

**Electronic Supplementary Information (ESI) for:**

**A photocatalytic graphene quantum dots-Cu<sub>2</sub>O/bipolar membrane as  
separator for water splitting**

Xian Liu, Xuan Jian, Huimin Yang, Xiuli Song and Zhenhai Liang\*

College of Chemistry and Chemical Engineering, Taiyuan University of  
Technology, Taiyuan, 030024, (P.R. China), E-mail: liangzhenhai@tyut.edu.cn

## 1. Preparation of GQDs-Cu<sub>2</sub>O/BPM

A three-step process was used to prepare GQDs-Cu<sub>2</sub>O/BPM by a paste method.

Firstly, carboxymethyl cellulose (CMC, with 6.5-8.5% Na-content, Guoyao Chemicals Co. Ltd.) aqueous solution (3.0 wt.%) together with polyvinyl alcohol (PVA, molecular weight of 105000 g mol<sup>-1</sup>) aqueous solution (3.0 wt%) was stirred for 2h and poured on a clean glass plate to form a membrane. Then, the membrane was cross-linked with FeCl<sub>3</sub> (8.0 wt.%, 10 min) and dried to obtain CM.

Secondly, GQDs-Cu<sub>2</sub>O composite is prepared by facile one-step ultrasonic treatment. Typically, 150 mL NaOH (1 mol L<sup>-1</sup>) was added dropwise into 150 mL CuSO<sub>4</sub> (0.1 mol L<sup>-1</sup>) solution at the rate of one drop per 10 seconds to form a flocculent suspension. Then, 20 mL polyvinylpyrrolidone (PVP, 50 g L<sup>-1</sup>) solution was added into it after ultrasonic treatment for 15 min. Next, 100 mL glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>, 1 mol L<sup>-1</sup>) solution was added with stirring, and followed by an ultrasonic treatment for 60 min. Finally, GQDs-Cu<sub>2</sub>O was obtained by centrifuging and washing several times with deionized water and ethanol respectively. The prepared GQDs-Cu<sub>2</sub>O photocatalyst was added to 100 mL deionized water with ultrasonication to prevent aggregation, then poured on to the surface of CM and dried to obtain GQDs-Cu<sub>2</sub>O interlayer.

Thirdly, Chitosan (CS, with 90 % N-deacetylation) aqueous solution (3.0 wt.%) together with PVA aqueous solution (3.0 wt%) was stirred for 2h. Then, 2 mL glutaraldehyde (25 % by volume in water) was added and stirred for another 2 h. Next, the mixture was poured on to the surface of GQDs-Cu<sub>2</sub>O interlayer to form AM. Finally, the GQDs-Cu<sub>2</sub>O/BPM sandwich structure composite was allowed to be totally dried at room temperature.

## **2. Measurement of the current-voltage curve (I-V curve) of the BPMs-equipped cell**

The I-V curve of the BPMs-equipped cell was measured by use of a direct current source. The BPMs was fixed between the cathode and anode chambers, as a separator. The catholyte and anolyte were both 200 mL 0.5 mol/L Na<sub>2</sub>SO<sub>4</sub> solution. The anode and cathode were both graphite electrodes (area 2 cm<sup>2</sup>). The I-V curve were measured both with and without sunlight irradiation.

## **3. AC impedance spectroscopy of the BPMs**

First, a clean graphite electrode was placed into the thick CMC aqueous solution, removed, and dried to obtain CM. The CM was cross-linked with FeCl<sub>3</sub> solution for 10 min and dried. Subsequently, the prepared GQDs-Cu<sub>2</sub>O photocatalyst was coated on the CM surface. Finally, the coated electrode was placed into a thick, glutaraldehyde-modified CS solution, removed, and dried.

The coated graphite electrode served as the working electrode. A Pt wire acted as the counter electrode, and an Ag/AgCl electrode functioned as the reference electrode. KCl solution (100 mL, 0.5 mol L<sup>-1</sup>) served as the electrolyte. AC impedance spectroscopy was performed on an electrochemical workstation (CHI660C; Shanghai Chenhua Instrument Company, China).

In the illustration of Figure 3, Cd is the capacitive impedance of the interlayer, Rr is the impedance of the membrane, and R1 the impedance of the bulk solution. The size of the high-frequency semicircle indicated the approximate impedance of different BPMs.

## **4. The current efficiency and energy consumption of H<sub>2</sub> generation**

The water system used the GQDs-Cu<sub>2</sub>O/BPM sandwich structure as a diaphragm to perform H<sub>2</sub> production from water splitting. The electrolyte was 0.5 mol/L Na<sub>2</sub>SO<sub>4</sub> solution. Two platinum plate working electrodes (ca. 2 cm<sup>2</sup> each) were connected by a direct current source. The

average light intensity of solar-light was  $1.16 \times 10^5$  lx during the experiments.

$$\text{Efficiency (\%)} = \frac{V_{real}}{V_{ideal}}$$

( $V_{ideal} = St/nF \times RT/P$ ,  $S$ : stoichiometric coefficient;  $I$ : applied current;  $t$ : operation time;  $n$ : number of electrons transfer;  $F$ : Faradic constant;  $R$ : ideal gas constant;  $T$ : operation temperature;  $P$ : atmosphere).

### **5. XPS survey spectrum of GQDs-Cu<sub>2</sub>O and XPS spectra of Cu 2p, O 1s and C 1s.**

To investigate further the surface composition of the GQDs-Cu<sub>2</sub>O composites, the XPS measurement was carried out. Fig. S1(A) shows an XPS survey spectrum of the GQDs-Cu<sub>2</sub>O, which clearly displays the presence of C, O and Cu. The Cu 2p spectra was shown in Fig. S1(B), the Cu 2p<sub>3/2</sub> and Cu 2p<sub>1/2</sub> peaks of Cu (I) were located at binding energies of 932.6 eV and 952.1 eV, respectively, which proves the presence of Cu<sub>2</sub>O in the nanocomposite.<sup>[S1]</sup> The O 1s spectrum was shown in Fig. S1(C). A broad peak was observed and fitted into three peaks at 530.1 eV, 531.6 eV and 533.2 eV, which were assigned to the adsorbed molecular H<sub>2</sub>O, hydroxyl oxygen and lattice oxygen, respectively.<sup>[S2]</sup> The C1s spectrum in Fig. S1(D) contains three components at 284.5eV, 285.6eV and 288.5eV, which are assigned to the C-C or C=C bonds, C-O bond and C=O bond, respectively.<sup>[S3]</sup>

### **6. The recyclability reaction and stability test over GQDs-Cu<sub>2</sub>O/BPM photocatalyst.**

The experiments were repeated ten times to test the stability of GQDs-Cu<sub>2</sub>O/BPM under sunlight irradiation, and each test circle time is 60min. The results showed that current efficiencies and energy consumptions kept nearly unchanged, indicating this system has a good reusability.

(Fig. S6)

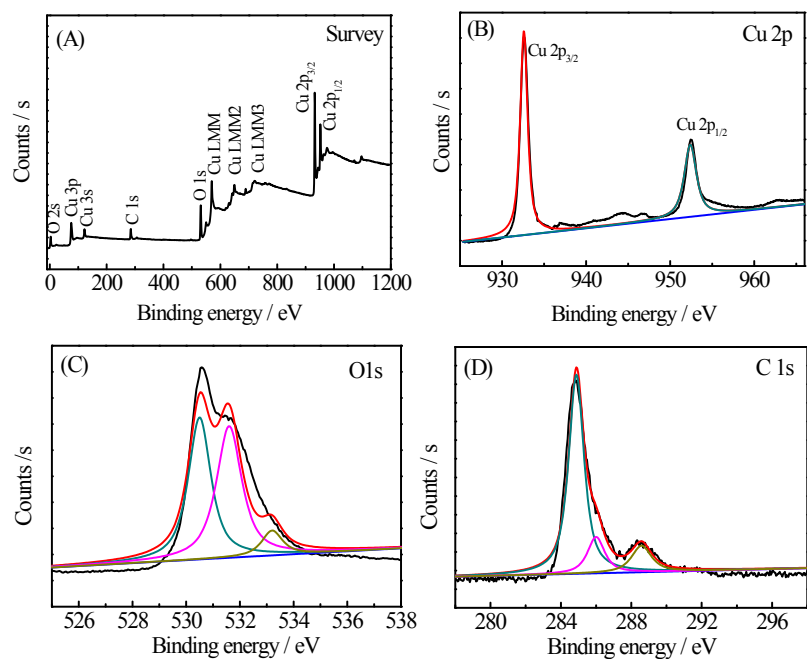


Fig. S1 XPS survey spectrum of GQDs-Cu<sub>2</sub>O (A) and XPS spectra of Cu 2p (B), O 1s (C) and C 1s (D).

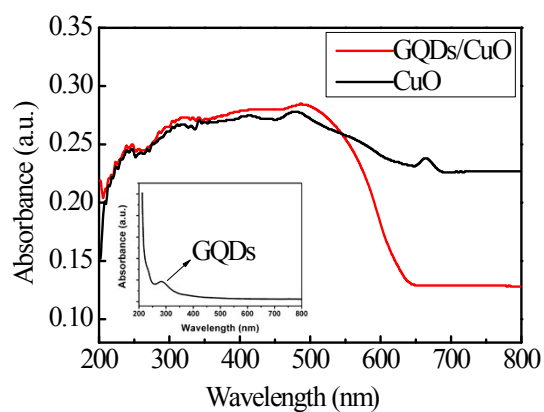


Fig. S2 DRS absorption spectral of GQDs-Cu<sub>2</sub>O, Cu<sub>2</sub>O and GQDs.

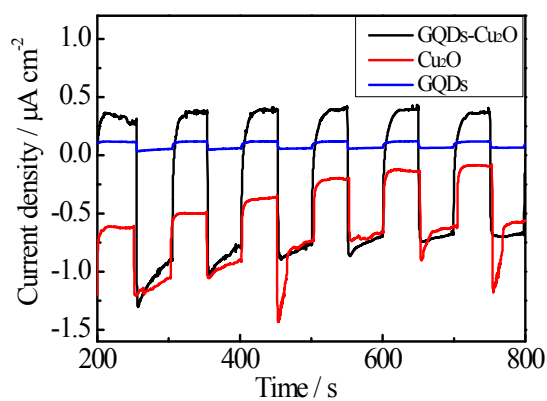


Fig. S3. Photocurrent responses of GQDs-Cu<sub>2</sub>O, Cu<sub>2</sub>O and GQDs under chopped illumination.



Fig. S4 Optical image of GQDs-Cu<sub>2</sub>O/BPM

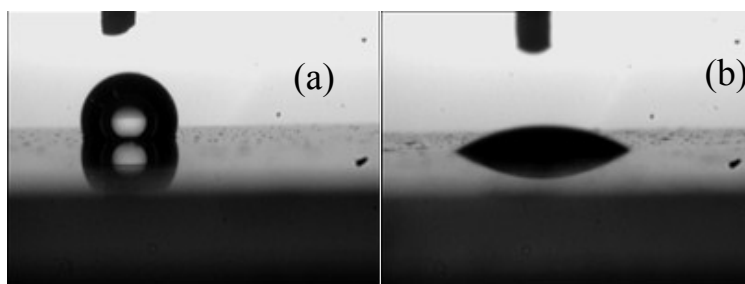


Fig.S5 Contact angles of the BPM (a) and GQDs-Cu<sub>2</sub>O/BPM (b).

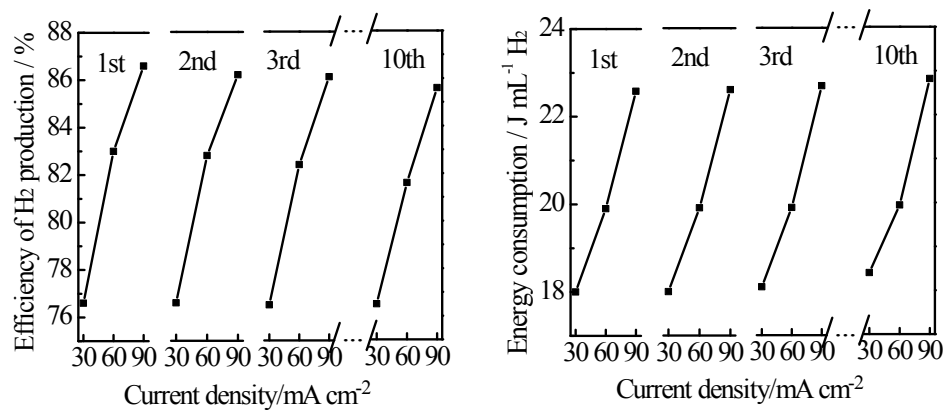


Fig. S6 The cycling runs in the presence of the GQDs-Cu<sub>2</sub>O/BPM.

**References:**

[S1] Y. Zhang, X. Wang, L. Zeng, S. Song and D. Liu, Dalton Trans., 2012, **41**, 4316.

[S2] W. Cui, W. An, L. Liu, J. Hu and Y. Liang, J. Hazard. Mater., 2014, **280**, 417.

[S3] Y. Li, Q. Wang, P. Liu, X. Yang, G. Dun and Y. Liu, Ceram. Int., 2015, **41**, 4248.