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Supplementary Materials

Hollow Nanospheres Organized by Ultra-Small $CuFe_2O_4$/C Subunits with Efficient Photo-Fenton-Like Performance for Antibiotic Degradation and Cr(VI) Reduction

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Abstract: Hollow transition metal oxides have important applications in the degradation of organic pollutants by a photo-Fenton-like process. Herein, uniform, highly dispersible hollow $CuFe_2O_4$/C nanospheres (denoted as CFO/C-PNSs) were prepared by a one-pot approach. Scanning electron microscope (SEM) and transmission electron microscope (TEM) images verified that the CFO/C-PNS catalyst mainly presents hollow nanosphere morphology with a diameter of 250 ± 30 nm. Surprisingly, the photodegradation test results revealed that CFO/C-PNSs had an excellent photocatalytic performance in the elimination of various organic contaminants under visible light through the efficient Fenton catalytic process. Due to the unique hollow structure formed by the assembly of ultra-small CFO/C subunits, the catalyst exposes more reaction sites, improving its photocatalytic activity. More importantly, the resulting magnetically separable CFO/C-PNSs exhibited excellent stability. Finally, the possible photocatalytic reaction mechanism of the CFO/C-PNSs was proposed, which enables us to have a clearer understanding of the photo-Fenton mechanism. Through a series of characterization and analysis of degradation behavior of CFO/C-PNS samples over antibiotic degradation and Cr(VI) reduction, •OH radicals generated from H_2O_2 decomposition played an essential role in enhancing the reaction efficiency. The present work offered a convenient method to fabricate hollow transition metal oxides, which provided impetus for further development in environmental and energy applications. **Highlights:** Novel hollow $CuFe_2O_4$/C nanospheres were prepared by a facile and cost-effective method. $CuFe_2O_4$/C exhibited excellent photo-Fenton-like performance for antibiotic degradation. Outstanding photocatalytic performance was attributed to the specific hollow cavity-porous structure. A possible mechanism for H_2O_2 activation over hollow $CuFe_2O_4$/C nanospheres was detailed and discussed.

Keywords: hollow $CuFe_2O_4$/C nanospheres; photo-Fenton; photodegradation of various pollutants; photocatalytic reaction mechanism

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1.1 Chemicals and materials

All the reagents and chemicals Polyacrylic acid (PAA), Cupric chloride dihydrate (CuCl2•2H2O), Ferrous chloride tetrahydrate (FeCl2•4H2O,), isopropanol (IPA) and aqueous ammonia solution (NH3•H2O) were purchased from Macklin biochemical technology Co. Ltd., China. They are analytical (AR) purity and used without further purified.

1.2. Experimental

1.2.1. Preparation of Fe(OH)3/PAA-Cu (OH)2 nanocomposites

For the preparation of Fe(OH)3/PAA/Cu (OH)2 nanocomposites, PAA solution (1 mL, 0.2 g• mL-1) and NH3•H2O（1mL, 2 mol·L-1） were added into 100 mL of deionized water for 40 min by stirring in a 1000 mL beaker. Then, 400 mL of IPA was added drop wise (1 drop/s) into the above solution under magnetic stirring. The 1.5 mmol FeCl2•4H2O was then added into the above solution with constant stirring for 180 min. Finally, the 0.75 mmol CuCl2·2H2O was added into the mixture for 12 h continuously in order to obtain a well-dispersed mixture. The Fe(OH)3/PAA/Cu(OH)2 was centrifuged and washed several times with deionized water and ethanol, and then dried at 400℃ for 12 h. The obtained Fe(OH)3/PAA/Cu(OH)2 NSs were stored at room temperature for further experiments.

1.2.2. Preparation of CFO/C-PNSs.

The collected Fe(OH)3/PAA/Cu (OH)2 NSs was transferred into an alumina crucible and calcined, which was at 400 ℃ with a heating rate of 2 ℃ min-1 and then maintained at 400 ℃ for 2 h under N2 atmosphere, which was denoted as CFO/C-PNSs.

1.2.3. Preparation of CFO -PNSs.

The procedure to fabricate CFO-PNSs was almost the same with CFO/C-PNSs, except that Fe(OH)3/PAA/Cu (OH)2 NSs was calcined in air atmosphere.

1.2. Material Characterization

The crystal structures of as-prepared composites were measured using X-ray diffraction (XRD, Rigaku D/Max-RB X-ray diffractometer) in the range of 5o-90o. The morphologies of synthesized photocatalysts were determined by field emission scanning electron microscopy (FESEM, JEOL 7500F, Japan) and transmission electron microscope (TEM, JEM-2100F, JEOL, Japan). Ultraviolet/visible diffuse-reflectance spectra were recorded by using spectrophotometer (Lambda-750, PerkinElmer, USA) with BaSO4 as a reference. The chemical states of elements were studied using an X-ray photoelectron spectroscopy (XPS) measurements. The Brunauer-Emmett-Teller (BET) surface areas of the samples were carried out via a nitrogen adsorption apparatus (ASAP 2020, Micromeritics, USA) and Barrett-Joyner-Halenda (BJH) method was used to study pore diameter distribution with adsorption data.

1.3. Photocatalytic degradation experiment

All the photocatalytic degradation experiments were carried out at room temperature, and the photocatalytic activity of different samples was also tested by the photodegradation of antibiotics, using a glass vessel with a water-cooling jacket as reactor (the temperature is about 15 ℃). Briefly, a certain amount of samples was dispersed into 30 mL of OTC (40 ppm), NFX(20 ppm), TCH(20 ppm), RhB(20 ppm), MO(40 ppm), Cr6+(160 ppm) and aqueous solution. Before irradiation, the mixture solution was placed in darkness for 30 min to make the adsorption-desorption equilibrium between the contaminant solution and catalyst. The photo-Fenton experiments were carried out by adding a certain amount of H2O2 (200 μL, 35vol.%), which was added into the above suspension and meanwhile was irradiated by a UV-Vis light (300 W Xe lamp). The vertical distance

between the mixture solution and lamp was about 12 cm. At a given time, 3 mL of the suspension was taken out and collected by centrifugation to remove the catalyst completely. The absorbance of antibiotic and industrial dyes solution was immediately analyzed by using a UV-vis spectrophotometer at the characteristic absorption peak. Every experiment was repeated at least twice. Typically, 18 mg CFO/C-PNSs photocatalyst with different scavengers were dispersed into 30 mL certain concentration contaminant aqueous solution, and the following processes were similar to the photodegradation process.

1.4. Active species trapping experiment and ESR measurements.

The free radicals capture tests were employed to study the mechanism for TCH degradation. Typically, 18 mg CFO/C-PNSs were dispersed into 30 mL of 20 ppm TCH aqueous solution with different scavengers. The active species were detected by adding isopropanol (IPA), riethanolamine (TEOA) and 4-hydroxy-TEMPO, which were respectively served as hydroxyl radicals (•OH), hole (h+) and superoxide radicals (•O2−) quencher into the photocatalytic reaction systems, respectively. The processes were similar to the TCH photodegradation process.

Electron spin-resonance spectroscopy (ESR) was collected on a magnettech MS-5000 instrument. The ESR measurement with 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as the spin trap was adopted to distinguish intermediate species especially such as superoxide anion radicals (·O2-) generated during the reaction. Electron spin-resonance spectroscopy (ESR) for ·O2- (superoxide radicals) was determined in dark and under visible light (methanol solution volume, 1.0 mL; sample, 3 mg; DMPO, 0.2 mL (1 M)).

1.5. Electrochemical measurements.

Electrochemical measurements were conducted through the electrochemical workstation (CHI760E, Shanghai Chen Hua Instrument Co., Ltd., China) by using a three-electrode system. The electrolyte was a 0.5 M Na2SO4 aqueous solution. The Ag/AgCl electrode, samples deposited fluoride-tin oxide (FTO) glass and Pt foil were served as reference electrode, the working electrode and counter electrode, respectively. The working photoelectrodes were prepared as follows: 30 mg catalyst was dispersed in 3 mL of ethanol and grounded for 8 min. Thereafter, the suspension was transferred onto a 1.2×2.5 cm2 FTO conductive glass by using a spin-coating method. Finally, the working electrode was obtained after dried at room temperature overnight.

The photocurrent response curves were obtained at 0 V with a 300 W Xe lamp irradiation. The electrochemical impedance spectroscopy (EIS) analyses were carried out at open circuit voltage in 0.1 M KCl solution containing 5 mM Fe(CN)63−/4− with a frequency range from 0.01 Hz to 10 kHz. The linear sweep voltammetry (LSV) was recorded in the potential scanning ranging from 0.8 to -0.8 V under a 300 W Xe-lamp irradiation with sample interval of 0.001 V. The Mott-Schottky (M-S) data was recorded in the potential range from 0.8 to -0.8 V with a frequency of 1000Hz.

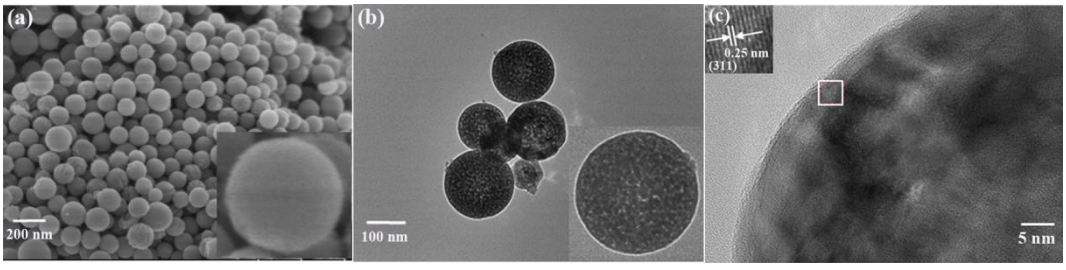

Figure S1. The SEM (a), TEM (b) and HRTEM (c) images for CFO-PNSs sample.

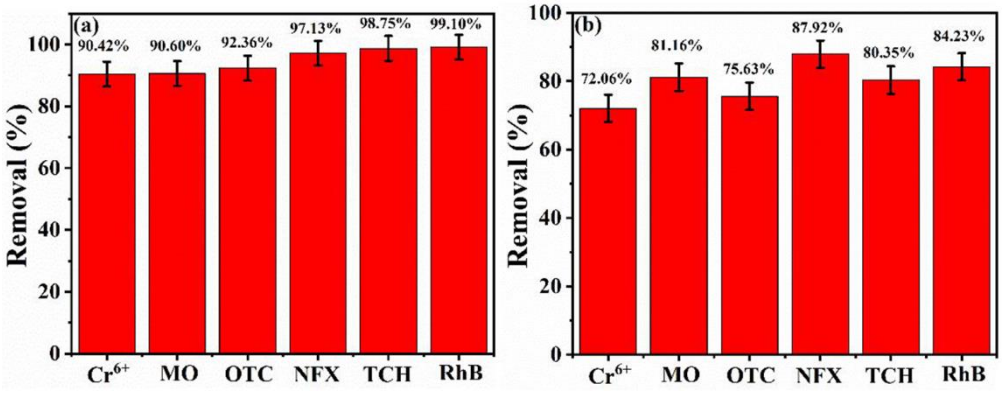

Figure S2. The removal rate of (a) CFO/C-PNSs and (b) CFO-PNSs for Cr^{6+} MO, OTC, NFX, TCH and RhB.

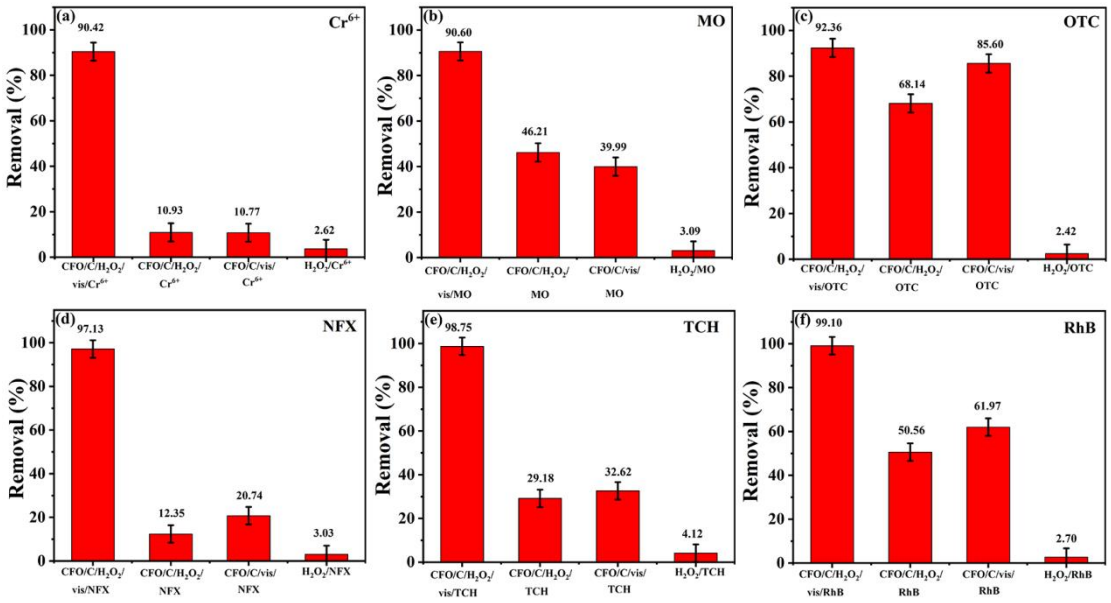

Figure S3. The photocatalytic degradation of (a) Cr^{6+}, (b) MO, (c) OTC, (d) NFX, (e) TCH and (f) RhB by CFO/C-PNSs with different conditions under visible light irradiation.

Table S1. The comparison of TCH photo-Fenton degradation activity of CFO/C-PNSs with previous literatures.

Photocatalyst	TCH Concentration ($mg \cdot L^{-1}$)	Dosage ($g \cdot L^{-1}$)	Time (min)	Removal (%)	Light source	Reference
$ZnFe_2O_4$-10	60	0.3	40	98	LED lamp; λ = 420 nm	1
α-Fe_2O_3/g-C_3N_4 (Fe:C=1: 2)	10	1	150	90	300 W Xe-lamp	2
Fe^{2+}	100	0.005	60	94.2	4 W low pressure Hg UV lamps; λ = 254 nm	3
CQDs/α-FeOOH (CQDs 1 wt %)	20	0.25	60	94.5	350 W Xe-lamp; λ > 420 nm	4
Fe-MOFs MIL-101	50	0.15	20	82.52	300 W Xe-lamp; $\lambda \geq$420 nm	5
g-C_3N_4/FeOCl -20	50	0.1	60	90	300 W Xe-lamp; λ = 400 nm	6
0.9%FeOOH/-Bi_2WO_6	50	1	50	91	300 W metal halide lamp; $\lambda \leq$ 420 nm	7

Ag_3PO_4@MIL-53(Fe)M:A=10:1	10		60	95.18		8
10%α-Fe_2O_3/BiOI	20	1	30	82.1	Xe-lamp; λ < 420 nm	9
$CuCo_2O_4$	50	0.2	5	89.1	400 W MW oven;T=90℃	10
{110} facets Fe_3O_4 NPs	50	0.3	60	96.7	10 W UVC-lamp; λ = 220—275 nm	11
0.1% CuS/Bi_2WO_6	40	1	50	73	300 W metal halide lamp; λ ≥420 nm	12
$MnFe_2O_4$/bio-char	40	0.5	120	95	300 W Xe-lamp; λ ≥420 nm	13
(0.75:1.5) $NiFe_2O_4$/C	20	0.3	60	97.25	visible-light; (λ > 400 nm)	14
α-Fe_2O_3@TiO_2	50	0.5	90	100	300W Xe-lamp; λ>420 nm	15
Fe_3O_4@void@TiO_2	40	0.25	6	100	300W Xe-lamp; λ=200—1000 nm	16
$CuFe_2O_4$/C	20	0.6	60	98.75	300 W Xe-lamp; λ ≥400 nm	This work

Table S2. The comparison of photo-Fenton degradation activity of CFO/C-PNSs with previous literatures.

Catalyst	Concentration ($mg•L^{-1}$)	Dosage ($g•L^{-1}$)	Time (min)	pollutant	Removal (%)	Light source	morphology	preparation methods	Reference
$CuFe_2O_4$/NC	15	0.3	90	Levofloxacin (LVFX)	84.87%	—	nanoparticle	solvothermal method	17
$CuFe_2O_4$	20	0.16	150	Malachite Green (MG)	82.8%	300 W Xenon lamp	Porous and spongy	solution combustion synthesis	18
oxygen vacancies-$CuFe_2O_4$	10	0.1	90	sulfamethazine (SMT)	95%	500 W Xenon lamp; λ > 420 nm	raw expanded perlite	precipitation-calcination method	19
$CuFe_2O_4$/AgBr	16.34	1.51	120	acid red 88 (AR88)	94.7%	300 W Xenon lamp	particle	hydrothermal method	20
$CuFe_2O_4$/g-C_3N_4	103.7	1	120	propranolol (PRO)	82.2%	350W Xenon lamp; λ > 420 nm	layered structure	sol-gel combustion method	21
Ag_3PO_4/NrGO/$CuFe_2O_4$	15	0.3	60	2,4-dichlorophenol (2,4-DCP)	95.3%	Xe lamp 250 W; λ ≤ 420 nm	tetrahedronnano particles morphology	Coprecipitation method	22
Bi_2Te_3/CdS/$CuFe_2O_4$	40	1.4	180	Methylene Blue (MB)	97.15%	ungsten-halogen lamp	Nanorod with anoparticles	wet impregnation method	23
$CuFe_2O_4$/ C	20	0.6	60	rhodamine B (RhB)	99.1%	350W Xenon lamp	Hollow nanospheres	one pot synthetic calcination method	This work

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