

# Supporting Information

## Cobalt Phthalocyanine-Graphene Oxide Nano-composite: Complicated Mutual Electronic Interaction

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### Experimental

#### *Reagents and materials*

Graphite flake (nature, 300 mesh) was taken from Liu Mao mine. Nafion (5wt. %, Alfa Aesar) was diluted to 0.1 w.t. % with distilled water. ACOP and ASA were obtained from Alfa Aesar. Other reagents were purchased from Beijing Chemical Company. All stock solutions were prepared with deionized water (18.2m $\Omega$ ).

#### *Characterization*

TEM images were obtained with a Tecnai G220 S-Twin microscope operating at an accelerating voltage of 200 kV. XPS spectra were obtained using an Axis Ultra spectrometer (Kratos, UK). A mono Al-K $\alpha$  (1486.6 eV) X-ray source was used at a power of 225 W (15 kV, 15 mA). To compensate for surface charge effects, binding energies were calibrated using the C 1s hydrocarbon peak at 284.8 eV. UV-visible spectroscopy (Cary Varian 50) with a 1 cm quartz cell was used. Electrochemical measurements were conducted using CHI660D electrochemical workstation (CHI, Shang Hai) with three-electrode setup. Glassy carbon electrode (GCE, 3 mm diameter, Tian Jin Aida, Inc.) acted as the working electrode, with SCE as the reference electrode, and platinum wire as the counter. XRD patterns of the catalysts were recorded using a D/max-rB X-ray diffractometer (Japan) with a Cu-K $\alpha$  radiation source operating at 45 kV and 100 mA. Raman spectroscopy was obtained using a Horiba HR800 Raman system with three laser lines, a 632.8 nm line from He-Ne laser. FTIR spectra of the samples were measured on a Bruker Tensor spectrometer with KBr as the solid dispersant.

#### *Preparation of modified Glassy carbon electrodes*

Glassy carbon electrode (GCE) was polished with 70 nm Al<sub>2</sub>O<sub>3</sub> powder, rinsed by deionized water, ethanol and deionized water, and dried at room temperature. 5 mg CoPc, GO or CoPc-GO was dispersed in 1 ml of 0.1 wt. % nafion solution. A 10  $\mu$ L aliquot of this dispersion was placed as a droplet on the pre-treated GCE to fabricate the modified GCE. The solvent was evaporated under an infra-red lamp.

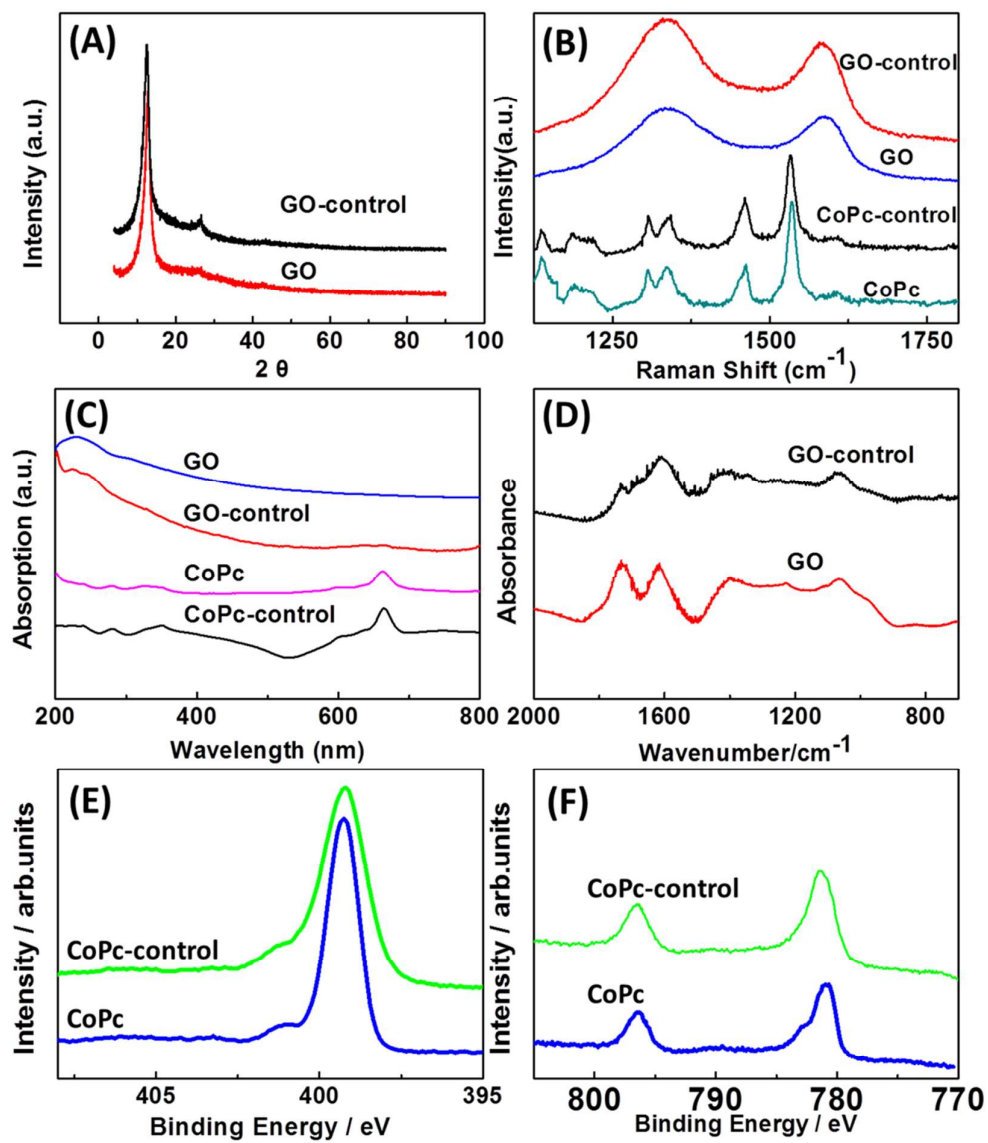
#### *Preparation of GO*

Graphene oxide (GO) was prepared from graphite powder by a modified Hummers method. The

GO was synthesized by oxidation of purified natural small graphite according to a modified Hummer's method<sup>1</sup>. Typically, the mixture of graphite (10 g) and sodium nitrate (5 g) was stirred by mechanical agitator in the concentrated sulfuric acid (230 ml) in the ice bath, and then 30 g of potassium permanganate was slowly put into the system within 10 minutes. After 3 h, the mixture was heated to 35 °C for 4 h, and then the deionized water (460 ml) was added to the mixture slowly (< 90 °C). After the water was added completely, the temperature of the slurry was increased until 98 °C, and it was kept at that temperature for 3 h. The batch was poured into a 3 L beaker filled with 2 L deionized water. Immediately, the hydrogen peroxide (100 ml, 30%) and hydrochloric acid (300 ml, 37%) was added into the mixture. Remove that supernatant twice a day until it did not show any precipitation with AgNO<sub>3</sub> solution. The mixture was filtered and the cake was put into oven (60 °C) for 2 weeks and then carefully powdered to get GO.

#### *Preparation of CoPc-GO*

0.3 (0.02) g CoPc was put into the mixed solvent containing 1.5 g AlCl<sub>3</sub> and 200 ml acetone and then the mixture was stirred for 2 hours after being ultrasonically dispersed for 1 hours following the adding of 1 g GO. The stirring mixture was then put into the oil bath at 333 K until the solvent was evaporated. The powder obtained was washed first with a mixture containing ethanol, water and ammonia (volume ratio: 90% CH<sub>3</sub>CH<sub>2</sub>OH, 5% H<sub>2</sub>O, 5% NH<sub>3</sub> • H<sub>2</sub>O) and then with pure ethanol until filtrate was colorless. The sample was dried at 333 K for 24 hours to get Cobalt Phthalocyanine-Graphene Oxide Nano-composite containing 2.6 w.t. % Cobalt Phthalocyanine (2.6%CoPc-GO) and 1 w.t. % Cobalt Phthalocyanine (1% CoPc-GO).



**Fig. S1** The XRD patterns (A), Raman spectra (B), UV-Vis spectra (C), FTIR spectra (D), N 1s (E)

XPS, Co 2p (F) XPS of sample and control sample.