Study on the Photo-Assisted Activation of PMS by $CuMo_{1-x}W_xO_4$ for Degradation of Tetracycline

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1. Experimental Reagents

Sodium tungstate dihydrate ($Na_2WO_4 \cdot 2H_2O$), Sodium molybdate dihydrate ($Na_2MoO_4 \cdot 2H_2O$), and tetracycline ($C_{22}H_{24}N_2O_8 \cdot xH_2O$) were purchased from Aladdin Chemical Reagent Co., Ltd.; copper nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$), disodium ethylenediaminetetraacetic acid (EDTA-2Na), anhydrous ethanol (C_2H_5OH), hydrochloric acid (HCl), PMS ($K_4H_3S_4O_{18}$), and isopropanol were purchased from Sinopharm Chemical Reagent Co., Ltd.; p-benzoquinone and L-histidine (L-his) were purchased from Aladdin Biochemical Technology Co., Ltd.; sodium hydroxide (NaOH) was purchased from Tianjin Damao Chemical Reagent Factory. All reagents were of analytical grade and were used without further purification. All aqueous solutions used in the experiments were prepared with ultrapure water.

2. Characterization

The crystal phases of the prepared samples were determined using an X-ray diffractometer (XRD, Bruker D8 Advance) with Cu Kα radiation at 40 kV and 40 mA. The morphology, structure, and grain size of the samples were characterized using a scanning electron microscope (SEM, Zeiss Sigma 300), a transmission electron microscope (TEM, FEI-Technai G2 F20), and a high-angle annular dark field detector (HAADF). The chemical states, surface elemental composition, and molecular structure of the samples were analyzed using X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific Nexsa). The Brunauer-Emmett-Teller (BET) specific surface area of the catalysts was analyzed using a nitrogen adsorption apparatus (Micromeritics ASAP 2460). The presence of reactive species during the catalytic reaction was verified using an electron paramagnetic resonance spectrometer (Bruker ESR A300). The formation of $\cdot OH$ and $SO_4^{\cdot -}$ was detected using the spin trap 5,5-dimethyl-1-pyrroline-N-oxide (DMPO), and the formation of $^1O_2$ was detected using 4-oxo-2,2,6,6-tetramethylpiperidine-1-oxyl (TMPO). The ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) of the catalysts were analyzed using a UV/Vis/NIR diffuse reflectance spectrophotometer (Lambda 1050+, PerkinElmer, GER). The photoluminescence (PL) spectra of the samples were recorded using a fluorescence spectrometer (FLS 980, Edinburgh, UK).

3. Radical Scavenging Experiments

In the radical scavenging experiments, L-histidine (L-his), isopropanol (IPA), ethanol (EtOH), p-benzoquinone (BQ), and disodium ethylenediaminetetraacetic acid (EDTA-2Na) were used as scavengers for $^1O_2$, $\cdot OH$, $SO_4^{\cdot -}$, $\cdot O_2^-$, and h^+, respectively. The specific operations are as follows:

A 50 mL aliquot of a 30 ppm TC solution was measured and 2 mL of a 10 $mmol \cdot L^{-1}$ scavenger solution (such as L-his, IPA, EtOH, BQ, or EDTA-2Na) was added, stirring thoroughly to mix. Twenty milligrams of the catalyst was weighed and added to the mixed solution, which was stirred for 1 hour to achieve adsorption-desorption equilibrium. The equilibrated mixture was then transferred to a photoreactor, the light source was turned on, and 1.5 mL of a 2 mmol·L^{-1} PMS solution was added to initiate the reaction. The reaction time was set to 40 minutes. The sample solution was drawn using a syringe with a 0.45 μm PTFE filter head, filtered, and injected into a cuvette to measure the TC concentration.

4. Photoelectrochemical Performance Test

The electrochemical impedance, transient photocurrent response, and Mott-Schottky plots of the catalysts were tested using a CHI760E electrochemical workstation. The test conditions were as follows: a 0.5 M Na_2SO_4 solution was used as the electrolyte, a platinum wire electrode as the counter electrode, and Ag/AgCl as the reference electrode. A working electrode was prepared by adding 10 mg of the catalyst to a mixture of Nafion and ethanol (volume ratio 1:9), ultrasonically dispersing it evenly, and drop-casting it onto FTO conductive glass. The transient photocurrent response was tested using the Amperometric i-t curve mode, with a bias voltage of 0.3 V (vs Ag/AgCl) and a total test duration of 200 seconds, with light on/off intervals of 20 seconds. Electrochemical impedance spectroscopy (EIS) was measured using the A.C. Impedance Parameters mode in a three-electrode system, with a frequency range of 10^{-1}–10^{6} Hz and a test voltage amplitude of 0.3 V. The Mott-Schottky plots were measured in the dark using the Impedance-Potential Parameters mode in a three-electrode system, with a 0.5 M Na_2SO_4 electrolyte solution and a frequency of 1 kHz.

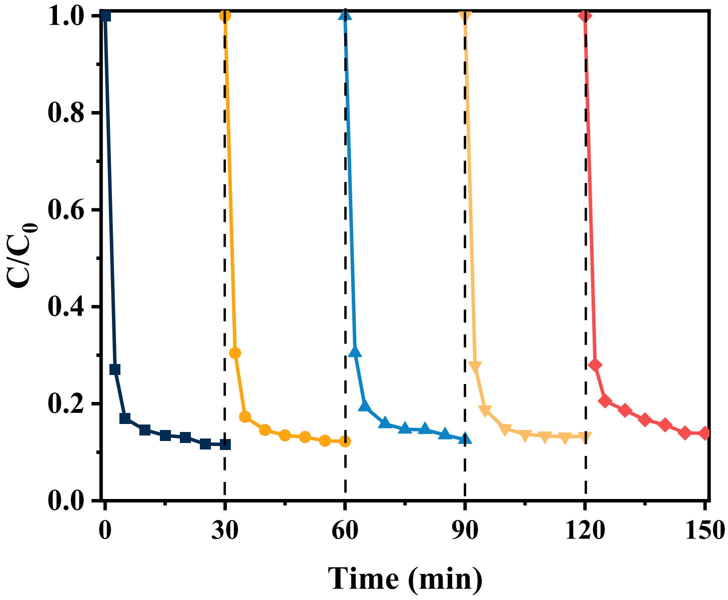

Fig. S1. Cyclic test for TC degradation by CMWO-3.

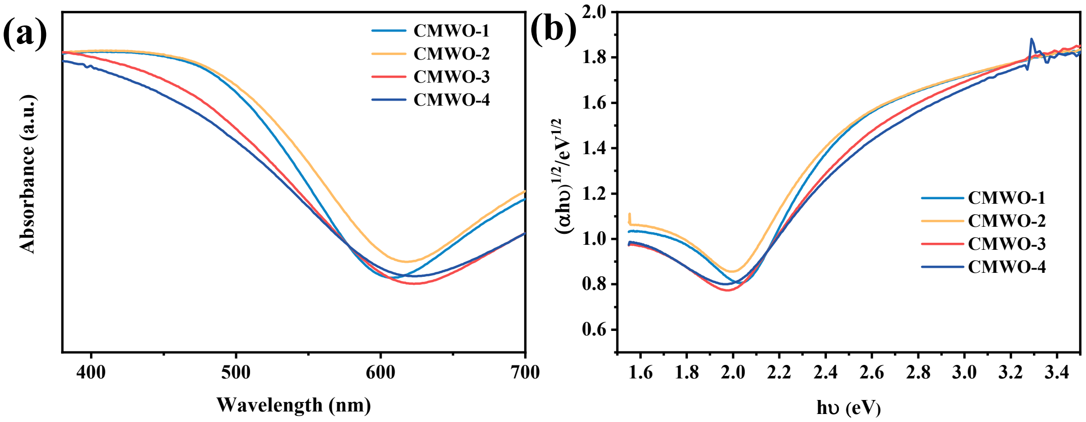

Fig. S2. (a) DRS spectra of CMWO-1, CMWO-2, CMWO-3 and CMWO-4 catalysts; (b) Tauc plots of CMWO-1, CMWO-2, CMWO-3 and CMWO-4 catalysts

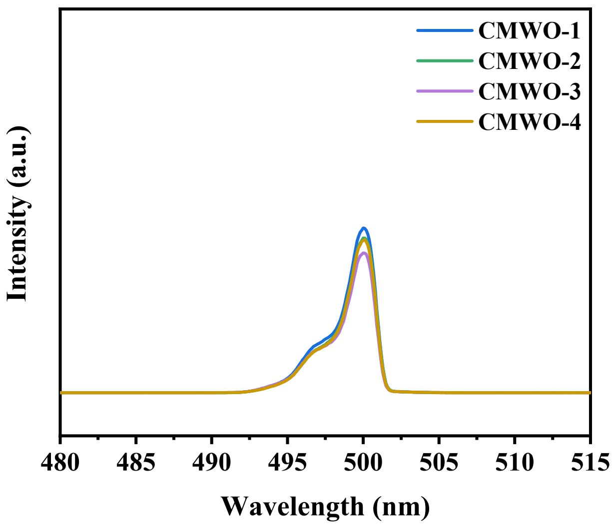

Fig. S3. PL spectra of CMWO-1, CMWO-2, CMWO-3 and CMWO-4 catalysts

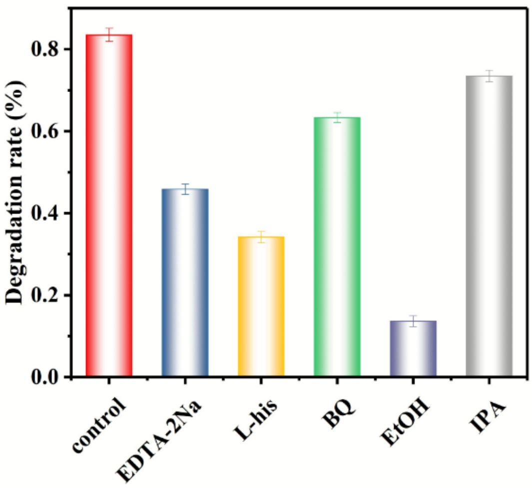

Fig. S4. Free radicals capture experiment

Table S1. BET surface area, pore distribution and average pore size of CMO, CWO and CMWO-3

Sample	S_{BET} (m^2/g)	Average pore size (nm)	Pore volume (m^2/g)
CMO	4.10	10.74	0.01
CWO	5.71	21.11	0.03
CMWO-3	5.91	14.95	0.02