

# Hybrid Catalyst Composed of Reduced Graphene Oxide/Cu<sub>2</sub>S Quantum Dots as a Transparent Counter Electrode for Dye Sensitized Solar Cells

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## **1 Experimental detail**

### **1.1 Synthesis of the hybrid catalyst of RGO/Cu<sub>2</sub>S QDs hybrid.**

GO sheets for the RGO-Cu<sub>2</sub>S QDs hybrid in this work were prepared by the oxidation and exfoliation of natural graphite using an improved Hummers' method.

Before the hybrid catalyst synthesis, 20 mg freeze-dried GO was added to 30 ml ethanol and the mixture were sonicated for 2 h until the GO was homogeneously dispersed in the solution. In a typical experiment, 1 mmol copper acetylacetonate (Cu (acac)<sub>2</sub>), 15 ml oleylamine (OLA), and 30 ml GO-ethanol solution were added into a three-necked flask (100 ml) at room temperature, followed by sonication for 30 min. After this, the mixture was heated to 120 °C and kept at this temperature for 30 min, while alternating between a vacuum (obtained using a vacuum pump) and a N<sub>2</sub> atmosphere (by bubbling N<sub>2</sub> through the mixture). Next, the GO-Cu(acac)<sub>2</sub>-OLA solution was heated to 200 °C and 5 ml of a sulfur-OLA solution (obtained by stirring 0.5 mmol sulfur powder and 5 ml OLA at 60 °C under a N<sub>2</sub> atmosphere) was injected and the mixture was kept at the same temperature under a N<sub>2</sub> atmosphere, with vigorous stirring, for 1 h. Finally, after cooling, the as-synthesized RGO-Cu<sub>2</sub>S QD hybrids were purified by repeated centrifugation and then washed using a mixture of solvent (chloroform) and anti-solvent (ethanol). The final product was redispersed in ethanol for deposition on the FTO glass by spray coating approach.

### **1.2 Preparation of counter electrodes:**

Moreover, the RGO/Cu<sub>2</sub>S QDs hybrid was prepared by 3 mg as-prepared RGO/Cu<sub>2</sub>S QDs hybrid dispersed in 10 mL ethanol using ultrasonication, and a thin layer of RGO/Cu<sub>2</sub>S QDs hybrids were deposited on FTO glass substrate (SnO<sub>2</sub>:F glass, 8 Ω/sq) by spraying coating method using an airbrush. The Cu<sub>2</sub>S QDs and RGO counter electrode was prepared in the same way. Before fabrication of the DSSCs devices, the electrodes were sintered at 400 °C in an Ar atmosphere for 2 h.

To prepare Pt CEs, 50 μL of H<sub>2</sub>PtCl<sub>6</sub> in ethanol was drop-cast on FTO glass substrates, followed by heat treatment at 380 °C for 30 min

### **1.3 Fabrication of Dye-sensitized solar cells:**

A TiO<sub>2</sub> film loaded on the FTO glass with dense transparent TiO<sub>2</sub> nanoparticle film (~13 μm in

thickness, 18 nm in diameter) and a scattering layer (~5  $\mu\text{m}$  in thickness, 400 nm in diameter) were prepared by a screen-printing method onto Fluorine doped Tin Oxide (FTO) glass, respectively. The substrate was sintered at 500  $^{\circ}\text{C}$  for 1 h and cooled to 100  $^{\circ}\text{C}$  to generate the anatase nanocrystals. After sintering, the  $\text{TiO}_2$  electrode was immersed in  $\text{TiCl}_4$  (40 mM) aqueous solution at 70  $^{\circ}\text{C}$  for 30 min. The film was then annealed at 450  $^{\circ}\text{C}$  for 30 min. In the following step, the mesoporous  $\text{TiO}_2$  was sensitized in N719 solution for 24 hours, the photoanode was sealed with a counter electrode by Surlyn films (40  $\mu\text{m}$  in thickness) by Hot-press machine. Further, an electrolyte which consists an acetonitrile solution of 0.6 M (1,2-dimethyl-3-propyl) imidazolium iodide, 0.05 M  $\text{I}_2$ , 0.5 M TBP, and 0.1 M LiI was to backfill through the hole in the counter electrodes of all the cells and then sealed them with a Surlyn film covered with a thin glass slide under heat.

#### **1.4 Characterization and Measurement:**

Morphologies of as-obtained products were observed on a field emission scanning electron microscopic (FESEM, FEI Sirion 200). Transmission electron microscopy (TEM, JEOL JEM-2100F) images were obtained under an acceleration voltage of 200 kV. UV-*vis* absorption spectra were recorded using a Hitachi U-4100 (Japan) spectrophotometer. The crystal structures of the counter electrode samples were characterized by powder X-ray diffraction (XRD) using a Goniometer Ultima IV (185 nm) diffractometer with  $\text{Cu K}_\alpha$  radiation, excited at 40 kV and 40 mA. Raman spectra were taken on a DXR Raman Microscope with an excitation length of 532nm.

Electrochemical impedance spectroscopy (EIS) measurements were obtained with an impedance analyzer (Zahner IM6, Germany) at zero bias potential. The impedance studies were carried out simulating open-circuit conditions in the atmosphere, and AC potential amplitude of 5 mV over a frequency range of 0.01– $10^5$  Hz in the dark conditions. The resultant impedance spectra were analyzed by means of the Z-view software. The Tafel polarization curves were measured using the Zahner electrochemical workstation system at a scan rate of 10  $\text{mV s}^{-1}$ . Additionally, all the EIS and Tafel measurements were based on a symmetric configuration consisting of two identical electrodes filled with the redox electrolyte which was to be used in the DSSCs. Cyclic voltammetry (CV) were executed in a three electrode system with different CEs as the working electrode, a platinum wire as the counter electrode, and  $\text{Ag}/\text{Ag}^+$  electrode as the pseudo reference electrode, which was

calibrated with a ferrocene solution after the CV measurements, at a scanning rate of  $50 \text{ mVs}^{-1}$ . The electrode was dipped in an anhydrous acetonitrile solution containing  $0.1 \text{ mM LiClO}_4$ ,  $10 \text{ mM LiI}$ , and  $1 \text{ mM I}_2$ .

For the photovoltaic measurements, devices were equipped with a UV cut-off filter and masked with a thin metal mask to give an active area of  $0.25 \text{ cm}^2$ . *J-V* curves of the DSSCs were measured with a digital source meter (Keithley 2400) under simulated solar illumination at  $100 \text{ mW cm}^{-2}$ , AM1.5 G standard (Wacom, Japan). During I-V measurements, a black mask was used with an aperture area of  $0.25 \text{ cm}^2$ .

## 2 Supporting Information

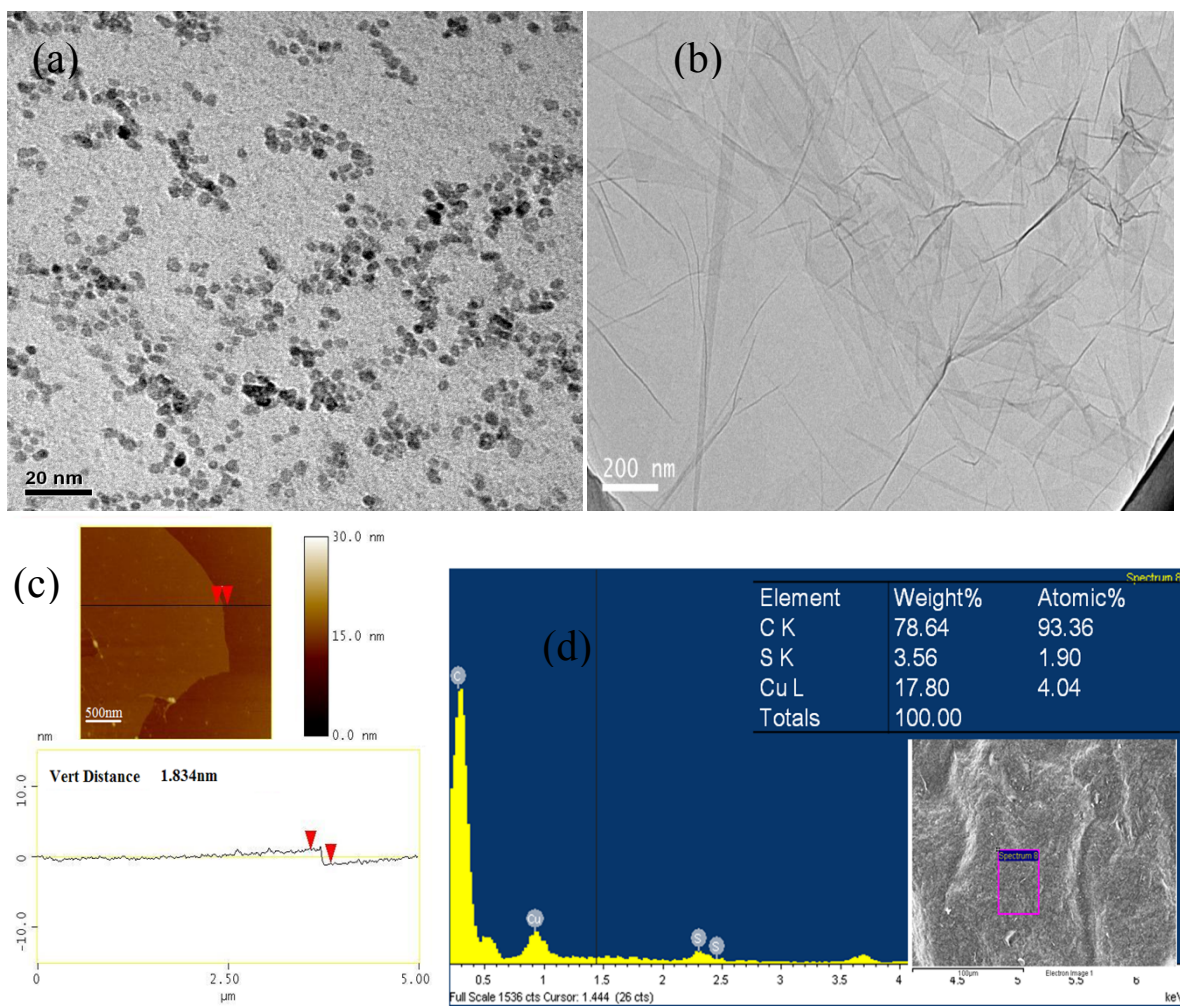


Fig.S1 (a) TEM image of Cu<sub>2</sub>S QDs; (b) TEM image of graphene oxide; (c) AFM images of graphene oxide; (d) EDS of RGO/Cu<sub>2</sub>S QDs hybrid.

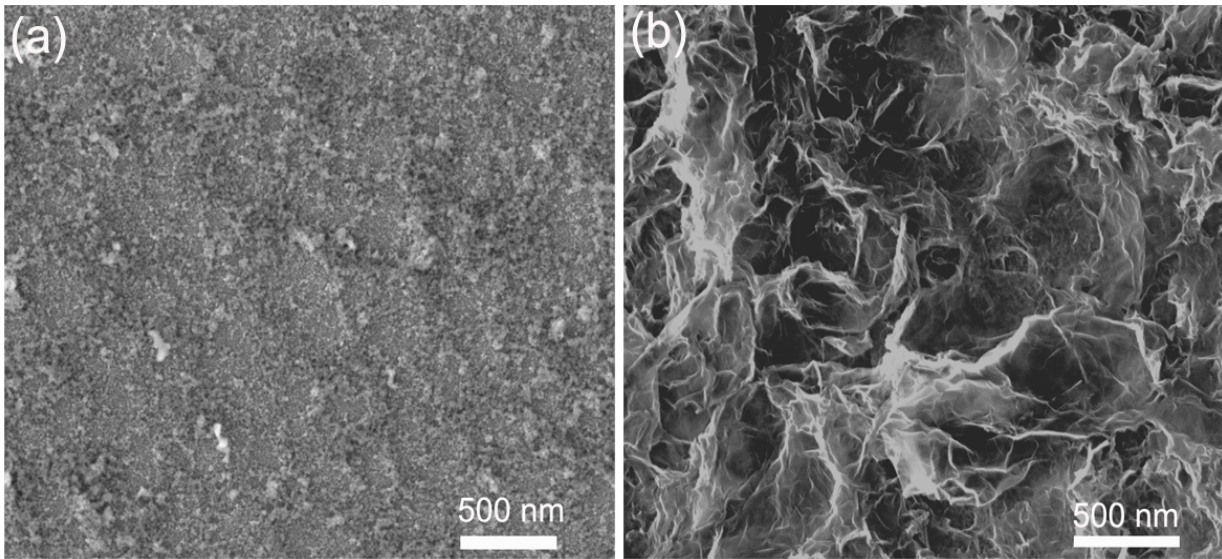


Fig.S2 SEM images of (a) Top view and (b) cross-section of  $\text{Cu}_2\text{S}$  QDs.

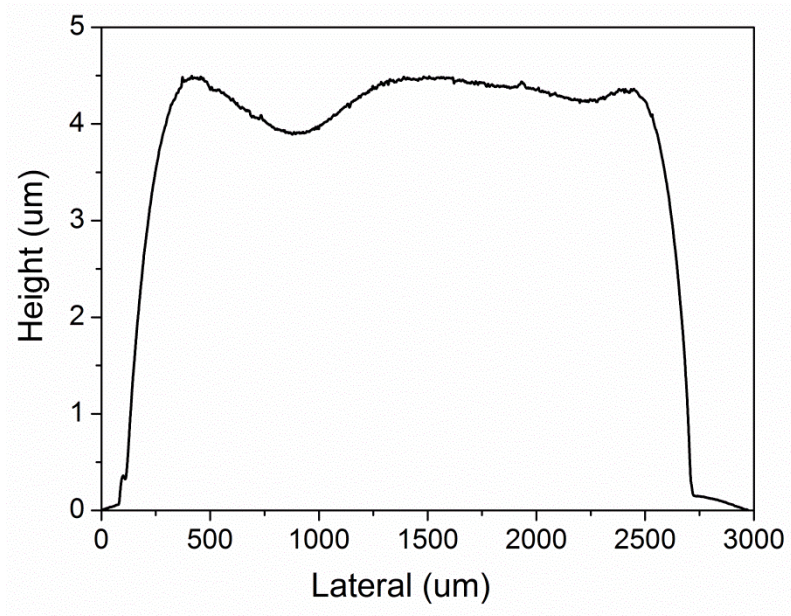


Fig.S3 The thickness of RGO/ $\text{Cu}_2\text{S}$  hybrid on FTO glass measured by a surface profiler.