Supporting Information

Carbon dots as electron extractant for enhanced photocatalytic antibacterial of covalent organic frameworks

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1 Experimental section

1.1 Chemicals and reagents

All reagents and starting materials were used without further purification. Citric acid, ethylenediamine, 1,2-dichlorobenzene (o-DCB), and anhydrous n-butanol (n-But), were purchased from Macklin Chemical. 4,4',4''-(1,3,5-triazine-2,4,6-triyl)trianiline (TTA) and 1,3,5-triformylphloroglucinol (Tp) were purchased from the Jilin Chinese Academy of Sciences, Yanshen Technology Co. Ltd.

1.2 Instruments

Powder X-ray diffraction (PXRD) patterns were obtained using a Rigaku Smartlab 600 X-ray diffractometer with Cu Kα line (λ = 1.540 56 Å). ^{13}C cross-polarization/magic-angle spinning (CP-MAS) solid-state nuclear magnetic resonance (NMR) spectra were recorded using a Bruker AVANCE III HD 400 WB (9.4T) spectrometer at a resonance frequency of 100.6 MHz. Fourier-transform infrared (FTIR) spectra were collected using a Nicolet Avatar 360 FT-IR spectrophotometer. X-ray photoelectron spectroscopy (XPS) data was obtained using a VG ESCALAB250 surface measurement system. High-resolution transmission electron microscopy (HRTEM) was performed using a JEM-2100F 90 transmission electron microscope. UV-Vis diffuse reflection spectra were recorded using a Shimadzu UV-2550 UV-Vis-NIR spectrophotometer. The fluorescence spectra and time-correlated single-photon counting measurements were measured using an Edinburgh Instruments FLS1000 instrument. Confocal laser scanning microscope (CLSM) was performed on Leica DMi8 microscope. Scanning electron microscopy (SEM) was performed using Zeiss (ULTRA Plus). Nitrogen isotherms were measured at 77 K using an Autosorb-iQ (Quantachrome) surface-area size analyzer. Before measurement, the samples were degassed in vacuum at 120 °C for 12 h. Using the N_2 adsorption isotherms, the surface areas were calculated over a pressure range 0.05-0.35 $=P/P_0$ using the Brunauer-Emmett-Teller (BET) method.

The working electrode analyzed in the electrochemical impedance spectroscopy

(EIS) test and the Mott-Schottky (MS) test as well as the transient photocurrent test, was formed as follows: 5 mg photocatalyst was scattered in a mixture liquid contain 20 μL 0.25% Nafion solution and 2 mL ethanol under ultrasonication to obtain a homogeneous paste. Then, the homogeneous paste (50 μL) was smeared on a piece of pre-cleaned 2×3.5 cm^2 FTO glass substrate. Then, it is dried under infrared light. Finally, the gained electrode was heated at 120 °C under the N_2 flow for 1 hour. Electrochemical impedance spectroscopy (EIS) and transient photocurrent experiments were conducted on an IM6e electrochemical workstation (Zahner Elektrik, Germany) with a standard three-electrode system, that employed as-fabricated electrodes as the working electrode, a platinum plate as the counter electrode, and Ag/AgCl (saturated KCl) as the reference electrode. A Xe arc lamp (300 W) with a cutoff filter ($\lambda \geq 420$ nm) was used as the light source. A 0.1 M Na_2SO_4 aqueous solution was used as the electrolyte. The similar electrochemical system was also employed to evaluate the working electrodes flat-band potential via the MS method. The MS measurements were carried out in the dark through scanning the electrode potential with of rate of 25 mV/s from -1.2 V to 1.6 V. The impedance-potential characteristics were registered at a frequency of 1000, 2000 and 3000 Hz. 0.1 M Na_2SO_4 aqueous solution was utilized as the electrolyte.

The working electrode examined in the Electrocatalytic H_2 evolution, was gained as follows: 6 mg photocatalyst was scattered in 2 mL deionized water by ultrasonication for 2 h to gain a homogeneous suspension. Then, 3 μL suspension was spread on the glassy carbon electrode and dry under infrared light. Finally, 3 μL 0.5% Nafion solution was dropped into the layer of catalyst and dry again under infrared lamp. Linear scanning voltammetry was accomplished in a standard three-electrode system with a scanning rate of 5 mV/s, including the as-obtained working electrode, the reference electrode of Ag/AgCl, the counter of Pt plate. A 0.5M H_2SO_4 aqueous solution was utilized as the electrolyte.

1.3 Synthesis of COF

4,4’,4’’-(1,3,5-triazine-2,4,6-triyl)trianiline (28.32 mg, 0.08 mmol) and 1,3,5-

triformylphloroglucinol (16.8 mg, 0.08 mmol) were charged into a Pyrex tube of size 10 × 8 mm (o.d × i.d) and mixed with *o*-dichlorobenzene/*n*-butanol solution (1:1 v/v, 1.0 mL) given solvent. The resulting suspension was sonicated at room temperature until the monomers were completely dissolved. Then 0.1 mL of pyrrolidine aqueous solution was added. After sonication for 10 min, the reaction solution in the Pyrex tube was sealed and subjected to three freeze-thaw cycles with liquid nitrogen. The reaction proceeded at 120 °C for three days. Subsequently, the product was filtered and washed with methanol, THF, and acetone. The yellow solid obtained was dried at 80 °C under vacuum for 8 h.

1.4 Synthesis of CDs

The synthetic methods for CDs were the same as those reported in the literature[1]. Briefly, citric acid (1.0507 g) and ethylenediamine (335 μL) were dissolved in 10 mL DI water. The solution was then transferred to a (polytetrafluoroethylene) (Teflon)-lined autoclave and heated at 200 °C for 5 h. After naturally cooling to room temperature, the brown-black solution was dialyzed for 24 h. Freeze-drying was then performed to obtain a dark brown powder.

1.5 Preparation of COF@CDs composite

An appropriate weight ratio of COF to CDs was mixed with a certain amount of water. The suspension was ultrasonicated for 1 h and heated at 80 °C until all of the solvent was evaporated. The weight percentage of CDs, with respect to the COF, was 4 wt% for characterization.

1.6 Bacterial culture and antibacterial experiments

To evaluate antibacterial activities, *E. coli* was selected as the model microorganism. Prior to determining the antibacterial activity, *E. coli* in the log phase (OD_{600} = 0.1) was diluted to a certain concentration. The diluted bacterial suspensions were mixed with the samples (50 μg mL^{-1}) in conical flasks, which were treated with or without light irradiation (300 W Xe lamp, λ≥420 nm) at a density of 100 mW cm^{-2} for different periods (0, 15, 30, 45, and 60 min). Untreated bacteria were used as control. Then, 10 μL of the bacterial suspension was dropped onto agar plates and spread uniformly. After

incubation at 37 °C for 20 h, viable bacterial colonies were counted using Image J software and recorded.

1.7 Dead/Live Staining Assay

Dead/live staining assay was performed to determine the viability of bacteria. First, the bacteria were co-cultured with sample for 1 h irradiated with and without visible light. The supernatant was removed and the sediment was washed three times using PBS. Bacteria were stained using propidium iodide (5 μM) /FDA (10 μM) for 15 min in the dark and images were captured using confocal laser scanning microscopy (CLSM) after washing the stained samples three times with PBS.

1.8 SEM characterization of bacteria

To further investigate the influence of COF@CDs on morphological changes of bacteria observed by scanning electron microscopy (SEM). Typically, sample-treated with and without light bacteria were harvested by centrifugation at 8000 rpm for 5 min. The precipitate was collected, washed with PBS three times, and then fixed with 2.5% glutaraldehyde for 6 h at 4 °C. After removing glutaraldehyde, these bacteria were sequentially dehydrated using a graded ethanol (50, 70, 90, 95, and 100%) for 10 min in 5 each step. Finally, these samples were obtained for SEM after freeze-drying.

1.9 ROS detection

ROS generation was detected by the electron paramagnetic resonance (EPR) spectrometer and fluorescence spectrometry. NaOH pretreated DCFH-DA (20 μL) was incubated with CDs, COF, COF@CDs samples (50 μg/mL) and then irradiated with Xenon lamp (mW/cm^2). At preset times, the fluorescence spectra were recorded (Ex: 488 nm, Em: 525 nm). The ROS generation ability was calculated as F_t/F_0. F_0 and F_t were the fluorescence intensities of the mixed solutions at 525 nm before and after irradiation.

1.10 ROS quenching experiment

COF@CDs (50 μg mL^{-1}) was mixed with the bacteria suspension with different ROS scavengers before irradiation. The scavengers were isopropanol (0.1%) for •OH,

2,2,6,6-tetramethylpiperidinyloxy (TEMPO) (100 μg mL^{-1}) for $•O^{2-}$, L-histidine (L-his) (100 μg mL^{-1}) for $^1O_2$. The scavenging experiments were conducted under the same conditions as the abovementioned antibacterial activity assay.

1.11 Cellular Toxicity Test

Human epithelial kidney cells 293T (10^4 cells per 200 μL) were cultured in 96-well plates first for 8 h in an incubator (37 °C, 5% CO_2) and for another 24 h after the culture medium was replaced by 100 μL of fresh medium containing COF@CDs with different concentrations (0, 25, 50, 100, and 200 μg/mL). Then, 10 μL of the CCK-8 solution (5 mg/mL) and 100 μL of the formation solvent were added to each cell well for further incubation for 4 h. The resulting mixture was shaken for 10 min at the incubator with low speed. The optical density (OD) of the mixture was measured at 450 nm.

2. Supplementary Figures

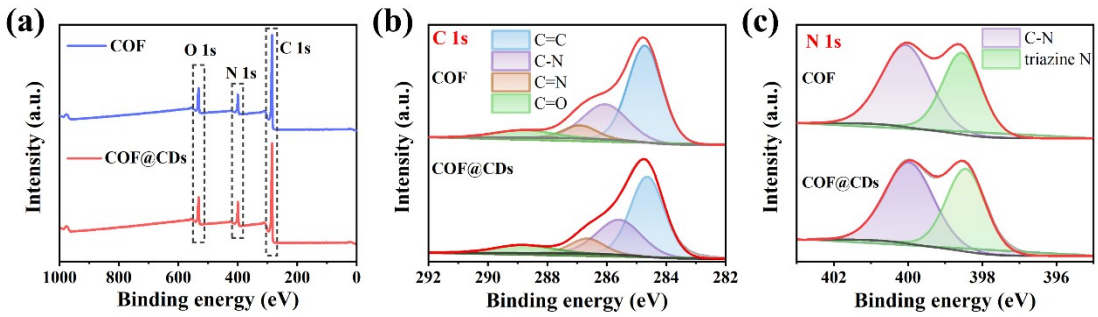

Fig. S1. (a) XPS survey spectra of COF and COF@CDs. High-resolution XPS spectra of (b) C 1s and (c) N 1s of COF and COF@CDs.

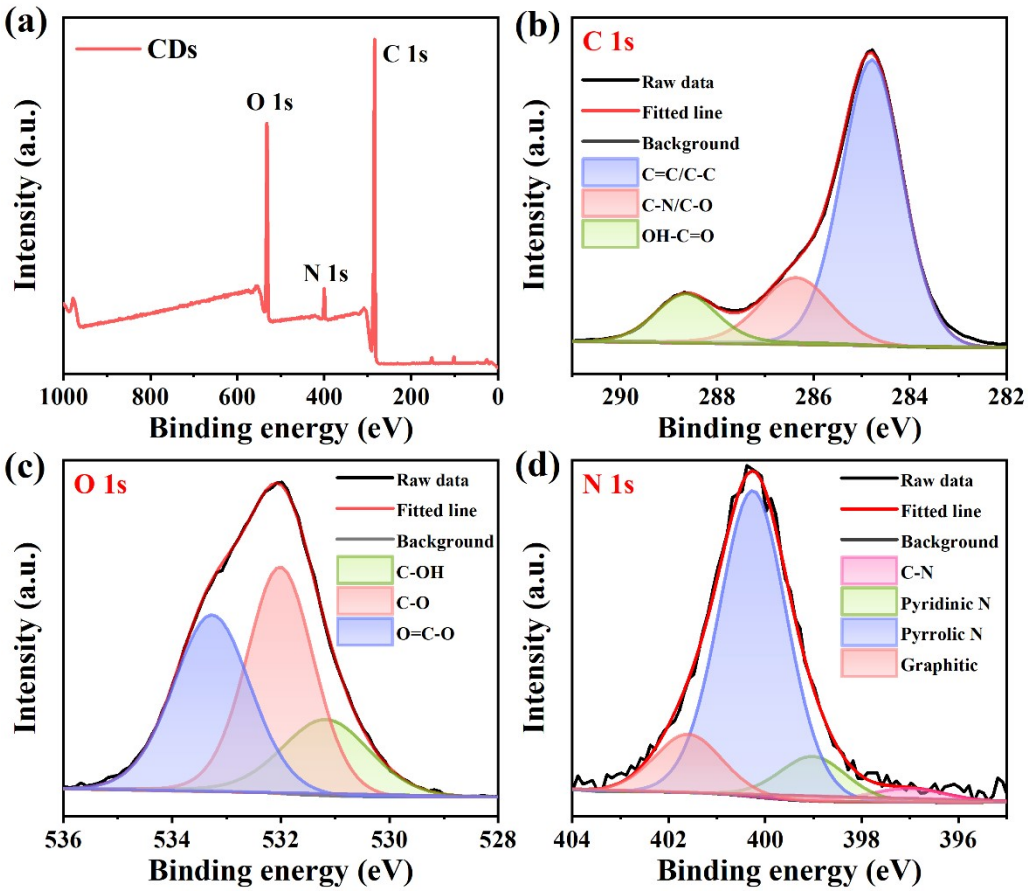

Fig. S2. (a) XPS survey spectra of CDs. High-resolution XPS spectra of (b) C 1s and (c) O 1s and (d)N 1s of CDs.

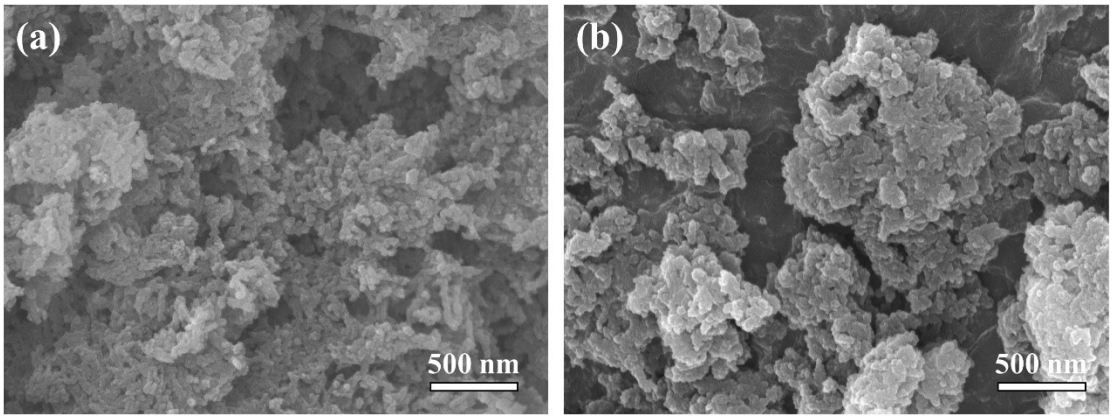

Fig. S3. SEM images of (a) COF and (b) COF@CDs.

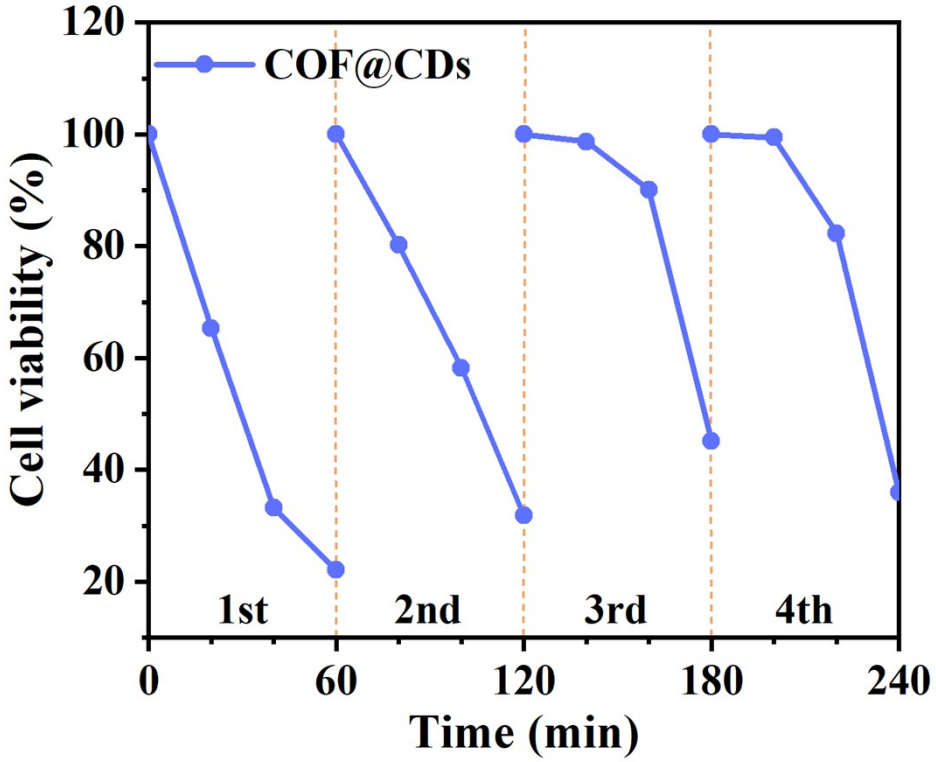

Fig. S4. Photocatalytic antibacterial stability of COF@CDs.

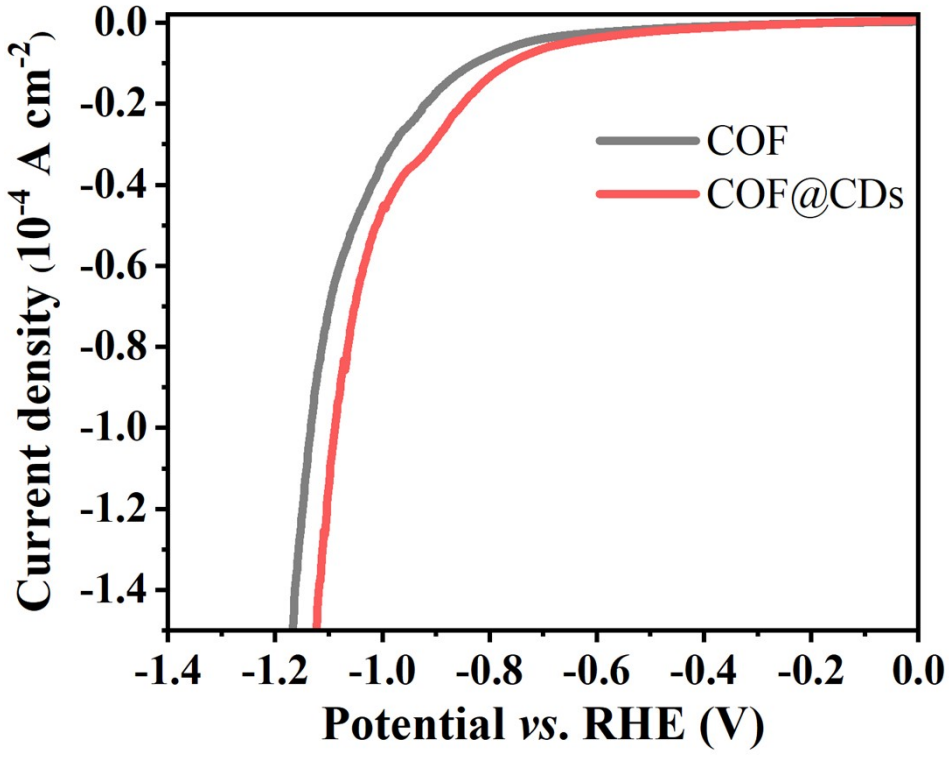

Fig. S5. Polarization curves of COF and COF@CDs.

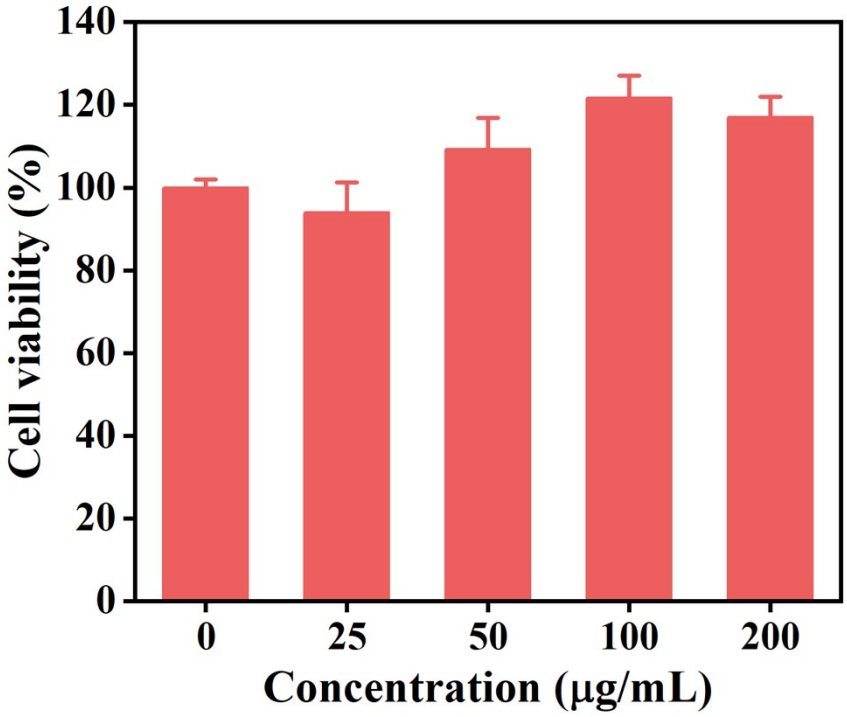

Fig. S6. Cytotoxicity of COF@CDs on human renal epithelial cells 293T.

Table S1. Exponential decay time constants of Time-correlated single-photon counting acquired from COF and COF@CDs.

Samples	t_1(ns)	A_1	t_2(ns)	A_2	t (ns)
COF	0.8968	0.0148	2.707	0.0193	2.34
COF@CDs	1.321	0.0213	3.773	0.0078	2.57

1. S. Zhu, Q. Meng, L. Wang, J. Zhang, Y. Song, H. Jin, K. Zhang, H. Sun, H. Wang and B. Yang, *Angew Chem. Int. Edit.*, 2013, **125**, 4045-4049.