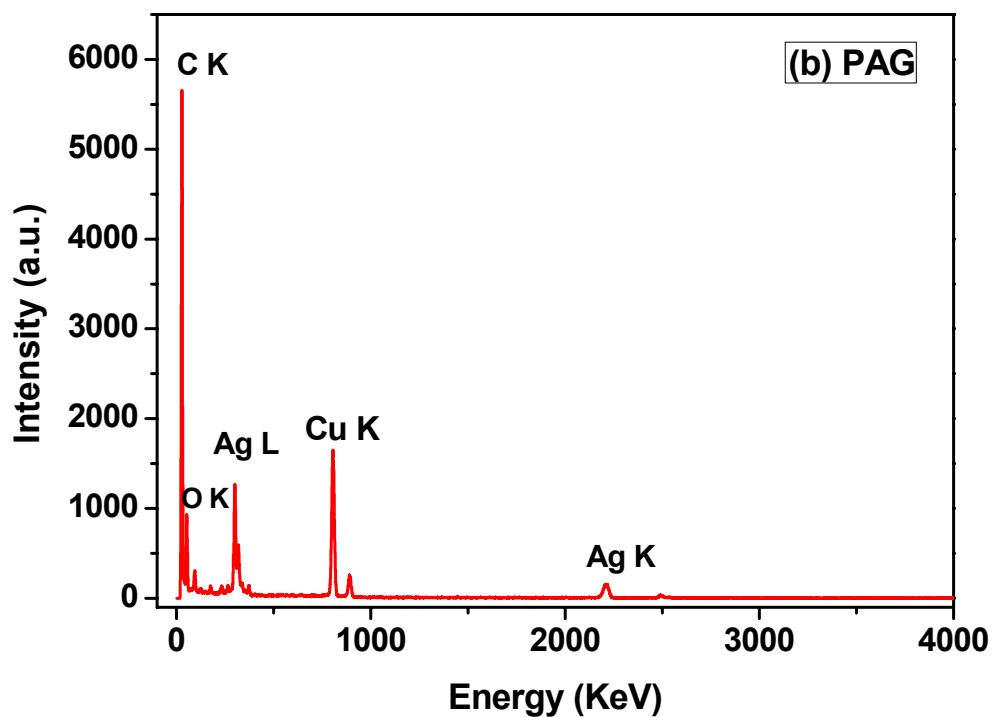
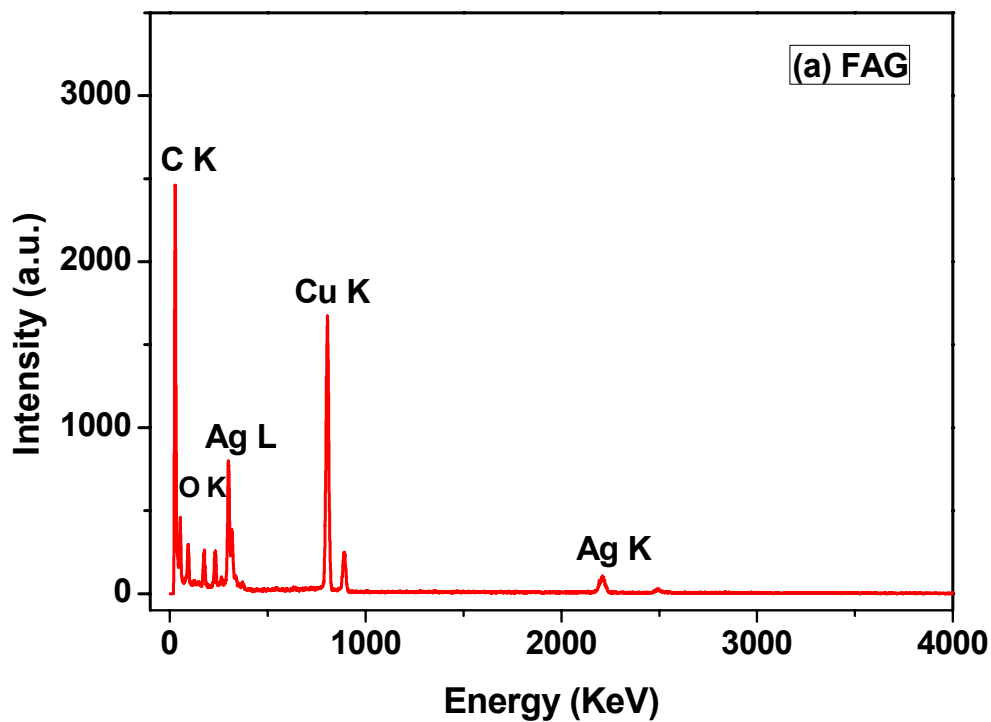


Fig. S3. EDS patterns of (a) FAG and (b) PAG.

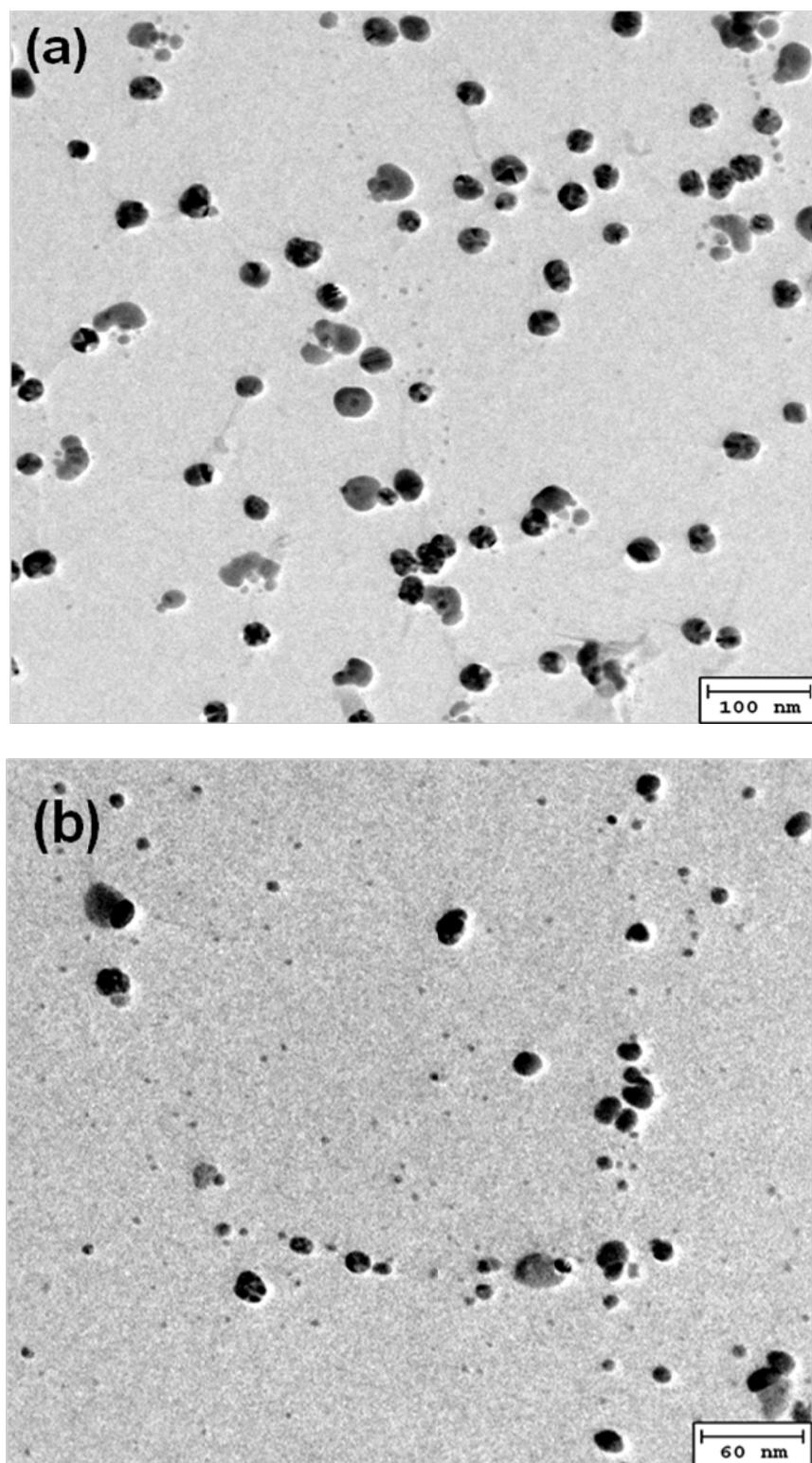


Fig. S4. HRTEM images of (a) FAG and (b) PAG.

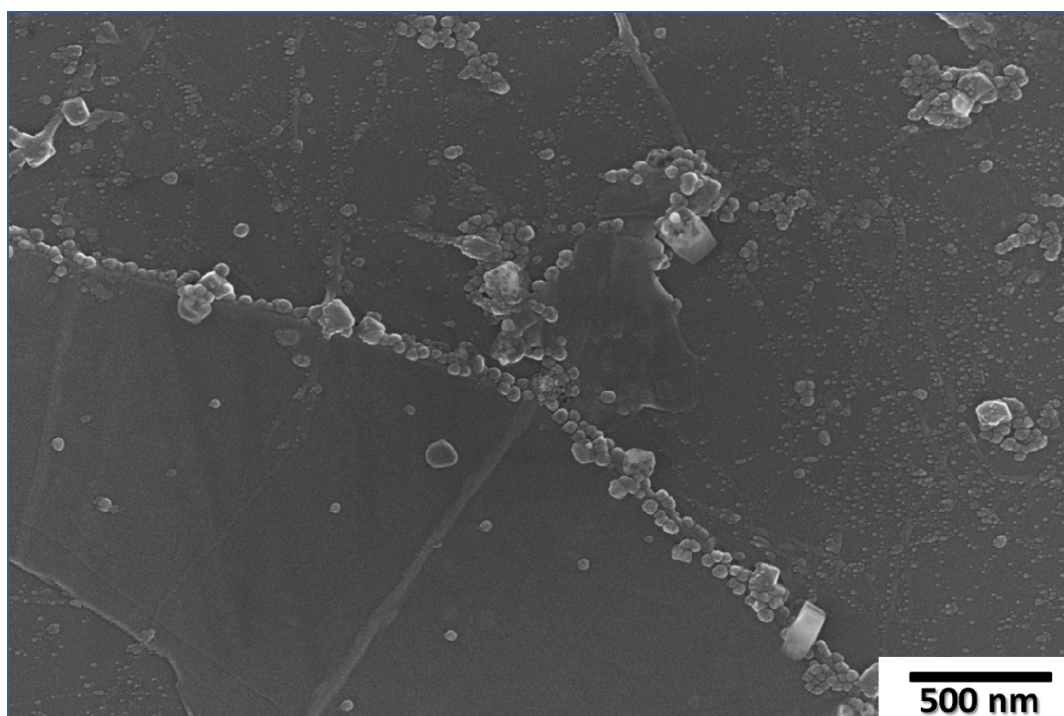


Fig. S5. SEM image of FAG. The Ag nanoparticles tend to locate at the edge of the graphene sheets.