Supplementary Material (ESI) for Chemical Communications

Fabrication of palladium nanoparticles/graphene nanosheets hybrid via sacrifice of copper template and its application in catalytic oxidation of formic acid

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Experimental methods

Materials: All chemical reagents were obtained from commercial sources without further purification.

Preparation of Graphene:

First, the graphene nanosheets were synthesized according to the literature [1]. Optimized conditions achieved: 20 g of polyacrylic weak-acid cation-exchanged resin (AC) was added to aqueous $FeCl_2$ (0.15 M, 500 ml), the solution was stirred for 12 h under the protection of nitrogen, and then the solid was separated by centrifugation. The above process was repeated several times to remove the excess Fe^{2+} into the AC resin as possible. The solid was collected after two centrifugation/washing cycles with water and dried under vacuum. The corresponding composite was then carbonized at 1100 °C under purity N_2 (99.999%) atmosphere for 45 min. The sample was treated in 10% hydrochloric acid at 90 °C for 8 h to remove the Fe species (catalyst) thoroughly. The solids were separated by several washing/centrifugating cycles with distilled water until neutral, and then dried in vacuum at 80°C for 6 h. The obtained supernatant after centrifugation treatment was filtered and dried, then graphene nanosheets collected to use.

Preparation of Cu/graphene Nanosheet (Cu/GN):

50 mg of obtained graphene nanosheets and 60 mg of copper sulfate were added into 100 ml of water, followed by 1 h sonication treatment. The homogeneous graphene nanosheets aqueous dispersion (0.5 mg/ml) was obtained. Then, to the resulting dispersion were added 100 ml of $NaBH_4$ solution (1% w/w), stirred with a magnetic

stirrer for 4 hours. After filtration, the obtained solid samples were dried for 2 h at 60°C in vacuum. Finally, the Cu/GN were prepared

Preparation of Pd/graphene Nanosheet (Pd/GN): 10mg of the obtained Cu/GN were dissolved with water, followed by the addition of 100 ml of $PdCl_2$ (1 % w/w). The mixture was stirrer for 6 hours at room temperature until the Cu NPs were oxided completely, with sonication treatment. Then, the solution was centrifuged and washed several times with double distilled water. Finally, the Pd/GN (named AP-Pd/GN) were obtained.

Electrocatalytic Experiment: Electrochemical experiments were performed in a three-electrode system, using a calomel electrode (SCE) as the reference electrode and Pt as the counter electrode, respectively. A 0.4 cm diameter glass carbon (GC) used as working electrode was polished with Al_2O_3 paste, followed by washing with water and ethanol. Prior to the surface coating, the GC electrode was polished carefully with alumina powder and rinsed with deionized water, followed by sonication in acetone and doubly distilled water successively. Then, 4mg of AP- Pd/GN, Pd/GN and Pd/Vulcan (Pd/GN and Pd/Vulcan synthesized by one-step procedure that Pd ions were reduced with $NaBH_4$ directly) were dispersed in 2ml ethanol and 20 µl of Nafion solution, respectively. 8.9µl of above mixture solution was dropped on the surface of the GC electrode and dried with an infrared lamp before electrochemical experiments. Ten electrodes coated with catalyst were used to electrochemical measurements in N_2-purged 0.5M H_2SO_4 solution and 0.5M HCOOH+0.5M H_2SO_4 solution, respectively. The CV curves of each electrode are obtained from the steady curves after scanning 20 cycles.

References:

[1] L. Wang, C. Tian, H. Wang, Y. Ma, B. Wang and H Fu, *J. Phys. Chem. C*, 2010, 114, 8727.

Characterization

TEM: Transmission electron microscopy (TEM) experiment was performed on a JEM-2100 electron microscope (JEOL, Japan) with an acceleration voltage of 200 kV. Carbon-coated copper grids were used as the sample holders. We disperse few as-prepared products ethanol. After mild sonication, the solution of Cu/GN and Pd/GN was dropped onto the TEM grids for following TEM measurement.

SEM: Scanning electron microscopy (SEM) micrographs were taken using a Hitachi S-4800 instrument operating at 10kV.

XPS: XPS measurement was performed on Aphi 5700 ESCA spectrometer with Al KαX-ray radiation as the X-ray source for excitation.

UV-vis-NIR: The solution-phase optical absorption data were recorded with a Shimadzu UV-3600 spectrophotometer using a quartz cell with a path length of 2 mm.

TGA: Thermogravimetric analysis (TGA) of sample was performed on a Pyris Diamond TG/DTA thermogravimetric analyzer (Perkin-Elmer Thermal Analysis). Sample was heated under an air atmosphere from room temperature to 900 at 10 °C/min^{-1}

CV: Electrochemical catalytic activity and stability were evaluated by BAS100B electrochemical workstation.

Reaction mechanism

In our experiment, Cu NPs with big size were fabricated on graphene nanosheets firstly. Reaction equations:

$$Cu^{2+} + 2BH_4^- = Cu + B_2H_6 + H_2$$

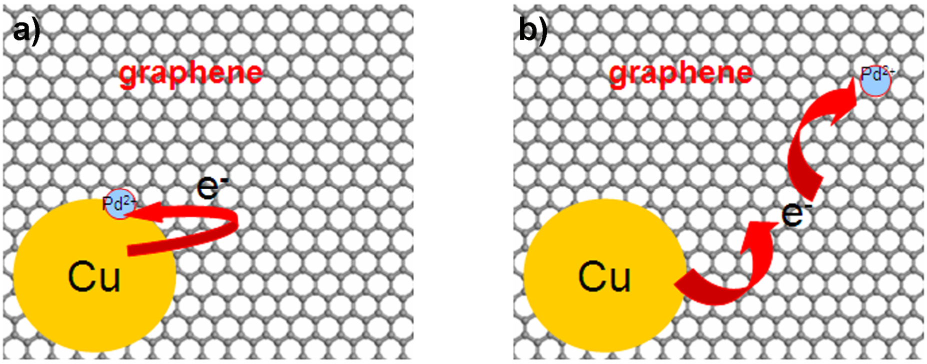
Cu NPs could be partly oxidized into Cu_2O: $4Cu + O_2 = 2Cu_2O$

Then, the big Cu NPs or Cu_2ONPs were oxidized by Pd ions and were replaced by small size Pd NPs completely. Reaction equations:

$$Cu + Pd^{2+} = Pd + Cu^{2+}$$

$$Cu_2O + Pd^{2+} + 2H^+ = Pd + 2Cu^{2+} + H_2O$$

Firstly, we considered the galvanic displacement process occurred between Pd ion and Cu contacted each other , in the same locations. Further, we also considered the galvanic displacement process occurred between Pd ion and Cu uncontacted, at the spatially separated locations. The graphene can shuttle electrons back and forth between these two half reactions, such that there need not be a correlation between the location of the Cu NPs and Pd NPs. By this strategy, though the dimensions of the obtained big size Cu NPs supported on graphene were nonuniform in the first step, but dimensions of the obtained small size Pd NPs were uniform. The two different mechanisms were shown as Scheme S1



Scheme S1 Different mechanisms (a, b) where the replacement reaction between Cu and Pd^{2+} occurred.

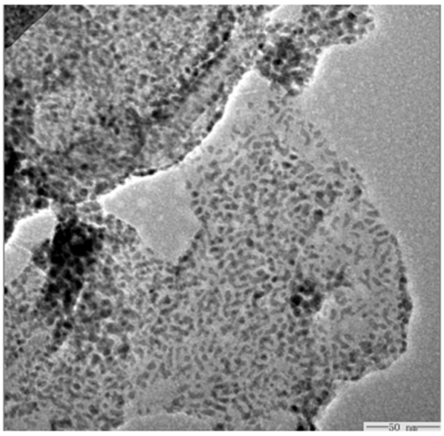


Fig. S1 TEM images of AP-Pd/GN at low-magnification.

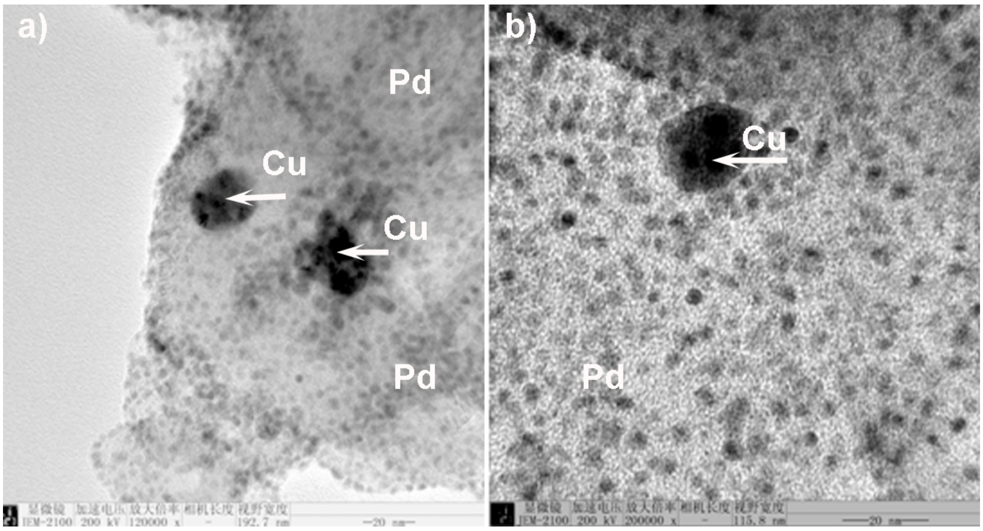


Fig. S2 TEM images with different magnifications (a, b) of the composite system after reacting for 1 h between Cu and Pd^{2+}.

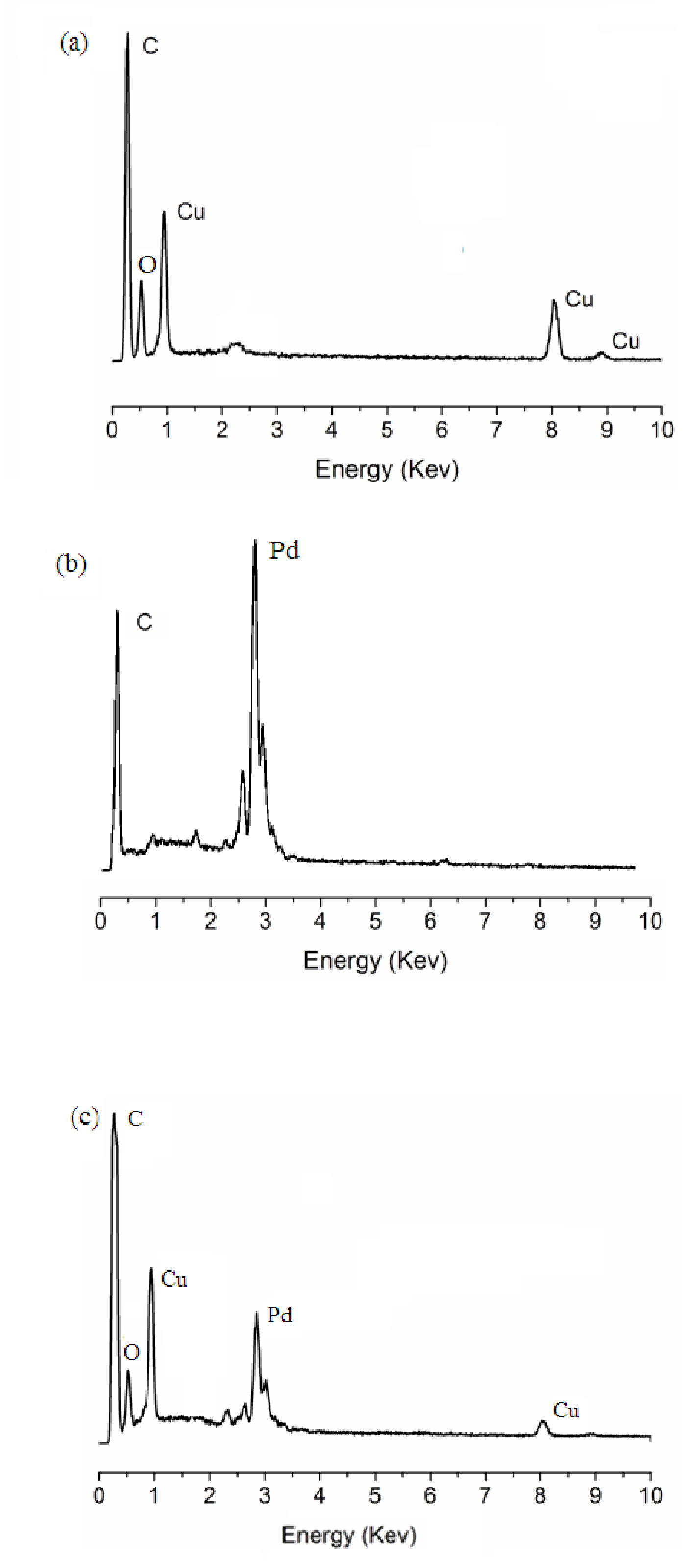


Fig. S3 EDX spectra of (a) Cu/GN and (b) AP-Pd/GN (c) Cu-Pd/GN

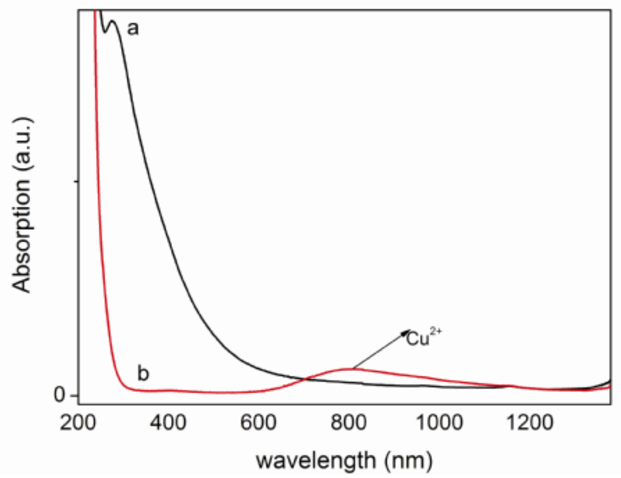


Fig. S4 UV-vis-NIR spectra of (curve a) the initialized $PdCl_2$ solution and (curve b) filtrate after the second step reaction.

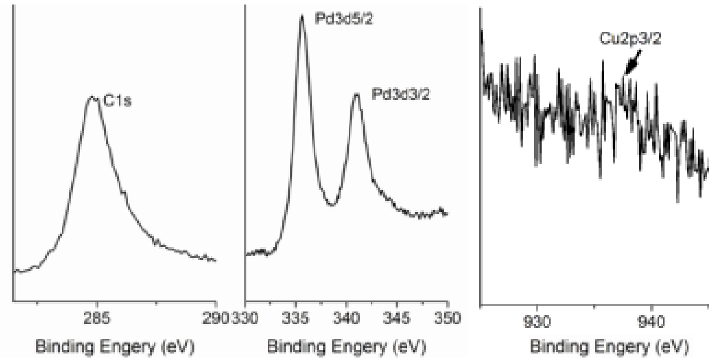


Fig. S5 XPS patterns of C, Pd and Cu for AP-Pd/GN.

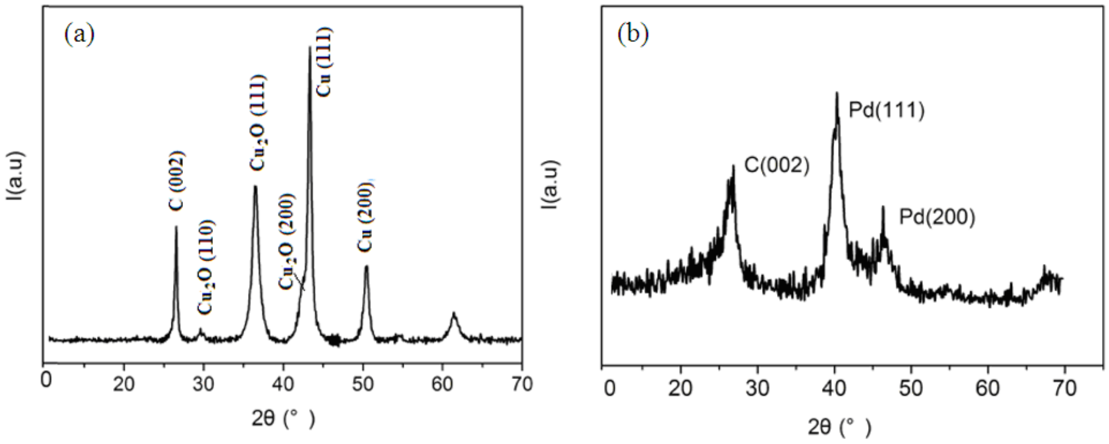


Fig.S6 XRD patterns for (a) Cu/GN and (b) AP-Pd/GN.

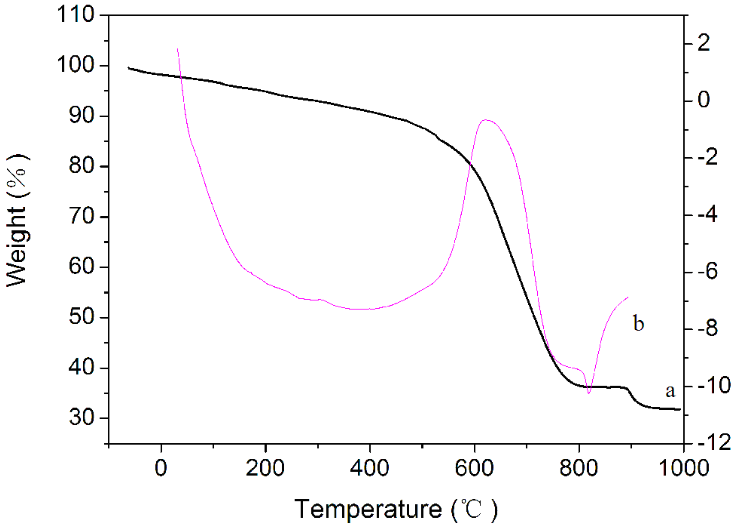


Fig. S7 TGA curve of AP-Pd/GN. The black line (a) showed the change in weight, while the purple (b) showed the derivative of the change in weight with respect to temperature.

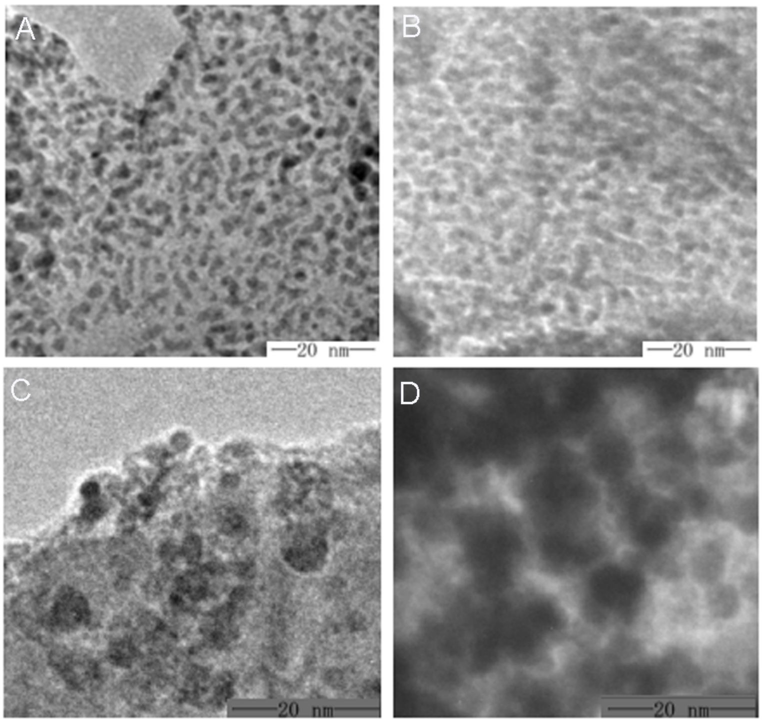


Fig. S8 TEM (A, C) images of AP-Pd/GN and Pd/GN before electrochemical measurements; TEM (B, D) images of AP-Pd/GN and Pd/GN after electrochemical measurements.

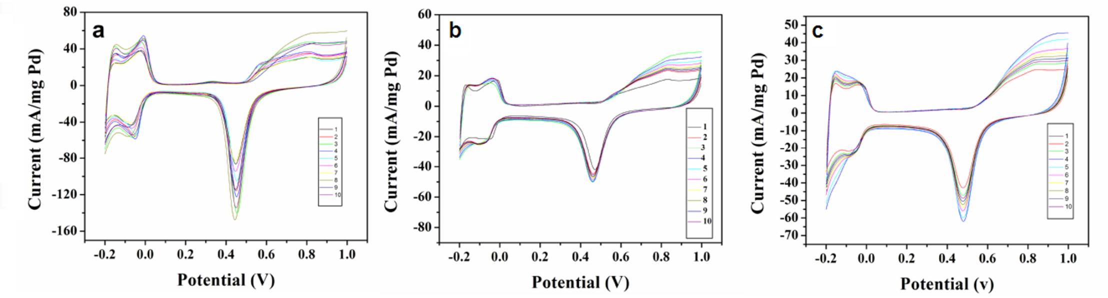


Fig. S9 Cyclic voltammograms of ten electrodes coated with (a) AP-Pd/GN; (b) Pd/GN; (c) Pd/VC catalysts in N2-purged 0.5 M H_2SO_4 at a scan rate of 50 mV/s.

In order to calculate the electrochemical activity surface area (ECSA) of catalysts, we have measured the cyclic voltammograms of ten electrodes coated with AP-Pd/GN, Pd/GN and Pd/Vulcan in 0.5M H_2SO_4 solution respectively. Thereinto, the cyclic voltammogram of each electrode is obtaind from the stabilized curve after scanning 20 cycles. we calculated average ECSA values of AP-Pd/GN, Pd/GN and Pd/Vulcan, respectively, according to the formula: **$ECSA=Q_H/0.21*[Pd]$.** Where Q_H (mC) is the charge due to the hydrogen adsorption/desorption in the hydrogenregion of the CVs shown in Fig. S9, 0.21 mC cm^{-2} is the electrical charge associated with monolayer adsorption of hydrogen on Pd, and [Pd] is the loading of Pd on the working electrode. Average ECSA values of AP-Pd/GN, Pd/GN and Pd/Vulcan are 72.72 m^2/g, 27.22m^2/g and 31.85 m^2/g, respectively.

Meanwhile, the cyclic voltammograms of ten elctrodes coated with AP-Pd/GN, Pd/GN and Pd/Vulcan were measured in the N_2-purged 0.5M + 0.5M H_2SO_4 solution. The results indicated that average J_m values of AP-Pd/GN, Pd/GN and

Pd/Vulcan catalysts are **446.3** mA/mg Pd, **213.0** mA/mg Pd and **191.9** mA/mg Pd**,** respectively. According to the calculated formula of activity on unit surface area (J_s): $\boldsymbol{J_s = J_m / ECSA\ value}$, the obtained J_s of AP-Pd/GN, Pd/Vulcan and Pd/GN are **6.14** A/m^2 Pd, **7.83** A/m^2 Pd and **6.03** A/m^2 Pd, respectively. Really, small size and better dispersion of Pd NPs on the graphene nanosheets could increase in ECSA, however, not sure to increase catalytic activity per unit surface area of Pd. Overlapping diffusion fields in a high density nanoelectrode array may saturate the overall electrochemical reaction rates. Moreover, the small-sized Pd NPs with more defects than big-sized ones, comparatively. There is no obvious available advantages in catalytic activity per unit surface area for AP-Pd/GN. However, just for its large ECSA value, AP-Pd/GN catalyst exhibit an especially high the J_m of AP-Pd/GN (**446.3** mA/mg Pd), compared with those for Pd/GN (**213.0** mA/mg Pd) and Pd/Vulcan catalyst (**191.9** mA/mg Pd). Economically, improving the activity in mass of catalyst and reducing dosage of precious metal are very significant for practical application.

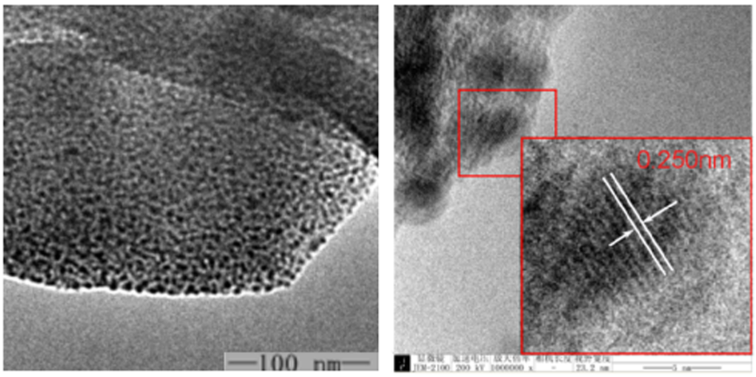


Fig. S10 TEM image of Ag/GN prepared by the proposed method