Supporting Information

One-step construction of NH_2-UiO-66 based heterojunction photocatalyst for adsorption-photocatalytic synergistic removal of antibiotics

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Additional Experimental Details

1. Experiment

1.1 Materials

Zirconyl chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$), acetic acid, hydrochloric acid, N, N dimethylformamide (DMF), 2-aminotheraphthalic acid (NH_2-BDC), $Bi(NO_3)_3 \cdot 5H_2O$ and KCl were obtained from Aladdin Co.

1.2 Synthesis of sample

The canonical NH_2-UiO-66 was synthesized using the solvothermal method. NH_2BDC (1.5 mmol) and $ZrOCl_2 \cdot 8H_2O$ (1.5 mmol) were dissolved in 43 mL of DMF, followed by the addition of acetic acid (7 mL) and hydrochloric acid (286 μL). The above mixture was transferred into 100 mL Teflon liner and reacted at 140°C for 16 hours. The synthesized composite materials were washed with DMF and methanol three times each, respectively. Finally, NH_2-UiO-66 power was obtained by vacuum drying at 80 °C.

The synthesis of NH_2-UiO-66/BiOCl composites (designated as UB-x), $Bi(NO_3)_3 \cdot 5H_2O$ and NH_2-UiO-66 (0.557 g) were added to an agate mortar and ground uniformly. KCl and deionized water (1 mL) were then added, and the mixture was ground for 15 min. The $Bi(NO_3)_3 \cdot 5H_2O$ and KCl are equal concentrations. The slurry products were washed three times with distilled water and absolute ethanol, respectively. Finally, the synthesized power was obtained by drying at 60 °C. The synthesized composite materials were marked as UB-x, where the mass ratios of NH_2-UiO-66 and BiOCl were represented as x (10%, 30%, 50% and 70%.).

1.3 Characterization

The X-ray diffraction (XRD) patterns are obtained on a Bruker D8 Advance X ray diffractometer with Cu Kα radiation source. Infrared spectra (FI-IR) are obtained using Fourier infrared spectrometer (Nicolet, iS 10). The morphological of NH_2-UiO-66, UB-50% were observed using transmission electron microscopy (TEM) with a JEM-ARM300F instrument from Japan. The microstructure of samples is characterized by field emission scanning electron microscope (HITACHI, SU8100) equipped with X-ray energy dispersive spectroscopy (EDS) for elemental mapping. The chemical state and molecular structure was carried by X-ray photoelectron spectrometer (XPS) with Al Kα X-ray source (Kratos, AXIS SUPRA). Optical absorbing property was acquired by ultraviolet and visible spectrophotometer (UV-Vis, Agilent, Cary 5000). Fluorescence spectra and Photoluminescence were characterized by fluorescence spectrophotometer (Edinburgh, FS5). Brunauer-Emmett-Teller (BET) of the sample were examined using N_2 adsorption and desorption to determine the surface area and pore structure of the photocatalysts (Tristar II 3020, USA). Photoelectrochemical data including transient photocurrents, electrochemical impedance (EIS), and Mott-Schottky experiments were tested using the electrochemical workstation (CorrTest, CS350).

1.4 Evaluation of photocatalytic activities

UB-50% was employed as the photocatalyst for degradation of CIP under full-spectrum irradiation. For this, 25 mg catalyst was added in 50 mL of CIP solution (20

mg/L), following by magnetically stirred in dark for 60 min to achieve the adsorption-desorption equilibrium. Afterward, a 300 W Xenon arc lamp ((CEL-S500, Beijing Zhongjiao Jinyuan Technology Co. Ltd) was used as light source to irradiate the reaction system. At the interval of 10 min, 2 mL of the suspension was collected and centrifuged to separate the catalyst. The absorbance of the solution was recorded on a UV-vis spectrophotometer at a wavelength of 273 nm.

To evaluate the recyclability and stability of as-prepared catalyst. After each cycle, the catalyst was collected by centrifugation and washed with ethanol several times, following by dried and used for the next cycle.

1.5 Degradation of different pollutants

In addition, in order to verify the wide applicability of UB-50% composites, CIP, tetracycline (TC) and Sulfamethoxazole (SMX) were selected as the target contaminants. The concentration of the target pollutants was 20 mg/L and the amount of catalyst was 25 mg. The reaction was stirred under dark treatment for 60 min and under the 300 W xenon lamp for 60 min.

1.6 Photoelectrochemical measurements

Photoelectrochemical measurements were conducted in a three-electrode cell, which consisted of a photoelectrode, an Ag/AgCl electrode, and a platinum sheet (10*10*0.1 mm) as working electrode, reference electrode, and counter electrode, respectively. The 0.5 M Na_2SO_4 solution was used as the electrolyte and a 300 W Xe lamp was served as a light source. A typical procedure to prepare the working electrodes was just as follows: 10 mg as-prepared sample was grounded with 0.2 mL ethanol and

30 μL 5% Nafion (Dupont) to make a slurry. Then, the slurry was coated on an ITO glass electrode (10*15 mm) with an active area of 1 cm^2. The electrochemical impedance spectroscopy (EIS) measurements were conducted at a frequency range of 100 kHz to 0.05 Hz. The transient photocurrent densities were tested at 0.5 V versus Ag/AgCl electrode under full-spectrum light irradiation with 300 W Xe lamp. The Motty- Schottky curves were tested at -0.8 ~ 1.2 V versus Ag/AgCl electrode with the frequencies of 750 and 1000 Hz.

1.7 Adsorption kinetic models

The adsorption amount (mg/g) of CIP on the samples at adsorption equilibrium (q_e) and different adsorption time (q_t), respectively, which were calculated by the following equations:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

where C_0 (mg/L) is the initial concentration of CIP, V (L) is the initial volume, m (g) is the mass of the adsorbent. C_e and C_t (mg/L) represent the equilibrium concentration of CIP and the residual concentration of CIP after adsorption for different time, respectively.

In order to obtain the adsorption kinetics, the experimental data of CIP adsorption on NH_2-UiO-66, BiOCl, and UB-x nanocomposites were fitted by pseudo-first order and pseudo-second order models, respectively.

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \quad \text{Pseudo-first order} \quad (3)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$$ Pseudo-second order (4)

where k_1 (min^{-1}) and k_2 (g/mg/min) are the adsorption rate constant of pseudo-first order model and pseudo-second order, respectively.

1.8 Adsorption isotherm models

The Langmuir and Freundlich models were used to simulate the adsorption isotherms of CIP onto UB-50% nanocomposites with nonlinear fitting.

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e}$$ Langmuir (5)

$$q_e = K_F C_e^n$$ Freundlich (6)

where C_e is the aqueous CIP concentration (mg/L) when equilibrium; q_e is the equilibrium CIP capacity (mg/g), which can be calculated from S1; q_m is the maximum adsorption capacity of UB-x nanocomposites (mg/g); K_L (L/mg) and K_F [(mg/g)/(mg/L)^n] stand for the adsorption coefficients of the Langmuir and Freundlich parameters; n is the exponential coefficient.

1.9 Effect of co-existing ions on CIP degradation

The degradation of tetracycline in the presence of 0.1 mM coexisting ions including $CaCl_2$, $MgCl_2$, KCl, Na_2SO_4 and NaCl were investigated for the effects of Ca^{2+}, Mg^{2+} and K^+, Ca^{2+}, SO_4^{2-} and Cl^-, respectively. The concentration of CIP was 20 mg/L and the amount of catalyst was 25 mg. The reaction was stirred for 60 min in the dark and then irradiated under the 300 W xenon lamp for 60 min.

1.10 Active species elimination experiments

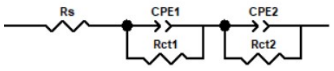
In order to investigate the main reactive species for the photocatalytic degradation

of CIP, radical trapping experiments were performed. In this study, benzoquinone (BQ), tert-Butanol (t-BuOH) and methanol (MeOH), were used as scavengers for superoxide radicals ($\bullet O_2^-$) hydroxyl radicals (•OH), and vacancies (h^+), respectively. The concentration of CIP was 20 mg/L and the amount of catalyst was 25 mg. The reaction was stirred for 60 min in the dark and then irradiated under the 300 W xenon lamp for 60 min.

Table S1 The adsorption performance of different kinds of MOFs

MOFs	Preparation T (°C)	Preparation Time (h)	S_{BET} (m^2/g)	Adsorbent quality (mg)	Adsorption time (min)	Pollutants and their concentrations	Equilibrium adsorption capacity (mg g^{-1})	Evaluate
ZIF-8 [1]	-	24	1555.07	75	30	2,4-DCP-100 mg·L^{-1}	89.482	Large specific surface area Single adsorption performance
UiO-66 [2]	120	24	1184.6	25	150	DMP-100 μg/L	37.80	Large specific surface area Single adsorption performance
MIL-101(Fe) [3]	110	24	194.0	5	180	As(V)-10 mg·L^{-1}	59.64	Low specific surface area Single adsorption performance
Ce-MOF [4]	150	12	41.54	25	120	Minocycline-50 mg·L^{-1}	344.8	Complex preparation process Low specific surface area Large adsorption capacity Single adsorption performance
ZIF-67 [5]	-	24	1918.9	30	720	UDMH-50 mg·L^{-1}	1.03	Simple preparation Low adsorption capacity Single adsorption performance
NH_2-UiO-66 (This work)	140	16	896.96	25	30	CIP- 20 mg·L^{-1}	30.67	Short adsorption equilibrium time synergistic integration of adsorption and photocatalytic

Table S2 Fitting results of the Nyquist plots for NH_2-UiO-66, BiOCl and UB-50%

Photocatalyst	Rs (Ω)	Rct1 (Ω)	Rct2 (Ω)	Equivalent Circuits
NH_2-UiO-66	20.35	$1.38x10^6$	27571	
BiOCl	18.51	98.12	15593	
UB-50%	16.62	106.8	12890	

Supplementary figures

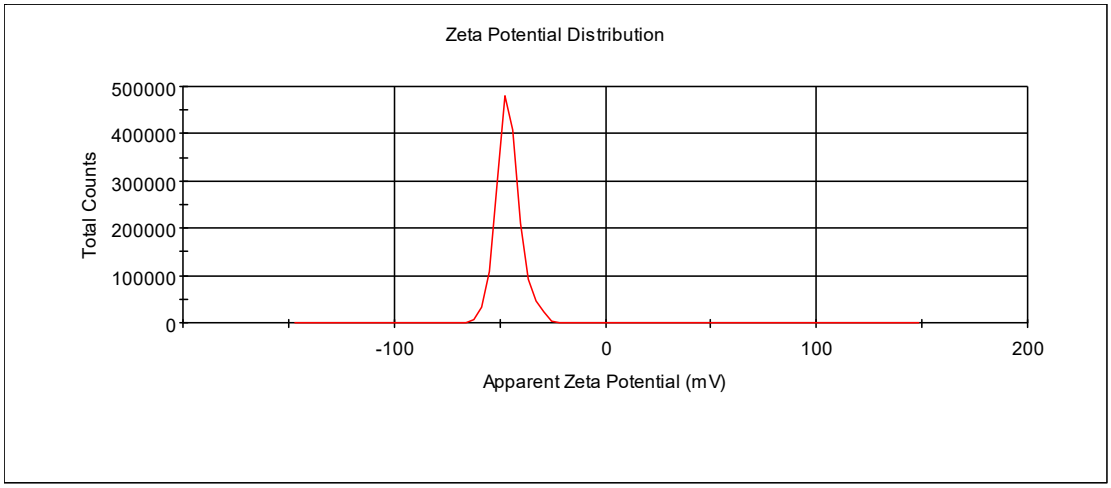


Fig.S1. The Zeta potential of UB-50% under pH=7 solution.

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