Supplementary Materials: Constructing String-Cage Structure of α-MnO_2@CoS_2 Photoelectrocatalyst for Efficient Detoxification Sulfonamides Wastewater

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Experimental

1. Materials

2-methylimidazole (2-MIM), Polyvinylpyrrolidone (PVP), Sulfamethoxazole ($C_{10}H_{11}N_3O_4S$) and anhydrous ethanol (C_2H_6O) nitrate were offered by Aladdin Industrial Corporation. Cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$), potassium permanganate ($KMnO_4$), oxalate ($C_2H_2O_4$), ammonium fluoride (NH_4F) and methanol (CH_4O) were purchased from Tianjin Kemi European Chemical Reagent Co., Ltd. (Tianjin, China). All the reagents in the experiments were analytically pure and did not require pretreatment. Deionized water was used throughout.

2. Fabrication of Ti/α-MnO_2

The α-MnO_2 nanowire (NWs) array was prepared by a simple hydrothermal reaction on Ti substrate. Typically, 1.0 mmol $KMnO_4$, 1 mmol NH_4F, and 40 mL of deionized water are added to a beaker and stirred to form a uniform solution. The treated Ti substrate and uniform solution are transferred to a stainless-steel autoclave (Teflon liner) and heated at 150 °C for 24 h. After natural cooling to room temperature, rinsed with deionized water for several times, dried in a constant temperature oven (70 °C) for 10 h, the sample was obtained, labeled Ti/α-MnO_2.

3. Fabrication of Ti/α-MnO_2@ZIF-67

Configure solution A and solution B respectively. Solution A: Dissolve 1.5 mmol $Co(NO_3)_2{\cdot}6H_2O$ in 20 mL methanol and stir continuously until completely dissolved. Solution B: Dissolve 12 mmol 2-methylimidazole (2-MIM) and 4.5 mmol polyvinylpyrrolidone (PVP) in 20 mL methanol and stir continuously until completely dissolved. Then, the prepared Ti/α-MnO_2 NWs was immersed in solution A for 30 min, and then solution B was added to solution A and stirred for 10 min. After aging at room temperature (30 °C) for 1 h, the purple electrode sheet was obtained, washed with methanol several times, and dried in a constant temperature oven (60 °C) for 12 h.

4. Fabrication of Ti/α-MnO_2@CoS_2

Dip Ti/α-MnO_2@ZIF-67 into 45 mL of TAA (0.2 mM) ethanol solution. The sample Ti/α-MnO_2@CoS_2 was synthesized by hydrothermal reaction at 90 ℃ for 4 h. The same experimental procedure was used for the experiment, while TAA of 0.1 mM, 0.3 mM and 0.4 mM were added respectively. They were labeled Ti/α-MnO_2@CoS_2-0.1, Ti/α-MnO_2@CoS_2-0.3, and Ti/α-MnO_2@CoS_2-0.4, respectively

5. Structural Characterization

X-ray diffractometer (XRD) can clearly show the atom and the electron distribution between them. The XRD of the sample in this paper was implemented on the Shimazu XRD-6100X diffractometer (Shimadzu Corporation, Kyoto, Japan). Cu Kα radiation (λ = 0.15406 nm) was used as the X-ray source to study the phase, crystal type and crystal structure of the electrode material. The tube pressure and tube flow of the diffractometer were 30 kV and 20 mA respectively, using copper target and Ni filter and the scanning range of θ–2θ was 5–80°, the scanning frequency was about 8°/min, and the diffraction wavelength is 0.1540 nm.

In this study, field emission scanning electron microscopy (Hitachi SU1510 (Hitachi High-Technologies Corporation, Tokyo, Japan); Talos F200X (Thermo Fisher Scientific, Waltham, MA, USA)) and field emission Scanning electron microscope (FESEM; JSM-7800F (JEOL Ltd., Tokyo, Japan)) was used for EDS surface scan analysis of core-shell heterostructures. X-ray photoelectron spectroscopy (XPS) can identify and analyze the elemental composition, bonding state and chemical properties of the sample surface by measuring the binding energy of photoelectrons. In this paper, VG ESCALAB 250 (Thermo Fisher Scientific, East Grinstead, UK) spectrometer was used, and Al Kα monochromatic radiation was used as the X-ray source. The measured sample state was powder, and XPS Peak software (Avantage Version 6.7.0) was used for analysis. Note that all XPS spectra were calibrated using a C1s spectrum with the highest binding energy at 284.6 eV, and the instrument calibration method for XPS was Au, Ag, Cu standard samples, specifically by surface chemical analysis X-ray photoelectron Spectrometer energy calibration (GB/T 22571-2008).

6. Degradation Performance Test

The simulated wastewater (250 mL) used 30 mg·L^{-1} SMX aqueous solution with Na_2SO_4 as a supporting electrolyte (0.1 mol·L^{-1} concentration). The degradation experiment of simulated solution was carried out in quartz reactor to evaluate the PEC performance of sample material electrode. 15 W ultraviolet lamp (for simulating ultraviolet light) and 175 W xenon lamp (for simulating daylight) were used as light sources during the PEC degradation process. The PEC reaction was carried out in a quartz internal reactor with a double cold trap. The prepared electrode was connected to a power source and decomposed simulated wastewater in PEC synergy. The light source was built into the quartz reactor, the condensation device was used to reduce the influence of the heat generated by the light on the degradation of PEC, and the magnetic stirrer kept the simulated wastewater in the reactor in a uniform state. Before the experiment began, a dark reaction (30 min) was performed to achieve an adsorption/desorption balance between the electrode system and the simulated wastewater. Under constant current density (15 mA·cm^{-2}), the PEC oxidation experiment was carried out using a DC voltage regulated power supply, and samples were taken from the reactor at fixed intervals for testing.

7. Photoelectric Characterization

Simulated wastewater was quantitatively analyzed using high performance liquid chromatography (LC-5990 HPLC (Hitachi, Ltd., Tokyo, Japan)) with an UV-VIS detector and reversed phase column (Ai-chrom-YWM-C18 (AiChrom Technologies, Shanghai, China) (4.6 mm 250 mm, 5 μm)). The operating conditions for the analysis of simulated wastewater SMX were as follows: single sample size of 20 μL = 270 nm, mobile phase of acetonitrile: ultra-pure water containing 0.1% acetic acid, is degree condition of 45%–65%, flow rate of 1 mL·min^{-1}. The collected samples are filtered with a 0.22 μm aqueous polyether sulfone filter and stored at 4 °C for future analysis. All experiments and measurements were repeated, and arithmetic mean values were taken for data analysis. The degradation performance of PEC was evaluated by comparing the peak area before and after degradation (C/C_0 was represented by S/S_0).

8. Computational Method

All calculations were implemented using the Vienna Ab-initio Simulation Package (VASP) code based on Density Functional Theory (DFT) [57]. The generalized gradient approximation (GGA) proposed by Perdew-Burke-Ernzerhof (PBE) is selected for the exchange-correlation potential [58]. The cut-off energy for plane wave is set to 450 eV. The energy criterion is set to 10^{-4} eV in iterative solution of the Kohn-Sham equation. For all models the vacuum space along the z-direction was set to be 15 Å, which was enough to avoid interaction between the two neighboring images. The Brillouin zone integration is performed using a 2 × 2 × 1 k-mesh. All the structures are relaxed until the residual forces on the atoms have declined to less than 0.02 eV/Å. The Gibbs free energy diagrams were estimated by the following equation:

$$\Delta G_i = \Delta E + \Delta ZPE - T\Delta S$$

where ΔE is the energy difference from reactants to products, obtained from DFT calculations; ΔZPE and ΔS are the contributions to the free energy from the zero-point vibration energy and entropy, respectively. T is 298.15 K

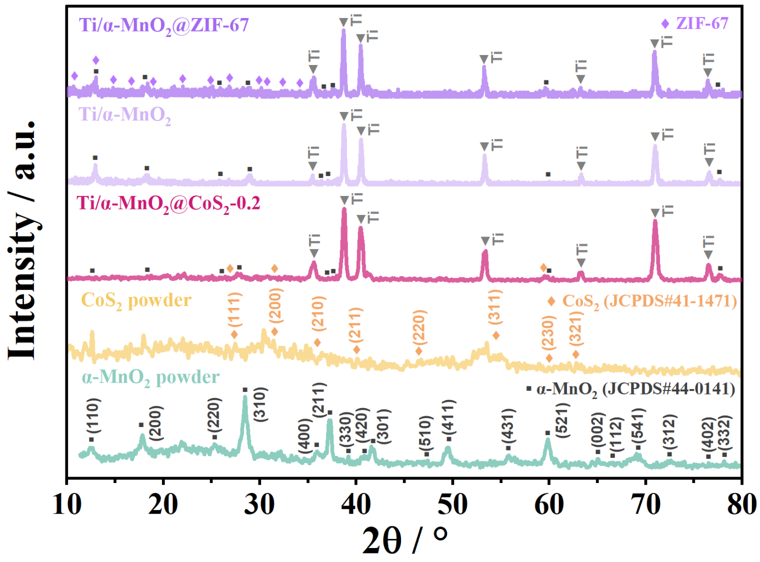

Figure S1. XRD patterns of pure α-MnO_2 powder, CoS_2 powder, Ti/α-MnO_2, Ti/α-MnO_2@ZIF-67 and Ti/α-MnO_2@ CoS_2-0.2, respectively.

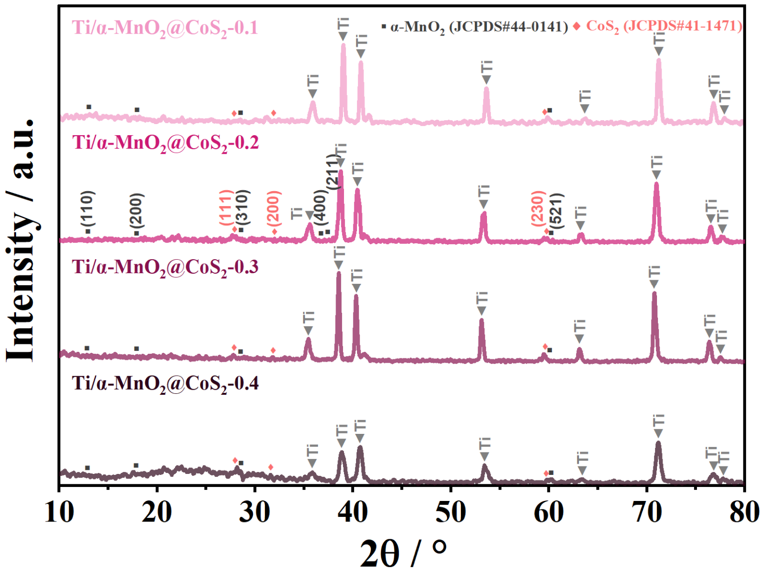

Figure S2. XRD patterns of CoS_2 nanocages wrapped α-MnO_2 nanoflower needles with different CoS_2 concentration.

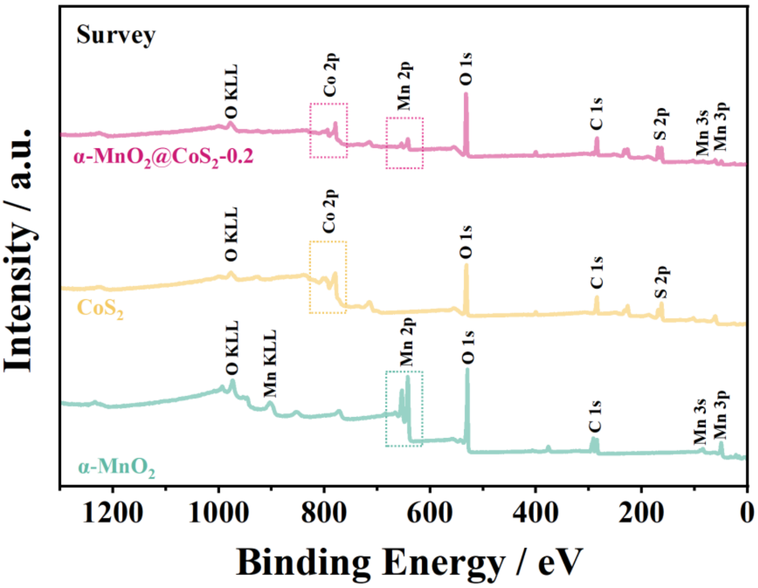

Figure S3. XPS survey spectra of α-MnO_2, CoS_2 and α-MnO_2@CoS_2-0.2.

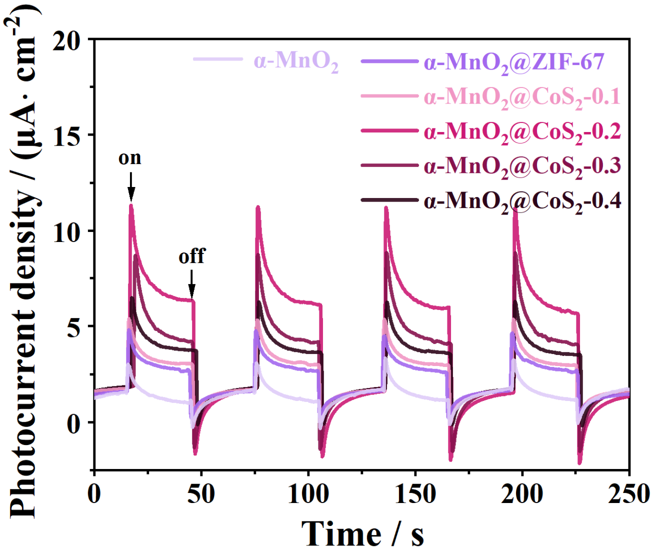

Figure S4. Transient photocurrent responses of α-MnO_2, α-MnO_2@ZIF-67 and various α-MnO_2@CoS_2-x electrodes.

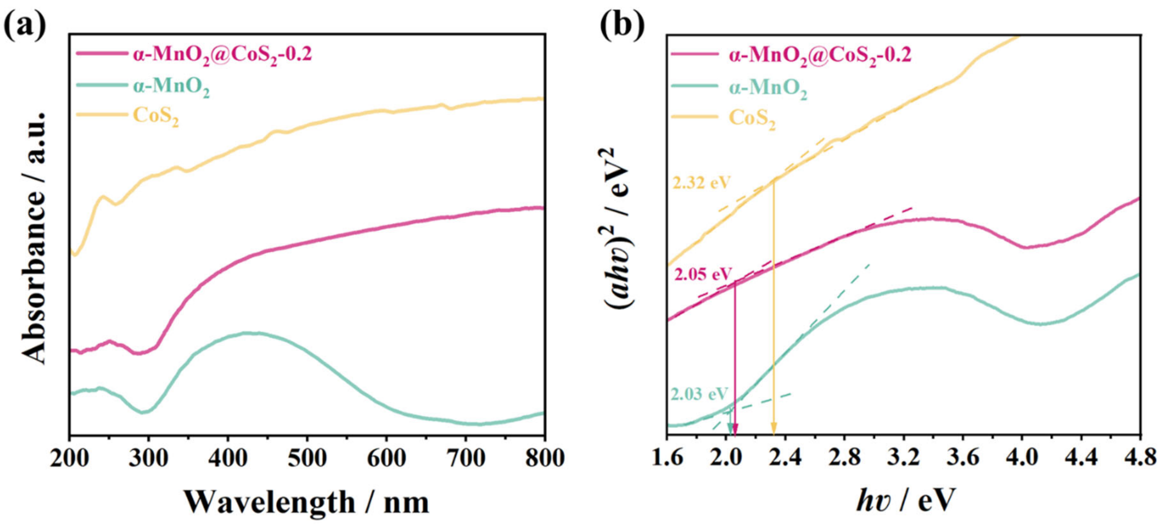

Figure S5. (**a**) UV-Vis diffuse reflectance spectra of α-MnO_2, CoS_2 and α-MnO_2@CoS_2-0.2; (**b**) The bandgap calculation of α-MnO_2, CoS_2 and α-MnO_2@CoS_2 by the Kubelka-Munk theorem.

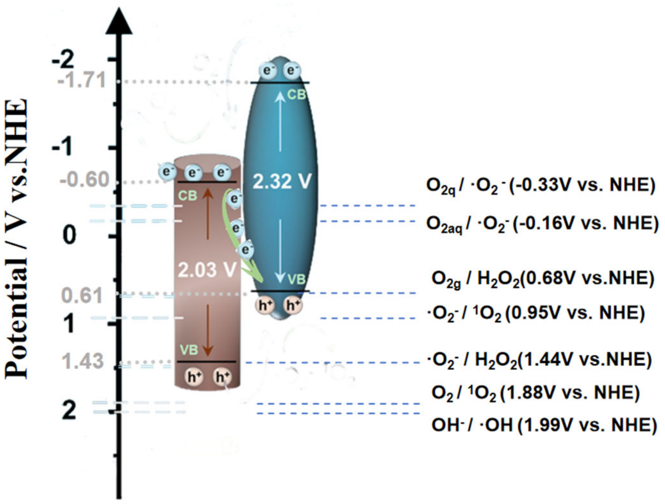

Figure S6. Proposed band structures of α-MnO_2@CoS_2.

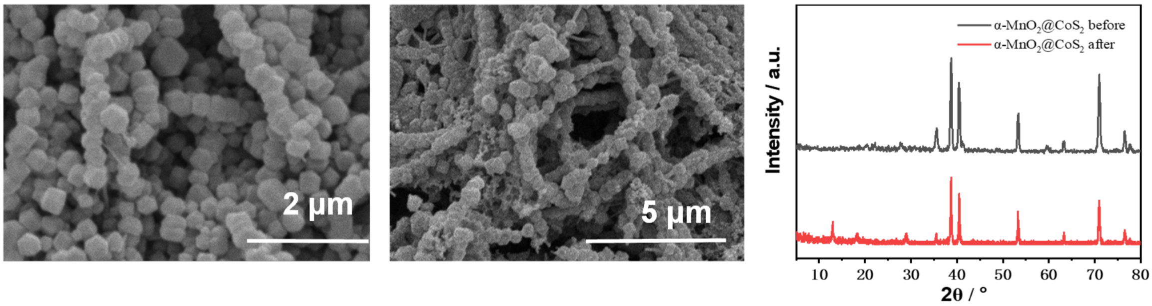

Figure S7. SEM and XRD analysis of α-MnO_2@CoS_2-0.2 after durability test.

Verification of Hydrogen Peroxide Generation

The content of H_2O_2 could be measured by the reaction system's solution and titration according to the standard cerium sulfate solution $Ce(SO_4)_2$ solution. Yellow Ce^{4+} could be reduced by H_2O_2 to colorless Ce^{3+}, and the amount of H_2O_2 could be determined by measuring the number of moles of Ce^{4+} consumed. Subsequently, the concentration of Ce^{4+} was determined by UV-vis spectroscopy, and the Ce^{4+} solution showed apparent adsorption strength at the wavelength of 316 nm, thus determining the presence of hydrogen peroxide, as shown in Figure S8.

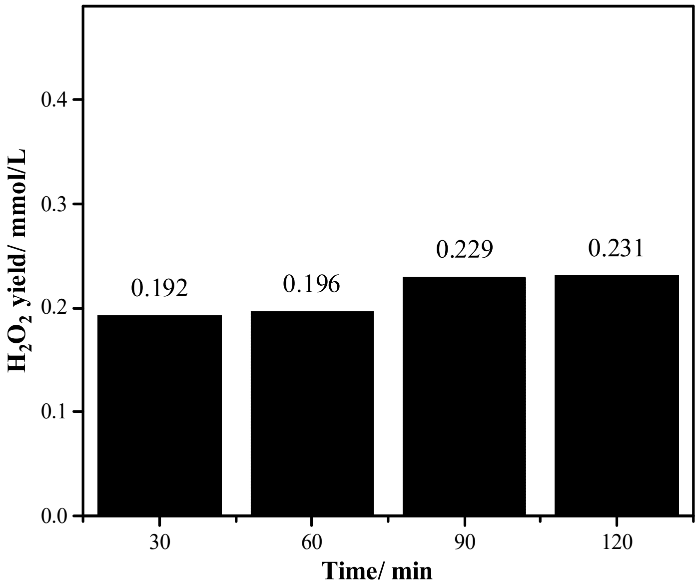

Figure S8. Verification of hydrogen peroxide generation.

Table S1. Experimental conditions of Ti/α-MnO_2@CoS_2 hierarchical heterogeneous core-shell structures.

Electrode	**TAA (mM)**
α-MnO_2@CoS_2-0.1	0.1
α-MnO_2@CoS_2-0.2	0.2
α-MnO_2@CoS_2-0.3	0.3
α-MnO_2@CoS_2-0.4	0.4

Table S2. Different catalyst applied in water purification and main result.

Material Features	**Catalytic Application**	**Remarks and Parameter Monitored**	**Reference**
α-MnO_2 nanowire composite CoS_2 nanocages	Photoelectrocatalytic for the degradation of sulfamethoxazole (SMX)	The concentration of sulfamethoxazole (SMX) was 30 mg/L. Using 250 mL aqueous solution with 0.1 mol/L Na_2SO_4 as the supporting electrolyte. The photoelectrocatalytic (PEC) degradation process was conducted in a quartz reactor using a 175 W xenon lamp (simulating sunlight). The degradation rate of SMX was 98.95%.	This work
Co_3O_4 nano-polyhedron wrapped α-MnO_2 nanowire	Photoelectrocatalytic for the degradation of reactive brilliant blue KN-R (anthraquinone dye)	The concentration of reactive brilliant blue KN-R was 60 mg/L. Using 250 mL aqueous solution with 0.1 mol/L Na_2SO_4 as electrolytes. The light illumination for photoelectrocatalytic procedure was conducted using 175-W xenon lamp. Organic degradation of reactive brilliant blue KN-R was 88.44%.	[29]
Ag decorated α-MnO_2 nanorods	Photocatalytic for the degradation of methylene blue (MB)	Under visible light irradiation, compared with pure α-MnO_2, Ag-doped α-MnO_2 achieved a higher degradation efficiency of up to 94% for methylene blue (MB).	[59]
Bi_2MoO_6 nanospheres encapsulated on the α-MnO_2 nanowires (Bi_2MoO_6@α-MnO_2)	Photoelectrocatalytic for the degradation of reactive brilliant KN-R (anthraquinone dye)	The concentration of reactive brilliant blue KN-R was 60 mg/L. Using 250 mL aqueous solution with 0.1 mol/L Na_2SO_4 as electrolytes. The light illumination for photoelectrocatalytic procedure was conducted using 175-W xenon lamp. Organic degradation of reactive brilliant blue KN-R was 88.64%.	[60]
α-MnO_2/BiOI	Photoelectrocatalytic for the degradation of tetracycline (TC)	Under visible light irradiation ($\lambda > 420$ nm), compared with pure α-MnO_2 and BiOI, the PEC degradation efficiency of tetracycline (TC) by the optimized α-MnO_2/BiOI composite is significantly enhanced, reaching up to 95.8% within two hours.	[34]
coconut shell fiber biochar decorated α-MnO_2 (α-MnO_2/CSB)	Photocatalytic degradation of bisphenol A (BPA)	The concentration of bisphenol A (BPA) was 0.01 mM. Using a 200 W LED lamp as the visible-light source, complete degradation of BPA was achieved within 45 min at a dosage of 0.1 g/L.	[61]
TiO_2 anchored α-MnO_2 nanorods (α-MnO_2/TiO_2)	Photocatalytic degradation of CBB R-250 dye	Under sunlight irradiation, compared with α-MnO_2 nanorods and TiO_2 nanoparticles alone, the hybrid α-MnO_2/TiO_2 photocatalyst significantly enhances the degradation efficiency of CBB R-250 dye (13 mg/L), achieving nearly 98.35% degradation within 30 min.	[62]
S-Scheme Co_3Se_4/$BiVO_4$ heterojunction	Photoelectrocatalytic for the degradation of sulfamethoxazole (SMX)	The concentration of sulfamethoxazole (SMX) was 10 mg/L. Using 100 mL aqueous solution with 0.1 mol/L Na_2SO_4 as the supporting electrolyte. The photoelectrocatalytic (PEC) degradation process was conducted in a quartz reactor using a 100 W xenon lamp (simulating sunlight). At optimum conditions, the SMX degradation efficiency reached 75% with a rate constant of 0.0115 min^{-1}.	[63]
g-C_3N_4/BiOI/EG p-n heterojunction	Photoelectrocatalytic for the degradation of sulfamethoxazole (SMX)	The concentration of sulfamethoxazole (SMX) was 30 mg/L. Using 100 mL aqueous solution with 0.1 mol/L Na_2SO_4 as the supporting electrolyte. The photoelectrocatalytic (PEC) degradation process was conducted in a quartz reactor using a 300-W compact xenon lamp (simulating sunlight). The degradation rate of SMX was 88%.	[64]
Ni-Co bimetallic decorated dodecahedral ZIF (BMZIF)	Photoelectrocatalytic for the degradation of sulfamethoxazole (SMX)	Dissolving SMX (10 mg L^{-1}) in 70mL 0.1 M Na_2SO_4 with the addition of PMS. The photoelectrocatalytic (PEC) degradation process was irradiated with a 100 mW cm^{-2} lamp (Xenon). The degradation rate of SMX was 99%.	[18]