Supporting Information

Efficient peroxymonosulfate activation by Fe-BiOCl hollow microsphere for carbamazepine removal

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1. Experimental Section

1.1. Chemicals and materials

All the materials were of analytical grade and used without further purification. Bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$), ferric nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$), potassium chloride (KCl), absolute ethanol, glycerol, methanol (MeOH), tert-butanol (TBA), p-benzoquinone (BQ) and ethylenediaminetetraacetate (EDTA-2Na) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Carbamazepine (CBZ), Potassium monopersulfate triple salt (PMS, $KHSO_5 \cdot 0.5KHSO_4 \cdot 0.5K_2SO_4$, ≥42% $KHSO_5$ basis) and L-histidine (HD) were purchased from Aladdin.

1.2. Synthesis of Fe-BiOCl and pure BiOCl hollow microsphere

Firstly, 15 mL of glycerol and 50 mL of absolute ethanol were mixed and stirred to form a homogeneous solvent. Subsequently, 0.149 g of KCl (2 mmol) and 0.970 g of $Bi(NO_3)_3 \cdot 5H_2O$ (2 mmol) was dissolved successively in the mixture solvent under constant stirring, then a certain amount of $Fe(NO_3)_3 \cdot 9H_2O$ (molar ratio, Fe: Bi = 0.01, 0.02, 0.03, 0.05 and 0.07) was added and continue stirring for 30 min. After that, the suspension was transferred into a 100 mL Teflon-lined stainless autoclave and maintained at 180°C for 12 h. The precipitate was obtained by centrifugation, washed several times with deionized water and ethanol, the final yellow products were collected after drying at 60°C for 12 h and denoted as 1%, 2%, 3%, 5% and 7% Fe-BOC for further characterization, respectively.

The preparation method of BiOCl hollow microsphere (denoted as BOC) was the same as that of Fe-BiOCl except that $Fe(NO_3)_3 \cdot 9H_2O$ is not added.

1.3. Photocatalytic measurement

Photocatalytic performance was evaluated by the degradation of carbamazepine (CBZ) under simulated visible light irradiation. In a typical procedure, a certain amount of photocatalyst powder and PMS were added in 50 mL of CBZ solution (10 mg/L), the mixture was ultrasonicated for 10 min to form a homogeneous suspension. After that, the suspension was magnetically stirred in dark for 30 min to establish the adsorption-desorption equilibrium before illumination. The photocatalytic process was

carried out in Pyrex glass bottles with circulating water, and a 300 W Xe lamp with the UV cutoff filter (λ > 420 nm) was used as the light source. About 3 mL of suspension was taken at certain intervals and filtered out by 0.22 μm membrane filters. The concentrations of CBZ were detected by UV-vis spectrophotometer (Shimadzu, Japan) and the detection wavelength was at 284 nm.

1.4. Characterization

The crystalline phases were characterized by powder X-ray diffraction (XRD) (Bruker D8 Advance, Cu Kα = 1.5404 Å, Germany). The morphology images were studied by field emission scanning electron microscope (FE-SEM, SU8010, Hitachi, Japan). Transmission electron microscope (TEM), high-resolution transmission electron microscope (HRTEM) and energy-dispersive X-ray spectroscopy (EDX) were observed on Talos F200X (Thermo Fisher, USA). X-ray photoelectron spectroscopy (XPS) was carried out on a VG Multilab 2000 (VG Inc.), photoelectron spectrometer using Al Kα radiation as the excitation source. The UV-vis diffuse reflectance spectroscopy (DRS) was obtained from a Cary-5000 spectrophotometer (Agilent) with $BaSO_4$ as reference substance. Photoluminescence (PL) measurements were carried out on an F-7000 (Hitachi) fluorescence spectrophotometer with a 150 W Xe lamp at 250 nm excitation wavelength. N_2 adsorption/desorption was tested on an ASAP 2020 PLUS adsorption analyzer (Micromeritics, USA) to obtain the Brunauer-Emmett Teller (BET) surface area and the pore size distribution.

The photoelectrochemical tests were carried out on CHI-760E electrochemical workstation (Shenzhen LAMPLIC Science Co. Ltd. China) with a standard three-electrode system. The electrolyte was 0.5 M Na_2SO_4 aqueous solution, Pt flake and an Hg/HgO electrode were used as the counter electrode and reference electrode, respectively. The catalyst solution (10 mg BiOCl, 500 μL ethanol and 450 μL ultrapure water, 50 μL Nafion) was uniformly coated on the ITO glass (1 cm × 1 cm) to prepare working electrodes. The frequency range of electrochemical impedance spectroscopy (EIS) test was 10^{-5}-10^{-1} Hz and no voltage was applied between the electrodes. A 3 W LED lamp was used as the light source (λ ≥ 420 nm) to trigger the photocurrent response.

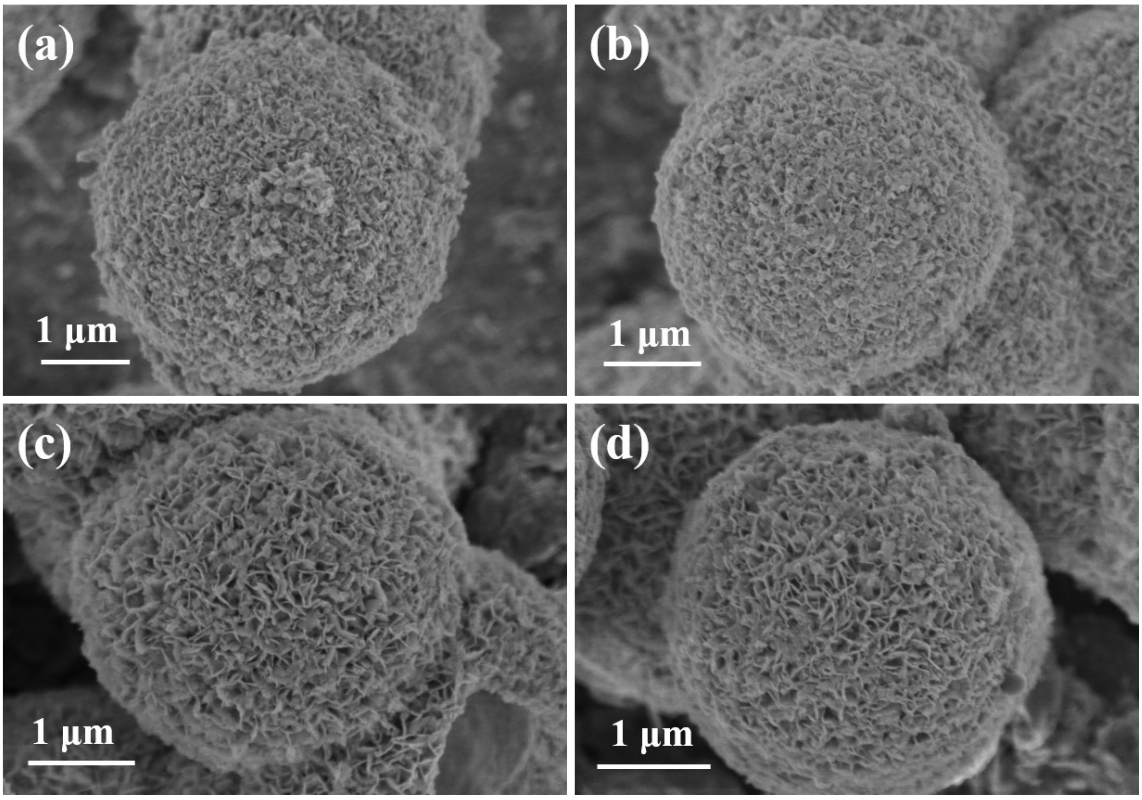

Fig. S1. SEM images of (a) 1% Fe-BOC, (b) 2% Fe-BOC, (c) 5% Fe-BOC and (d) 7% Fe-BOC samples.

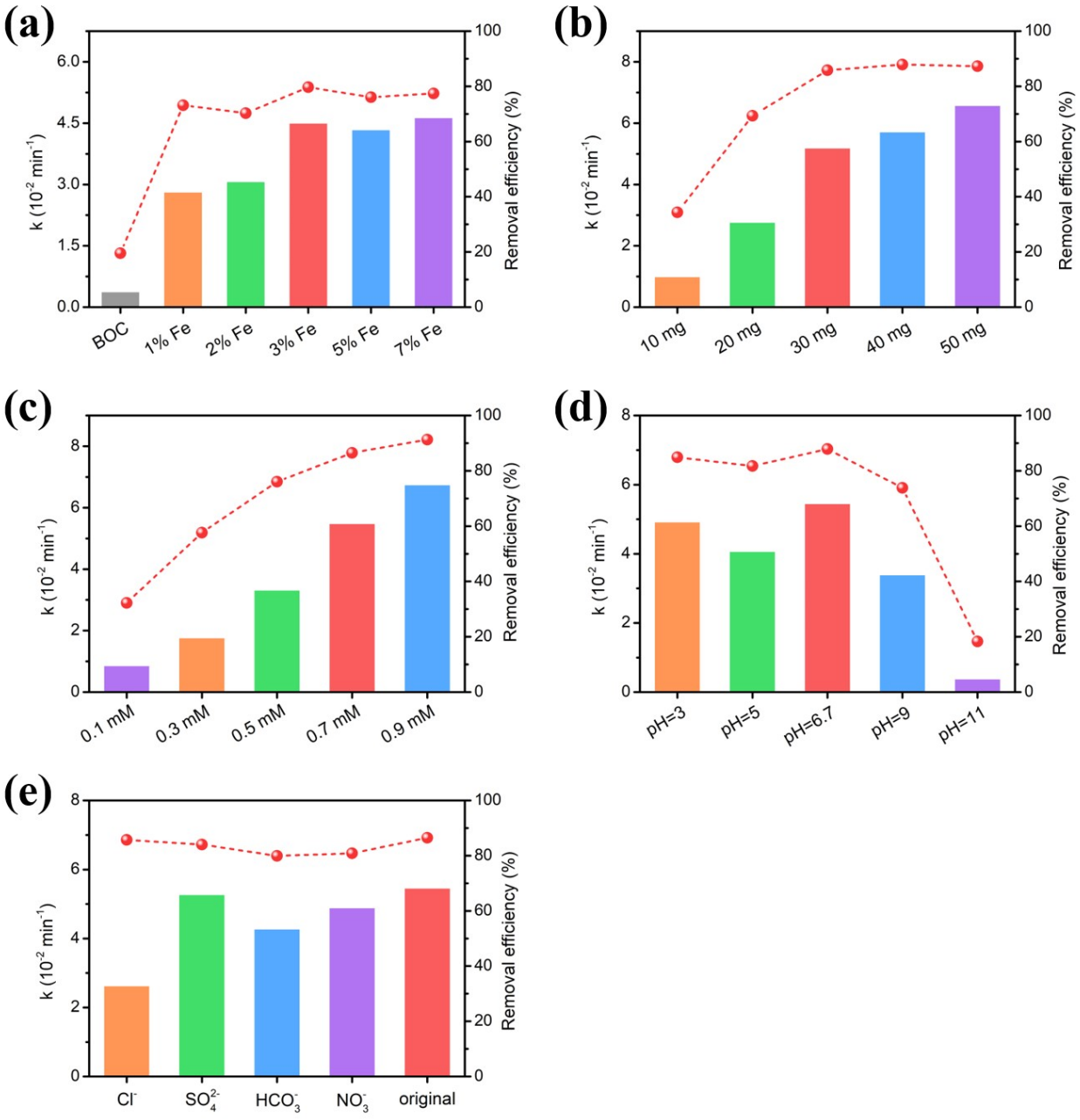

Fig. S2. Effects of (a) Fe doping amount, (b) catalyst dosage, (c) PMS concentrations, (d) initial pH values, (e) co-existing inorganic anions on the removal of CBZ.

Table S1. Degradation kinetic constants and removal rates for different samples.

Figure	Experimental conditions		k (10^{-2} min^{-1})	Removal rate (%)
(a)	30 mg catalyst, 0.5 mM PMS, pH=6.7	BOC	0.37	19.6
		1% Fe-BOC	2.80	76.2
		2% Fe-BOC	3.06	70.9
		3% Fe-BOC	4.49	79.7
		5% Fe-BOC	4.33	76.1
		7% Fe-BOC	4.62	77.5
(b)	3% Fe-BOC, 0.7 mM PMS, pH=6.7	10 mg	0.96	34.4
		20 mg	2.75	69.4
		30 mg	5.17	85.9
		40 mg	5.69	87.9
		50 mg	6.56	87.3
(c)	30 mg 3% Fe-BOC, pH=6.7	0.1 mM	0.85	32.3
		0.3 mM	1.74	57.7
		0.5 mM	3.31	76.1
		0.7 mM	5.47	86.5
		0.9 mM	6.73	90.3
(d)	30 mg 3% Fe-BOC, 0.7 mM PMS	pH=3	4.91	84.9
		pH=5	4.06	81.8
		pH=6.7	5.44	87.9
		pH=9	3.38	73.8
		pH=11	0.36	18.3
(e)	30 mg 3% Fe-BOC, 0.7 mM PMS, pH=6.7	Cl^-	2.62	85.7
		SO_4^{2-}	5.25	84.1
		HCO_3^-	4.26	79.9
		NO_3^-	4.87	80.9
		original	5.44	86.5

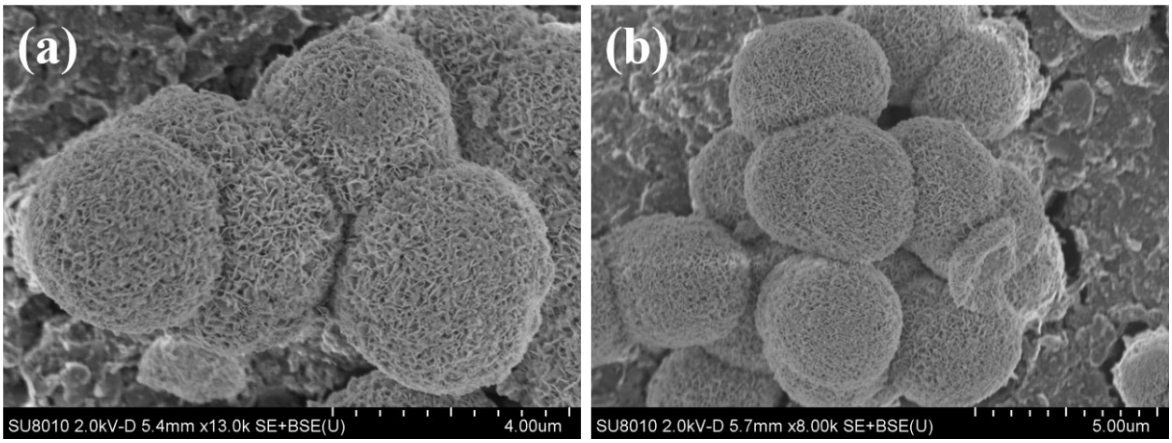

Fig. S3. SEM images of 3% Fe-BOC before (a) and after (b) the cycle experiment.

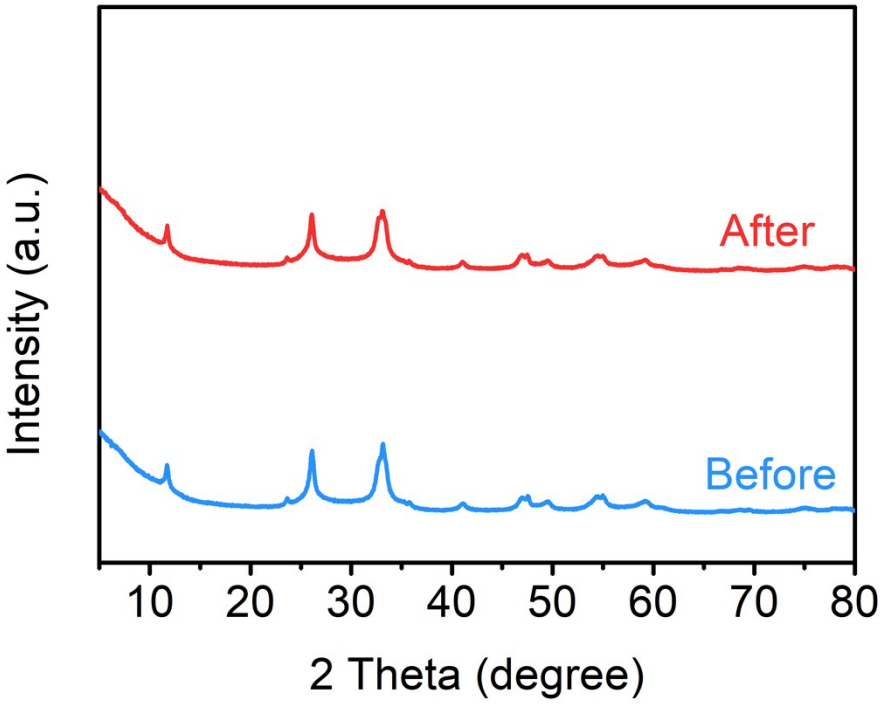

Fig. S4. XRD pattern before and after the cycle experiment.

Table S2. BET surface area, pore volume and average pore diameter of BOC and 3% Fe-BOC.

Sample	Surface Area (m^2/g)	Average pore size (nm)	Pore volume ($cm^3 \cdot g^{-1}$)
BOC	28.7	0.20	24.7
3% Fe-BOC	82.5	0.27	11.4

[a.] The surface area is measured with the Brunauer–Emmett–Teller (BET) method.
[b.] The pore volume is the single-point total pore volume at $P/P_0 = 0.998$.
[c.] The average pore size is calculated using the adsorption branch by Barrett–Joyner–Halenda (BJH) method.