

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 (18.2mΩ).

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 α (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 α 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 Al₂O₃ 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 μ 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 method¹. 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 AgNO₃ 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 AlCl₃ 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% CH₃CH₂OH, 5% H₂O, 5% NH₃ • H₂O) 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).

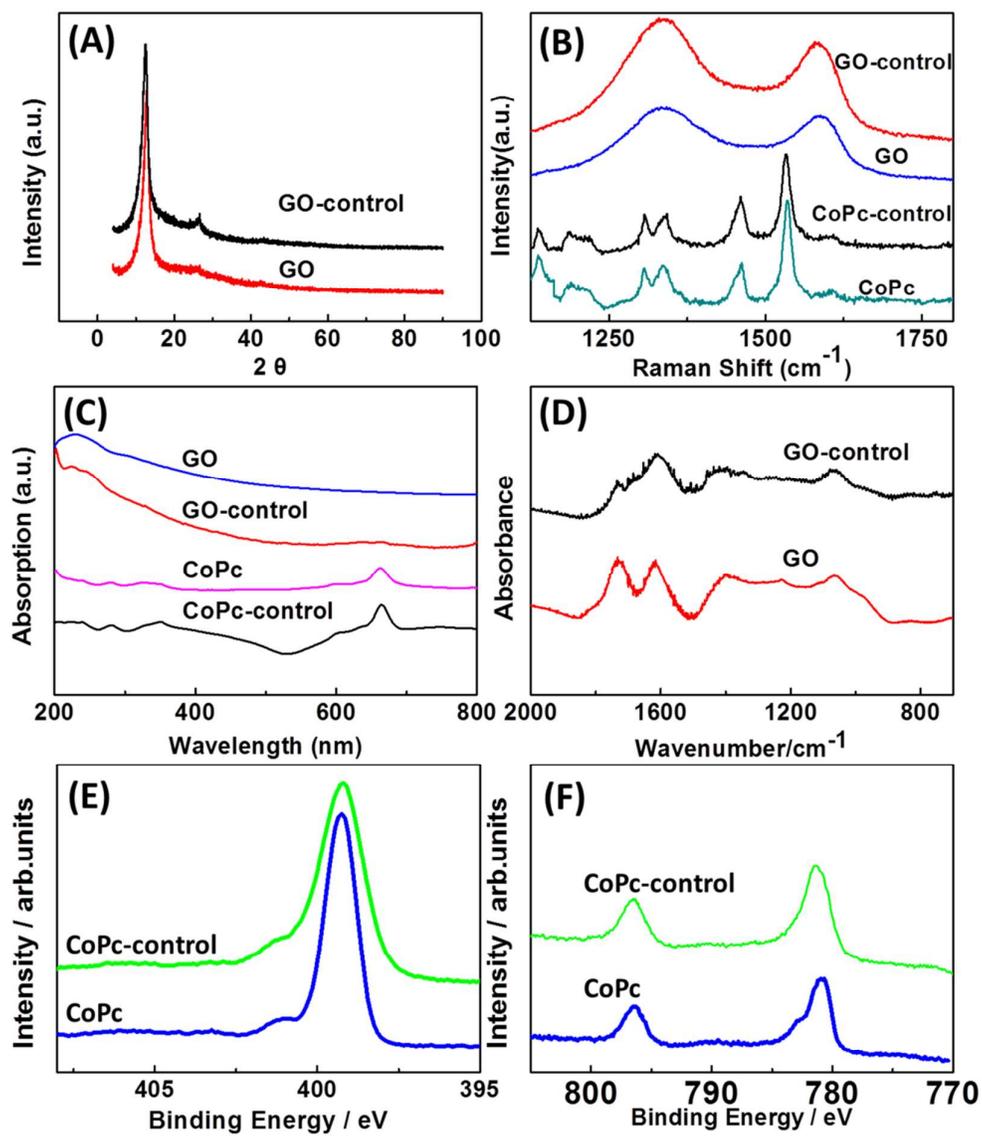


Fig. S1 The XRD patterns (A), Raman spectra (B), UV-Vis spectra (C), FTIR spectra (D), N 1s (E)

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