Supplementary Information

Carbon quantum Dots Aqueous Solution as Electrolyte for H₂O₂ Production Based on Photoelectrochemical Water Splitting

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1. Experimental Section

1.1 Materials

The CQDs precursors 3-Aminopropionic acid, 4-Aminobutyric acid and 6-Aminocaproic acid were purchased from Energy Chemical Co., Ltd. Hydrogen peroxide (30%) was purchased from Sinopharm Chemical Reagent Co., Ltd. DMPO (dimethyl pyridine N-oxide) used for EPR was obtained from Dongren Chemical Technology Co., Ltd. Peroxidase from horseradish was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. All the reagents were used without any further purification. A cellulose dialysis membrane with molecular weight cut off (MWCO) of 500 Da was purchased from Sangon Biotech (Shanghai) Co., Ltd.

1.2 Preparation of CQDs

The CQDs samples were prepared based on hydrothermal method.¹ Different from the strong electrolyte to complete ionization in aqueous solution, CQDs generated from aliphatic amino acids was weak electrolyte. For strong electrolyte, it is easy to obtain the identical charged particle concentration by controlling the concentration of electrolyte, which is infeasible in the system containing weak electrolyte. Based on the Kohlausch's law of independent ion movement,² the charged particles concentration is proportional to the electro-conductibility of the system. Therefore, the preparation conditions were different for 3-CQDs, 4-CQDs, and 6-CQDs in order to keep the almost identical electro-conductibility for PEC testing.

1.2.1 Preparation of 3-CQDs

Typically, 3-Aminopropionic acid (0.0267 g, 0.03 mmol) was dissolved in 10 ml deionized water to deliver 0.03 M aqueous solution, which was kept in an autoclave at 180 °C for 8 hours. The obtained system was filtered through a filter with diameter of 0.22 μ m. Then, the resulted solution was dialyzed by a cellulose dialysis membrane in a 1 L deionized water under subsequent stirring. Every 4 h, fresh deionized water was applied and the whole dialysis process lasted for 2 days. Finally, 68 mg 3-CQDs was obtained as a pale yellow powder after freeze-drying. It was found that 3-CQDs was

very hygroscopic, which was changed into light brown very quickly in the room condition.³

1.2.2 Preparation of 4-CQDs and 6-CQDs

The similar approach was carried out for the preparation of 4-CQDs or 6-CQDs, but 4-Aminobutyric acid (0.2062 g, 0.2 mmol) or 6-Aminohexanoic (0.1312 g, 0.1 mmol) was used instead. The compounds were dissolved in 10 ml deionized water respectively and delivered 0.2 M or 0.1 M aqueous solution. Additionally, the treatment temperature for the preparation of 4-CQDs or 6-CQDs was different from 3-CQDs, in which the solution was kept in an autoclave at 200 °C or 220 °C for 8 hours respectively. After filtration, dialysis and freeze-drying, 56 mg 4-CQDs was obtained as a yellow powder and 35 mg 6-CQDs was obtained as a brownish yellow powder respectively.

1.3 Preparation of BiVO₄ working electrode

Fabrication of BiVO₄-modified FTO photoanode was based on the reported method without further development.⁴

1.4 Characterization

1.4.1 Material Characterization

High-resolution transmission electron microscopy (HR-TEM) images were obtained on a Tecnai G2 F20 electron microscope at 200 kV. The photoluminescent (PL) spectrum was recorded on a fluorescence spectrometer (F-7000, Hitachi). X-ray photoelectron spectroscopy (XPS) analysis of the CQDs were performed on a Kratos AXIS ULTRA XPS instrument. The C 1s peak at 284.8 eV was chosen as the calibration for binding energy. Fourier transform infrared (FT-IR) spectrum was collected on a FT-IR spectrometer (Spectrum One, Perkin Elmer). An X-ray powder diffractometer (XRD) was operated to characterize the structures of materials on Bruker D8 Advance. UV-vis absorption spectrum was recorded on U-3900 UV-vis spectrophotometer (Hitachi). ¹³C NMR data were recorded on 400 MHz JEOL Ltd. Chemical shifts were expressed in parts per million (ppm) units with downfield from

TMS. The contact angle of water droplets was measured on Dataphysics OCA20 DCAT21. Zeta potential measurements were conducted on a Malvern laser particle size analyzer. To determine the electro-conductivity of CQDs solution, conductivity meter (DDSJ-319L) was applied. The German Bruker EMX-10/12 electron paramagnetic spectrometer was used to collect electron paramagnetic resonance spectroscopy (EPR) data, which provided the information for the genenration of free radicals in PEC system. For detecting the H₂O₂ degradation, standard Clark-type oxygraph electrode equipped with Oxygraph + software (Hansatech Instruments) was applied.

1.4.2 Electrochemical measurements with three-electrode cell

All electrochemical experiments were operated at 25 °C on a CH instruments electrochemical analyzer (model CHI660E). A three-electrode system was equipped with Ag/AgCl (3 M KCl) as reference electrode, graphite rod as a counter electrode, and 2 cm² FTO electrode covered by 1 cm² BiVO₄ as working electrode. Without further statement, all potentials were reported versus RHE (Reversible Hydrogen Electrode). The photocurrent density was determined after dividing photocurrent by photoanode areas. Flat-band potential measurements were performed using Mott-Schottky plots at potential varying from 0.6 V to 1.6 V with a frequency of 1 KHz.

1.4.3 The determination and quantification of H₂O₂ in PEC system

The and determination quantification of H_2O_2 based was on N,N-diethyl-1,4-phenylene-diamine (DPD) method.⁵ DPD (0.1 g) was dissolved in 10 mL 0.05 M H₂SO₄ solution to deliver DPD solution. Peroxidase (POD, 10 mg) was dissolved into 10 mL deionized water, which was kept in a refrigerator for storage. Before PEC process, the UV-vis spectrum was recorded for the mixture of 2 ml electrolysis solution, 0.4 ml potassium phosphate buffer solution (1 M), 3 mL water, 0.05 mL DPD solution and 0.05 mL POD solution. And then, 2 ml electrolysis solution was collected after PEC process proceeding for 10 min, which was further added with 0.4 ml potassium phosphate buffer solution (1 M), 3 mL water, 0.05 mL DPD solution and 0.05 mL POD solution. The system was well mixed and analyzed by UV-vis spectroscopy. The detection of H_2O_2 was based on the differences in UV-vis spectroscopy before and after PEC process, and its quantification was determined according to the job plot for the mixture of 2 ml H_2O_2 solution with different concentration, 0.4 ml potassium phosphate buffer solution (1 M), 3 mL water, 0.05 mL DPD and 0.05 mL POD solution.

1.4.4 The detection and quantification of O₂ generation in PEC system or degradation of H₂O₂

Oxygen was detected on a Shimadzu GC-14B instrument, and the amount was determined by injection Methane as an internal standard in the well-sealed PEC system. For detecting the H₂O₂ degradation properties of CQDs, standard Clark-type oxygraph electrode (Hansatech Instruments) was applied, which was separated from the sampled solution by a Teflon membrane. For all experiments, the cell was thermostated at 20°C. The signal was calibrated using air saturated aqueous solutions $([O_2] = 276 \ \mu\text{M}, T = 20^{\circ}\text{C})$, and then recorded for the entire duration of the measurement using Oxygraph + software (Hansatech Instruments) at 0.1 s intervals.

2. Tables and Figures



Figure S1. Excitation-wavelength dependent photoluminescence spectra of (a) 3-CQDs, (b) 4-CQDs and (c) 6-CQDs.



Figure S2. The Zeta potential of (a) 3-CQDs and (b) 4-CQDs.



Figure S3. FT-IR spectra of (a) 6-CQDs, (b) 4-CQDs and (c) 3-CQDs respectively.



Figure S4. The LSV curve on $BiVO_4$ photoanode in the aqueous solution with CQDs precursors in the dark or under irradiation of 420 nm LED lamp (the input optical power is 8.37 mW cm⁻²).



Figure S5. Long period PEC proceeding on BiVO₄ electrode in 6-CQDs solution at 1.23 V under the irradiation of 420 nm LED lamp.



Figure S6. (a) The UV-vis absorption spectra for the mixture with 2 ml H_2O_2 solution with different concentration (0 M, 0.006 M, 0.008M, 0.01M, 0.012M, 0.015M), 0.4 ml potassium phosphate buffer solution (1 M), 3 mL water, 0.05 mL DPD and 0.05 mL POD solution. The job plot for the quantification of H_2O_2 based on the absorption in the spectra at 510 nm (b) and 551 nm (c) respectively.



Figure S7. The UV-vis absorption spectra of the mixture with 2 ml electrolysis solution, 0.4 ml potassium phosphate buffer solution (1 M), 3 mL water, 0.05 mL DPD solution and 0.05 mL POD solution before and after PEC proceeding on BiVO₄ photoanode at 1.23 V for 10 min. The Figure stands for the detection of PEC H_2O_2 evolution in (a) 3-CQDs solution, (b) in 4-CQDs solution, (c) in 6-CQDs solution and (d) in KHCO₃ aqueous solution respectively. The detail for H_2O_2 detection was described in the Experimental Section. The insets were the images for the stated mixture before and after PEC proceeding.



Figure S8. The UV-vis absorption spectra of the mixture with 2 ml electrolysis solution, 0.4 ml potassium phosphate buffer solution (1 M), 3 mL water, 0.05 mL DPD solution and 0.05 mL POD solution after PEC proceeding on $BiVO_4$ photoanode at 1.23 V and 1.5 V respectively for 10 min.



Figure S9. The cyclic voltammetry (CV) spectra of (a) 3-CQDs and (b) 6-CQDs, which was carried out in the corresponding CDs solution with bare FTO electrode as working electrode, Ag/AgCl electrode as reference and graphite rod as a counter electrode.

The determination for the HOMO and LUMO band lever of CQDs was based on CV measurement, which was according to the following equations:⁶

$$E_{HOMO} = -(E_{OX} + 4.71) \, eV$$
 (1)

$$E_{LUMO} = -(E_{red} + 4.71) eV$$
 (2)

Here, E_{ox} and E_{red} represents the first oxidation and reduction potential respectively in CV measurement, in which the potentials were reference to the Ag/AgCl electrode. The values for E_{HOMO} and E_{LUMO} were evaluated versus vacuum level.



Figure S10. UV-vis absorption of the system before and after long period PEC proceeding on BiVO₄ photoanode in 6-CQDs solution at 1.23 V for 1 h.



Figure S11. Experimental EPR spectrum (black) and simulated spectra (blue and pink) of the system after PEC proceeding on BiVO₄ photoanode in 3-CQDs solution at 1.23 V for 10 min.



Figure S12. The absorption of in-situ UV-vis spectroelectrochemical spectra at 268 nm for the system with PEC water oxidation on $BiVO_4$ photoanode in 3-CQDs solution at 1.23 V.



Figure S13. O_2 evolution in the mixture of H_2O_2 and CQDs or KHCO₃ aqueous solution (V: V = 1: 1) determined by clark electrode in the dark.

Table S1. pH and electro-conductibility of CQDs and KHCO₃ solution.

	3-CQDs	4-CQDs	6-CQDs	KHCO₃
рН	7.13	7.47	5.76	8.46
Conductivity (S • cm ⁻¹)	1.663 × 10 ⁻³	1.638 × 10 ⁻³	1.690 × 10 ⁻³	1.688 × 10 ⁻³

3. Reference

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