

Supplementary Information

Synthesis of Hierarchical Porous β -FeOOH Catalysts in Ionic Liquid/Water/CH₂Cl₂ Ionogels

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Experimental Section

Materials: Ionic liquid, 1-decyl-3-methylimidazolium chloride (DmimCl, purity>99%) was purchased from the Centre of Green Chemistry and Catalysis, LICP, CAS. CH₂Cl₂ (A. R. grade), acetonitrile (A. R. grade) and toluene (A. R. grade) were provided by Sinopharm Chemical Reagent Co., Ltd. FeCl₃ (purity>98%), tert-butyl hydroperoxide (TBHP, 70 wt% aqueous solution) xanthene (purity>98%) and xanthone (purity>99%) were obtained from Alfa Aesar China Co., Ltd.

Ionogels preparation and characterization: To prepare the ionogels, 8 g IL, 2 g water and desired amount of CH₂Cl₂ were mixed at 50 °C to form homogeneous solution under vigorous stir and then cooled down to room temperature. The as-prepared mixture was photographed using a camera, and the pH value was determined by an acidimeter produced by Mettler-Toledo Instruments Co., Ltd. (Shanghai, China).

SAXS study: SAXS experiments were carried out at Beamline 1W2A at the Beijing Synchrotron Radiation Facility.^{S1} The data were collected using a CCD detector (MAR) with maximum resolution of 3450×3450 pixels. The wavelength of the X-ray was 1.54 Å, and the distance of the sample to detector was 1.56 m. In a typical experiment, the sample was added into the sample cell controlled at 25 °C, and the X-

ray scattering data were recorded. The 2-D SAXS images were obtained from the detector and then transformed into the profiles of intensity (I) vs wavevector (q) by the software SAXS Data Pre-process V2.0.0.

β -FeOOH synthesis in IL/water/CH₂Cl₂ ionogels with CH₂Cl₂ contents of 0-25 wt%: In a typical experiment, 20 g FeCl₃ aqueous solution (50 mM) was added into 20 g IL/water/ CH₂Cl₂ ionogel at room temperature. FeCl₃ diffused into the ionogel and hydrolyzed. After all the ionogel was completely destroyed, the mixture was stabilized for another 24 h. The obtained mixture containing the materials was centrifuged with a centrifugal speed of 5000 rpm. The obtained β -FeOOH particles were washed with water for 5 times (5×50 mL) and ethanol for 5 times (5×50 mL), and then dried in a vacuum oven at 40 °C for 24 h.

β -FeOOH synthesis in IL/water/CH₂Cl₂ with CH₂Cl₂ content of 50 wt%: In a typical experiment, 20 g FeCl₃ aqueous solution (50 mM) was added into 20 g IL/water/ CH₂Cl₂ solution at room temperature. The mixture was stirred for 48 h. The obtained mixture containing the materials was centrifuged with a centrifugal speed of 5000 rpm. The obtained β -FeOOH were washed with water for 5 times (5×50 mL) and ethanol for 5 times (5×50 mL), and then dried in a vacuum oven at 40 °C for 24 h.

β -FeOOH synthesis in water: The synthetic procedure was similar to that reported.^{S2} In the experiment, 10 mL FeCl₃ solution (1 M) and 10 mL NaOH solution (1 M) were mixed, and placed for 24 h at room temperature. After that, 20 mL NaOH (1 M) was introduced into the mixture and stirred at 70 °C for another 24 h. The suspension was separated by centrifugation and washed with water for 5 times, and then dried in a vacuum oven at 40 °C for 24 h.

Material Characterization: X-Ray diffraction (XRD) analysis of the samples was performed on the X-ray diffractometer (Model D/MAX2500, Rigaka) with Cu-K α radiation, and the scan speed was 5°/min. The morphologies of the products were characterized by JEOL-1011 TEM operated at 100 kV. The porosity properties of the materials were obtained from nitrogen adsorption-desorption isotherms determined using a Micromeritics ASAP 2020M system. Barrett-Joyner-Halenda method was used for mesopores.

Oxidation of xanthene: The reaction procedures were similar to that used by other researchers.^{S3} In the reaction, 50 mg xanthene and 10 mg catalyst were placed in 4 mL acetonitrile in a 10 mL glass flask, which was immersed in constant-temperature water bath. The mixture was stirred (800 rpm), and then TBHP (another reactant) was added and the reaction began. After suitable reaction time, the reaction mixture was cooled in ice-water, and was centrifuged to precipitate the β -FeOOH particles. The reaction mixture was analyzed by gas chromatograph (GC, HP 4890) equipped with a flame ionization detector (FID), and toluene was used as the internal standard. The used β -FeOOH catalyst was washed with ethanol and water for five times and dried in

a vacuum oven at 40 °C for 24 h. Then the recycled catalyst was used under the same condition for catalyzing the reaction.

Supplementary Figures

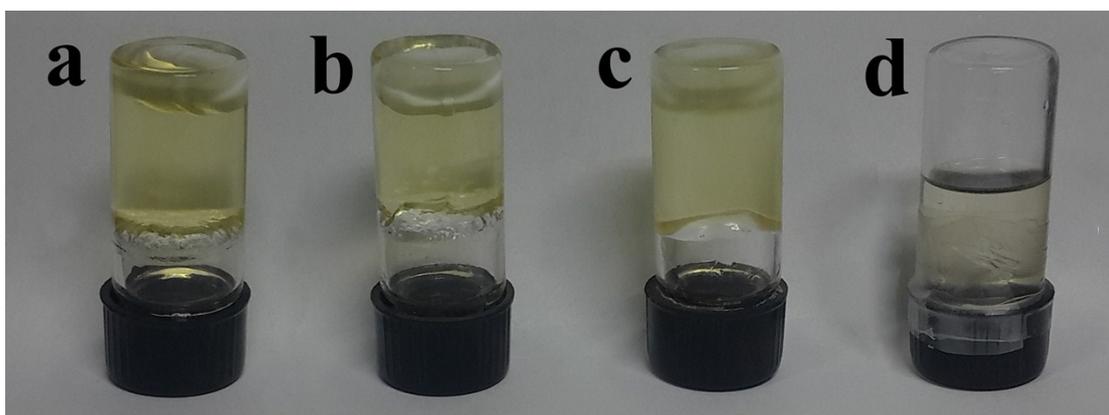


Fig. S1 The photographs of IL/water/ CH_2Cl_2 systems with CH_2Cl_2 contents of 0 (a), 15 wt% (b), 25 wt% (c) and 50 wt% (d) at 25 °C.

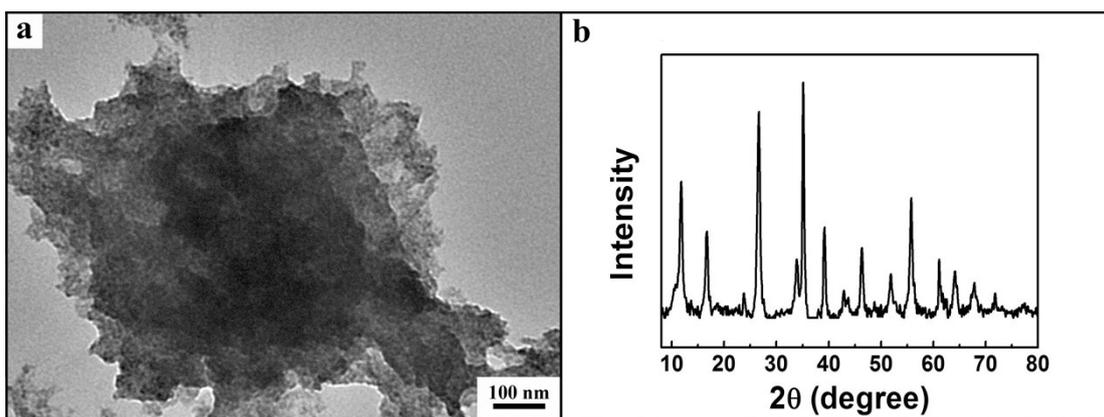


Fig. S2 The TEM image (a) and XRD pattern (b) of bulk $\beta\text{-FeOOH}$ synthesized in water.

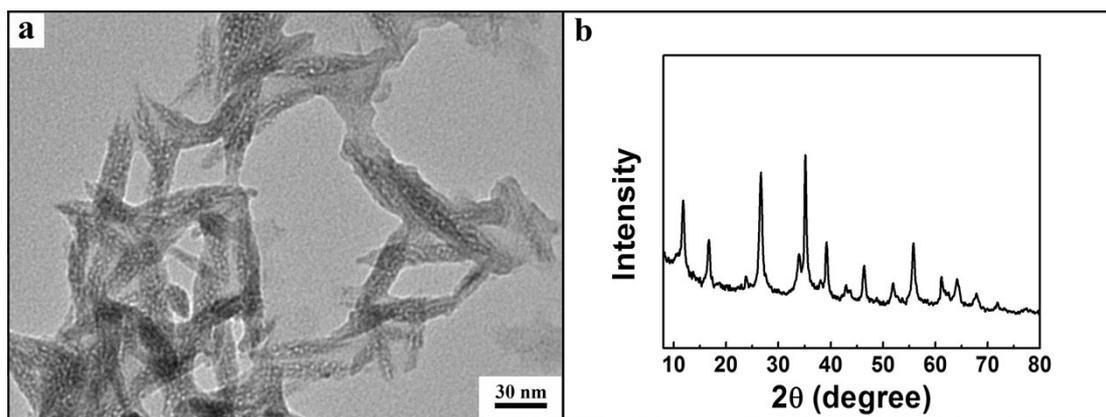


Fig. S3 TEM image (a) and XRD pattern (b) of the β -FeOOH synthesized in IL/water/ CH_2Cl_2 systems with CH_2Cl_2 content of 25 wt% after used five times.

Supplementary Tables

Table S1 The SAXS peak location, aggregate size and pH value of different IL/water/ CH_2Cl_2 systems.

Entry	ω (CH_2Cl_2) (wt%) ^a	q (nm^{-1})	d (nm)	pH
1	0	2.174	2.890	8.48
2	15	2.213	2.839	8.47
3	25	2.240	2.805	8.44
4	50	-	-	7.93

^a CH_2Cl_2 content in the IL/water/ CH_2Cl_2 system.

Table S2. The BET surface area (S) and total pore volume (V) of different β -FeOOH particles synthesized in IL/water/CH₂Cl₂ systems with CH₂Cl₂ content.

Entry	ω (CH ₂ Cl ₂ wt%) ^a	S (m ² ·g ⁻¹)	V (cm ³ ·g ⁻¹)
1	0	148.1	0.24
2	15	171.5	0.51
3	25	233.2	0.78
4	50	107.8	0.61
5 ^b	-	37.7	-

^aCH₂Cl₂ content in the IL/water/CH₂Cl₂ systems. ^bBulk β -FeOOH synthesized in water.

References

- S1** X. C. Kang, J. L. Zhang, W. T. Shang, T. B. Wu, P. Zhang, B. X. Han, Z. H. Wu, G. Mo and X. Q. Xing, *J. Am. Chem. Soc.*, 2014, **136**, 3768-3771.
S2 J. Kim, W. Li, B. L. Philips and C. P. Grey, *Energ. Environ. Sci.*, 2011, **4**, 4298-4305.
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