Electronic Supplementary Material

Cuprous oxide/copper oxide interpenetrated into ordered mesoporous cellulose-based carbon aerogels for efficient photocatalytic degradation of methylene blue

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1. Experiments

1.1. Materials

Cellulose nanofibers (CNFs), carboxymethylcellulose sodium (CMC, >98.0%), sodium hydroxide (NaOH, >95.0%), hexadecyl trimethyl ammonium bromide (CTAB, >98.0%), cupric nitrate ($Cu(NO_3)_2 \cdot 3H_2O$, ≥99.5%), ethanol (C_2H_5OH, ≥95.0%) are purchased from Aladdin Industrial Corporation. Methylene blue (>90.0%), isopropanol (>99.9%), tryptophan (>98.0%), benzoquinone (>99.5%), potassium iodide (≥99.0%) are provided by Macklin Industrial Corporation (Shanghai, China). Potassium hydroxide (KOH, >95.0%), liquid nitrogen and other reagents are obtained from Dalian Chemical Reagent Factory, China. All chemicals were analysis grade and used directly without further purification.

1.2. Characterization

The morphologies of all samples were explored by scanning electron microscopy (SEM, Hitachis-4800). Fourier transform infrared (FT-IR) spectra were taken on a Bruker Tensor 27 spectrophotometer. The powder X-ray diffraction (XRD) patterns were collected in the θ-2θ mode using a Bruker D8 Focus diffractometer (CuKα radiation, λ = 0.15418 nm), operated at 40 kV and 40 mA with a scattering angle (2θ) of 5-80^{o}. N_2 adsorption-desorption isotherm measurements were performed on a physisorption analyzer (Micromeritics, ASAP 2020) at 77 K for P/P0 of 0.01-0.99. The specific surface area (N_2 adsorption-desorption, 77 K) isotherms was obtained by the Brunauer-Emmett-Teller method (BET) using a Micromeritics ASAP 2020 apparatus. The X-ray photoelectron spectroscopy (XPS) analysis was performed with a Kratos Axis Ultra DLD spectrometer with a monochromatic Mg Kα X-ray source. The photocurrent-time was investigated in the irradiation of Xe lamp at a bias potential of 0.5 V vs. Ag/AgCl. The electrochemical impedance spectroscopy (EIS) was detected by an AC voltage amplitude of 10 mV at -0.3 V versus Ag/AgCl over the frequency range from 10 kHz to 0.01 Hz. The Mott-Schottky plot was studied in the electrolyte of Na_2SO_4 (0.5 M), and the frequency of the AC potential was set as 800, and 1000 Hz as well as the amplitude was 5 mV. Ultraviolet photoelectron spectroscopy (UPS) was measured by using a He I (21.22 eV) as monochromatic discharge light source and a VG Scienta R4000 analyzer. Inductively coupled plasma mass spectrometry (ICP-MS) was performed on Aglient 7800 equipment. Electron spin-resonance spectroscopy was used to study molecules and materials with unpaired electrons, and the 5,5-dimethyl-1-pyrroline N-oxide (DMPO) was chosen as a spin trap for the detection of hydroxyl radical (·OH) and superoxide ($\cdot O_2^-$), the 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) was applied to characterize electrons and holes, while the amino-2,2,6,6-tetramethylpiperidine (TEMPONE) was used to detect singlet oxygen.

1.3. Poisoning experiments

The effects of oxidation active species on the photocatalytic degradation of methylene blue with $Cu_2O/CuO@CA_{0.2}$ were examined by poisoning experiments. 5 mg of $Cu_2O/CuO@CA_{0.2}$ was added to 10 mL of methylene blue solution (100 ppm, pH = 8). Potassium iodide, benzoquinone, tryptophan (dosage of 2.5 mmol) and isopropanol (5 mmol) were added to the reaction system, respectively. The mixed system was first stirred at 500 rmp for 40 min under darkness to reach adsorption/desorption equilibrium. Then, the reaction was reacted for 60 min under the irradiation of a 300 W Xenon lamp. The reacted solution was filtered through a microporous filter (0.22 μm) and the concentrations were measured with a UV-vis spectrophotometer at a wavelength of 664 nm.

3. Results and discussion

Table S1 Photocatalytic degradation of methylene blue by copper oxide based photocatalysts.

Entry	Photocatalysts	Light source	Reaction conditions	Efficiency (%)	Ref.
1	$Cu_2O/CuO@CA$	Xenon lamp	Methylene blue 100 mg/L, Time 60 min	99.09	This work
2	$MgFe_2O_4/CuO/GO$	Sunlight	Methylene blue 10 mg/L, Time 27 min	98.8	[1]
3	CeO_2/CuO	Sunlight	Methylene blue 20 mg/L, Time 180 min	91	[2]
4	$CuO-Cu_2O$	Metal halide lamp	Methylene blue 5 mg/L, Time 180 min	80	[3]
5	$CuO-TiO_2$	Xenon lamp	Methylene blue 12 mg/L, Time 120 min	35	[4]
6	FGC[a)]	Visible light	Methylene blue 20 mg/L, Time 40 min	94.27	[5]
7	CS-CuO	Sunlight	Methylene blue 30 mg/L, Time 150 min	91.3	[6]

a) FGC: Fe_2O_3/graphene/CuO

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