Supplementary Material

Carbon-Dot-Modified Phloroglucinol-Glutaraldehyde Resin Photocatalysts for Hydrogen Peroxide Production

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1. Experimental section

1.1 Sample characterization

Scanning electron microscope (SEM) and transmission electron microscopy (TEM) characterizations were performed on JEOL JEM-F200 and FEI Tecnai G2 F20 microscope, respectively. X-ray diffraction (XRD) patterns of different samples were obtained on a Bruker D8 ADVANCE powder diffractometer at Cu K α with a scanning rate of 2° min⁻¹ in the 2 θ range of 10-90°. X-ray photoelectron spectroscopy (XPS) was tested on the Thermo Scientific ESCALAB 250Xi electron spectrometer with an Al Ka X-ray source for determining the composition and chemical bonding configurations. Solid-state ¹³C nuclear magnetic resonance (NMR) spectra were collected on Bruker AVANCE NEO 400 WB spectrometer operating at 100.6 MHz with a 3.2 mm double resonance MAS probe and 10 kHz spinning rate. The ^{13}C NMR results were analyzed combined with the prediction tool of NMR software. Fourier transform infrared (FT-IR) spectrum of samples were recorded with a Bruker Vertex 70 spectrometer from 4000 to 500 cm⁻¹. In situ FT-IR measurements were conducted by the Bruker INVENIOR FT-IR spectrometer equipped with an in situ diffuse reflectance cell. Brunauer-Emmett-Teller (BET) surface area and pore structure were characterized by ASAP 2460 Micropore Physisorption Analyzer. Light absorption spectra were collected on a Shimadzu UV-2550 UV-visible spectrometer. Fluorescence spectra were recorded with a Hitachi F4500 fluorescence spectrophotometer. Time-resolved PL lifetime measurements were conducted on Hamamatsu C11367 fluorescence spectrophotometer. The electron paramagnetic resonance (ESR) experiments were performed on Bruker EMXplus-6/1 with 5,5-dimethyl-1-pyrroline-Noxide (DMPO) as a spin-trapping reagent under illumination of 300W xenon lamp.

1.2 Electrochemical experiments

The electrochemical experiments were conducted by a BIO-Logic SP-200 electrochemical workstation. A three-electrodes system (ITO glass with loaded catalysts, Ag/AgCl standard electrodes, and Pt electrodes as working electrodes, reference electrodes and electrodes, respectively) was employed to measure the electrochemical impedance spectroscopy and transient photocurrent in the electrolyte of 0.5 M sodium sulfate solution. The EIS measurements were performed at an open-circuit voltage with an amplitude of 0.3 V. The photocurrent measurements were conducted at an open-circuit voltage with an amplitude of 0.4 V. The electron number (n) of ORR was examined by linear sweep voltammetry (LSV) on the RDE in phosphate buffered saline (PBS) solution (pH 7). The Pt wire electrode and Ag/AgCl electrode were used as the counter and reference electrode, respectively. The sample was coated on the disk electrode as working electrode. The scan rate was set to 10 mV s⁻¹, and the rotating speed was set as 900-2500 rpm. The n was acquired by the Koutecky-Levich equation as reported.

1.3 Photocatalytic Measurement

Typically, 5 mg of samples was added into 20 mL of aqueous solution (or containing the given acetic acids). After mixing thoroughly under dark conditions, the resultant suspension was irradiated using a light source of solar simulation (CEL-HXUV300, CEAULIGHT, China). Every 15 minutes, 2 mL of the reaction solution was extracted and filtered for determining H_2O_2 concentration through the cerium sulfate Ce(SO₄)₂ titration¹. The absorbance at 316 nm was monitored using a UV-Vis spectrophotometer. The calibration curve with a good linear relation ($R^2 = 0.999$)² was displayed in Figure S0.



Figure S0. Absorption spectra and the corresponding linear fitting relationship of H_2O_2 concentration and absorbance at 316 nm

1.4 Apparent quantum yield (AQY) measurement

To analyze the AQY, 30 mg of CDs-PG and 10 mL of acetic acid solution were put into a beaker with an area of 0.95 cm². Afterwards, the system was constantly stirred at 353 K for 1 h under light irradiation with a band-pass filter (λ = 420 nm, 500 nm, 600 nm, 700 nm).

The AQY for H₂O₂ formation was calculated using the following equation³:

$$AQY = \frac{2MN_A hc}{SPt \lambda} \times 100\%$$
(S3)

where *M* signifies the generated amount of H₂O₂ (mol), N_A is the Avogadro constant (6.022×10²³ mol⁻¹), *h* is the Planck constant (6.626×10⁻³⁴ J·s), *c* represents the velocity of light (3×10⁸ m·s⁻¹), *S* is the irradiation area (0.95 cm²), *P* is the intensity of irradiation light (20 mWcm⁻²), *t* is the photoreaction time (3600 s), λ signifies the wavelength of the incident monochromatic light (420×10⁻⁹ m, 500×10⁻⁹ m, 600×10⁻⁹ m, 700×10⁻⁹ m).

1.5 The solar-to-chemical energy conversion (SCC) efficiency measurement

SCC efficiency was determined by the photocatalytic experiments using an AM 1.5G solar simulator as the light source (100 mWcm⁻²). CDs-PG (30 mg) and acetic acid solution (10 mL)

were put in a 20 mL beaker. The SCC efficiency of CDs-PG was calculated by the following equation⁴:

$$SCC = \frac{E_{H2O2}}{E_{solar}} \times 100\% = \frac{\Delta GM}{PSt} \times 100\%$$
(S4)

where $E_{\text{H}_2\text{O}_2}$ and E_{solar} are the energy of produced H₂O₂ (J) and the total input energy (J) respectively, ΔG is the formation energy of H₂O₂ (117 kJmol⁻¹), *M* represents the generated amount of H₂O₂ (µmol), *P* is the light intensity (20 mWcm⁻²), *S* is the irradiation area (0.95 cm²), *t* is the reaction time (3600 s).

2. Computational methods

All quantum calculations were carried out by using the Gaussian 16 program. The Becke three parameters hybrid exchange-correlation functional (B3LYP) level of theory combined with the def2svp standard basis set⁵ was adopted to explore the reactions. The dispersion correction schemes by Grimme (denoted as D3) were used to calculate the van der Waals interactions⁶. For the geometry optimization procedure, the structures were optimized until the forces were < 10^{-5} hartree/bohr and the energy change was < 10^{-7} hartree. The convergence criterion for the energy calculation during the self-consistent-field procedure was set for < 10^{-8} hartree. The transition states were characterized by identifying the only single imaginary frequency along the reaction coordinate. All transition states were located using the Berny algorithm⁷. The connection between the transition state and two minima (reactants and products) was established by the intrinsic reaction coordinate (IRC) calculations based on the reaction path following algorithm of Gonzalez and Schlegel as coded in Gaussian $16^{8,9}$. We verified that none of the stationary points have imaginary frequencies and each transition state have only one imaginary frequency.

3. Supplementary Results



Figures S1. SEM images of PG (a, b) and CDs-PG (c, d) with different magnifications



Figures S2. (a) N_2 adsorption/desorption isotherm of PG and CDs-PG; (b) The corresponding pore size distribution of PG and CDs-PG



Figures S3. XRD patterns of PG and CDs-PG



Figures S4. TEM (a) and high resolution TEM (b) images of CDs-PG



Figures S5. (a) XPS full spectra of PG and CDs-PG; (b) XPS C1s spectra of PG and CDs-PG



Figures S6. FTIR spectra of PG and CDs-PG. **Note:** In the FTIR spectrum of the CDs-PG sample, the additional peak at around 1250 cm⁻¹ is attributed to the stretch vibrations of C-O bonds of carboxylic acid functional groups derived from CDs, while the additional peak at around 1360 cm⁻¹ is assigned to the bending vibration of the hydroxyl functional groups (*J. Photoch. Photobio. A*, 2008, **198**, 205).



Figures S7. (a and b) XPS valence-band spectra of PG and CDs-PG; (c and d) Mott-Schottky plots for identifying the flat-band potentials of PG and CDs-PG



Figures S8. EIS Nyquist plots of PG and CDs-PG



Figures S9. Photocurrent responses of PG and CDs-PG



Figures S10. The effect of the mass ratio of carbon dot to phloroglucinol on hydrogen peroxide production at the room temperature



Figures S11. The effect of light irradiation intensity on hydrogen peroxide production



Figures S12. The effect of catalyst amounts on hydrogen peroxide production



Figures S13. Decomposition test of hydrogen peroxide solution (0.25 mM) in the presence of

CDs-PG under light irradiation



Figures S14. Cyclic tests of the CDs-PG and PG



Figures S15. (a) The effect of aldehyde species on hydrogen peroxide production; (b and c) The effect of phenol species on hydrogen peroxide production.



Figures S16. The effect of photocatalytic reaction temperature on hydrogen peroxide production of CD-PG with and without acetic acids



Figures S17. Dependence of hydrogen peroxide production on pH values



Figures S18. Apparent quantum efficiency and absorption spectrum of CDs-PG



Figures S19. Absorption spectra of nitro blue tetrazorium (NBT) solution added in PG and CDs-PG at the different photocatalytic reaction temperatures for determining O_2^- formation, in which the decrease degree in characteristic absorption peak reflects the generated amount of $O_2^$ species¹⁰



Figures S20. LSV curves of CDs-PG (a) and PG (b) by RDE at different rotating speeds and their corresponding Koutecky-Levich plots (c)



Figures S21. Comparisons of hydrogen peroxide production of CDs-PG and PG in the present pbenzoquinone, histidine and isopropanol, which serve as the reactive species scavengers of O_2^- , 1O_2 and OH, respectively.



Figures S22. Oxygen adsorption energy of CDs-PG and PG



Figures S23. The transition state structures of O_2^* , OOH* (TS1) and HOOH* (TS2) hydrogenation at D-A pair of CDs-PG and PG



Figures S24. FTIR spectra evolution of the mixed solution of CDs-PG at different photocatalytic reaction time.

| Sample | $\tau_1(ns)$ | τ_2 (ns) | τ ₃ (ns) | τ_{ave} (ns) |
|--------|--------------|---------------|----------------------------|-------------------|
| PG | 2.56 | 9.03 | 35.76 | 5.27 |
| CDs-PG | 2.69 | 8.39 | 38.45 | 8.35 |

Table S1. Fluorescence lifetimes of PG and CDs-PG

| Catalyst | Condition | Light source | H ₂ O ₂ yield | | |
|--|---------------------------|--|---|-----------|--|
| | | | (µmol·g ⁻¹ · h ⁻¹) | Ref. | |
| g-C ₃ N ₄ /PDI/rGO | Pure water | Xe lamp (AM 1.5) | 23.4 | 11 | |
| RF523 | O ₂ -saturated | Xe lamp ($\lambda > 420 \text{ nm}$) | 65.8 | 12 | |
| RF-acid resins | O ₂ -saturated | Xe lamp ($\lambda > 420 \text{ nm}$) | 75 | 13 | |
| Cv-g-C3N4 | Pure water | Xe lamp (AM 1.5) | 95 | 14 | |
| CdS | O ₂ -saturated | Xe lamp ($\lambda > 420 \text{ nm}$) | 101.9 | 15 | |
| ZnPPc-NBCN | O ₂ -saturated | Xe lamp ($\lambda > 420 \text{ nm}$) | 114 | 16 | |
| CRF | O ₂ -saturated | Xe lamp ($\lambda > 420 \text{ nm}$) | 126.7 | 17 | |
| g-C3N4/NaBH4 | Pure water | $(\lambda > 420 \text{ nm})$ | 170 | 11 | |
| CRF/NCDs | O ₂ -saturated | Xe lamp ($\lambda > 420 \text{ nm}$) | 213 | 15 | |
| RF/P3HT-1.0 | O ₂ -saturated | Xe lamp ($\lambda > 420 \text{ nm}$) | 233.3 | 18 | |
| CDs-PG | Pure water | Xe lamp (AM 1.5) | 244 | This work | |
| CDs-PG | Acetic acid solution | Xe lamp (AM 1.5) | 685 | This work | |

Table S2. Performance comparisons of reported photocatalysts for H₂O₂ production

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