Large-pore mesoporous Mn_3O_4 crystals derived from metal-organic frameworks

Li Peng, Jianling Zhang*, Zhimin Xue, Buxing Han, Jianshen Li and Guanying Yang

Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Colloid and Interface and Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences

E-mail: zhangjl@iccas.ac.cn

1. Experimental section

Materials

The ILs 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6), 1-hexyl-3-methylimidazolium hexafluorophosphate ([hmim]PF_6), 1-octyl-3-methylimidazolium hexafluorophosphate ([omim]PF_6) (>98% purity) were provided by Lanzhou Greenchem ILS, LICP, CAS. Methylene blue was produced by TCI (>70% purity). Other starting materials (H_2O, benzene dicarboxylic acid (H_2BDC), $MnCl_2$, methyl ammonium, 30 wt% H_2O_2) were purchased from Alfa Aesar and used without further purification. The methyl ammonium salt of the ligand was made by dissolving the benzene dicarboxylic acid in a 40 wt % solution of methyl amine in water. The excess methyl amine and water were vaporated under reduced pressure, and the isolated salt was then redissolved in distilled water to give an aqueous solution of desired concentration.

Mn-MOF synthesis

To synthesize the Mn-BDC MOF, 2 mL of a 0.05 M benzene dicarboxylic acid methyl ammonium salt aqueous solution and 2 mL of a 0.05 M $MnCl_2$ aqueous solution were loaded into IL-water mixture with the IL volume ratio 0.375. The mixture was stirred for 18 h at room temperature. The product was collected and washed with acetone and ethanol for several times.

Mn_3O_4 synthesis

In a typical synthesis, the Mn-MOF underwent thermolysis under an inert environment (N_2) with a heating rate of 5 °C/min from room temperature to 400 °C. After reaching the target temperature, the material was calcined for 2 h and then naturally allowed to cool down to room temperature. The Mn_3O_4 crystals calcined from the Mn-MOFs synthesized in [bmim]PF_6-water, [hmim]PF_6-water and [omim]PF_6-water mixtures, respectively, are denoted as Mn_3O_4-1, Mn_3O_4-2 and Mn_3O_4-3.

Characterization

The morphologies of Mn-MOF and Mn_3O_4 were characterized by a HITACHI S-4800 scanning electron microscope equipped with EDX and TEM JeoL-1010 operated at 100 kV. XRD analysis was performed on the X-ray diffractometer (Model D/MAX2500, Rigaka) with Cu Kα radiation. Thermogravimetric analysis was carried out on a PerkinElmer TGA instrument. The temperature range was from 30 to 710 °C with a heating rate of 10 °C/min, and the experiment was carried out under nitrogen atmosphere. Furthermore, the fine-TGA test was carried out at 400 °C over 2 h under nitrogen atmosphere. X-ray photoelectron spectroscopy data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300W AlKα radiation. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. The porosity of Mn-MOF and Mn_3O_4 were determined by N_2 adsorption-desorption isotherms using a Quadrasorb SI-MP system. Raman spectra were obtained using a LabRAM ARAMIS spectrometer. The small angle X-ray (SAXS) experiment was carried out at Beamline 1W2A at the Beijing Synchrotron Radiation Facility (BSRF). The wavelength was 1.54 Å, and the distance of sample to detector was 1.596 m. The data were collected using a CCD detector (MAR) with a maximum resolution of 3450×3450 pixels. The UV-vis spectrometer was produced by the Beijing Instrument Company (TU-1901).

Catalytic test

The catalysis experiment was carried out in a 250 mL glass flask that contained an aqueous MB solution (100 mg/L, 20 mL), distilled water (65 mL), and Mn_3O_4 (20 mg). After 30 wt% H_2O_2 solution (15 mL) was added, the mixture was heated to 75 °C with continuous stirring. At given time intervals, 0.5 mL of the mixture was removed and quickly diluted with distilled water to 3 mL total volume prior to analysis.

2. Results

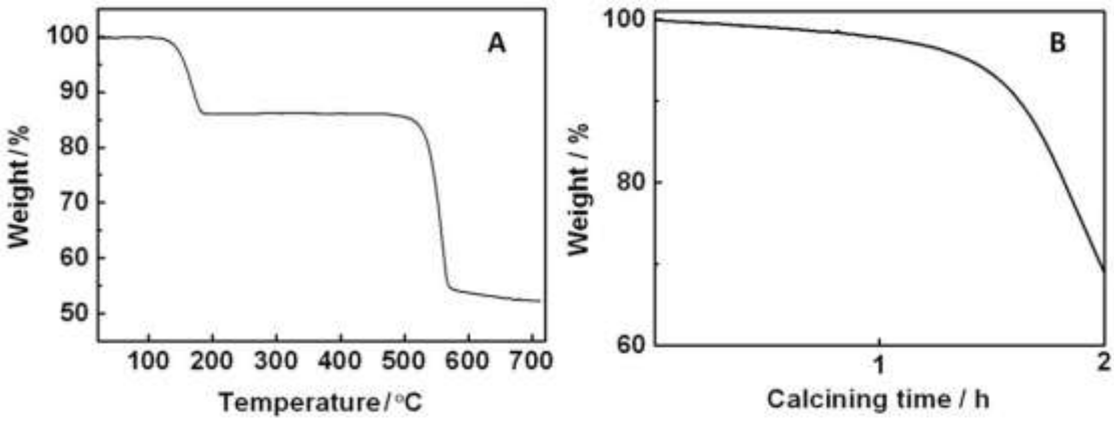

Fig. S1 Thermogravimetric curves of the Mn-MOF synthesized in [bmim]PF_6-water mixture under nitrogen atmosphere. The TGA curve A shows the first weight loss of about 14% between 100 °C and 200 °C, resulting from the decomposition of crystal water. Then Mn-MOF kept stable to 480 °C until the ligand began to decompose. In comparison, the TGA curve B shows that at 400 °C, Mn-MOF gradually decomposed over 2 h, and the weight loss about 31% agreed with the weight loss between 480-520 °C in TGA curve A. Because the decomposition of MOF was a slow process and the TGA test was a very fast heating process (10 °C/min), the decomposition of MOF could not be detected at 400 °C in the TGA curve A.[1] Based on the thermogravimetric analysis result, the decomposition of Mn-MOF was performed at 400 °C for 2 h under a nitrogen flow.

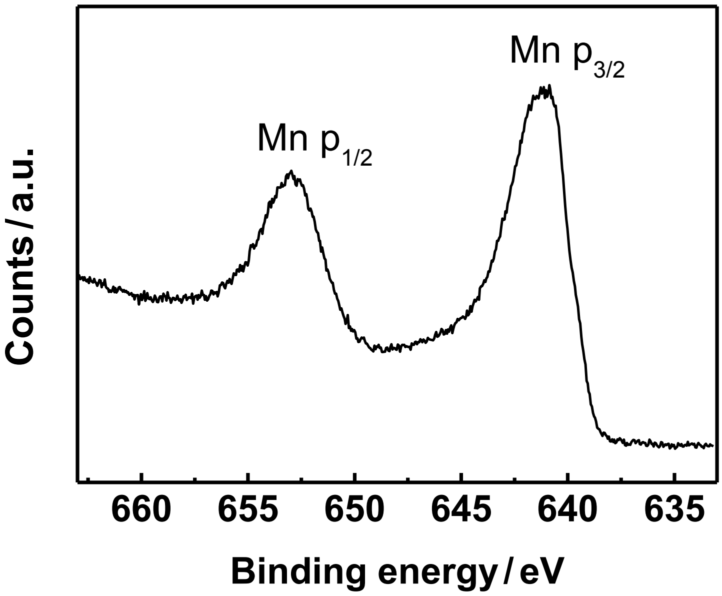

Fig. S2 X-ray photoelectron spectroscopy of Mn_3O_4-1. The binding energies of Mn $P_{3/2}$ and Mn $P_{1/2}$ are 641.4 and 652.6 eV, respectively, with the spin orbit splitting between Mn $P_{3/2}$ and Mn $P_{1/2}$ levels of 11.2 eV. These results are consistent with those of the reported Mn_3O_4.[2]

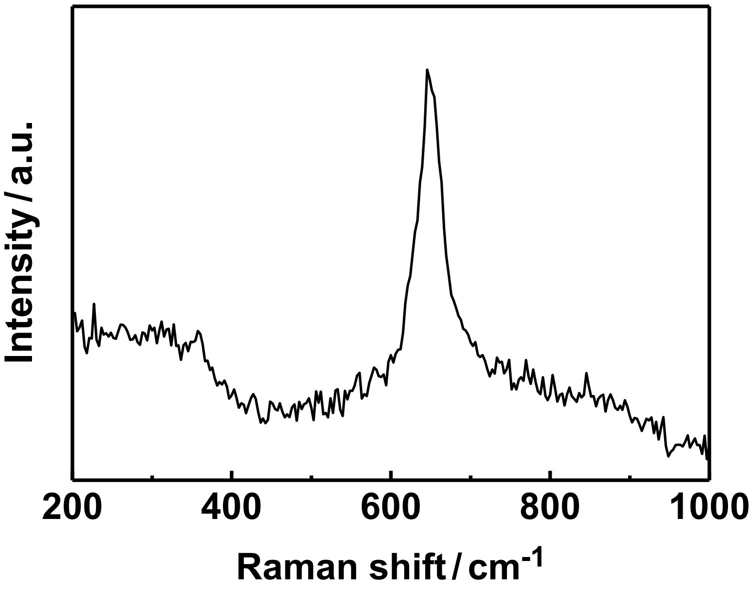

Fig. S3 Raman spectrum of Mn_3O_4-1. The dominant peak at 656 cm^{-1} was clearly observed, which is characteristic of Mn_3O_4.[3]

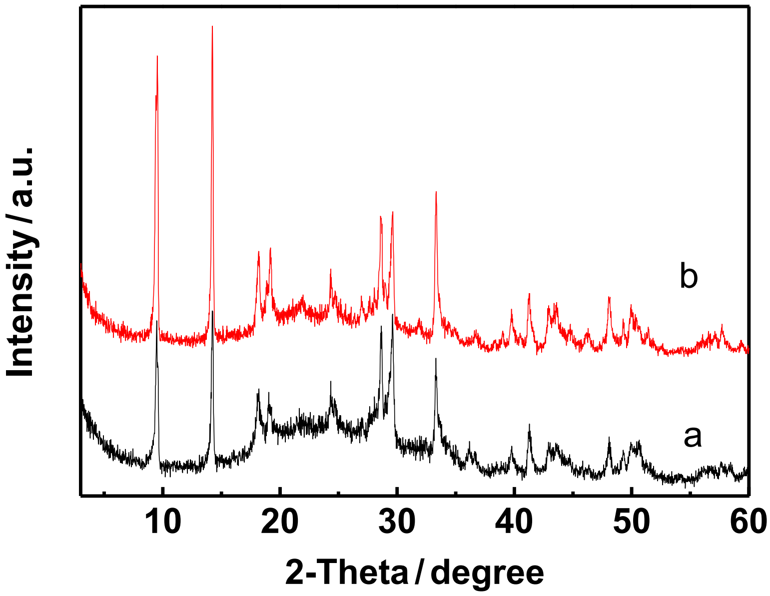

Fig. S4 XRD patterns of the Mn-MOFs synthesized in [hmim]PF_6-water mixture (a) and [omim]PF_6-water mixture (b).

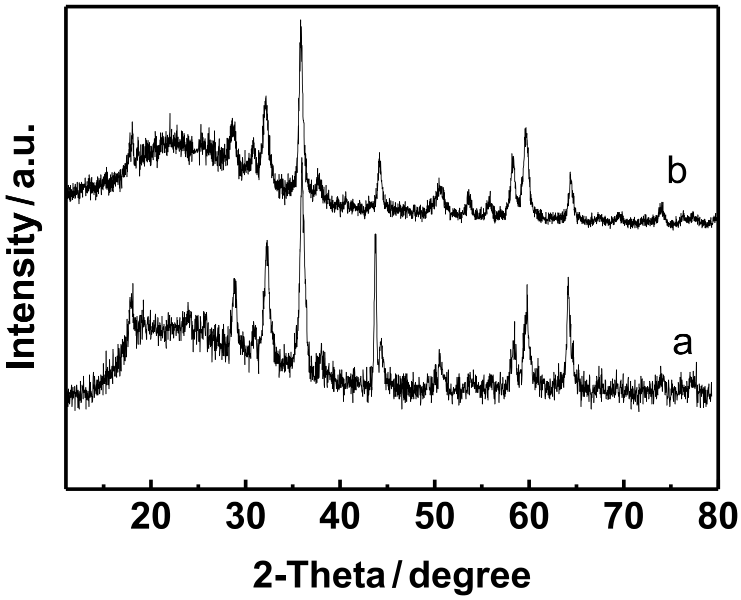

Fig. S5 XRD patterns of Mn_3O_4-2 (a) and Mn_3O_4-3 (b).

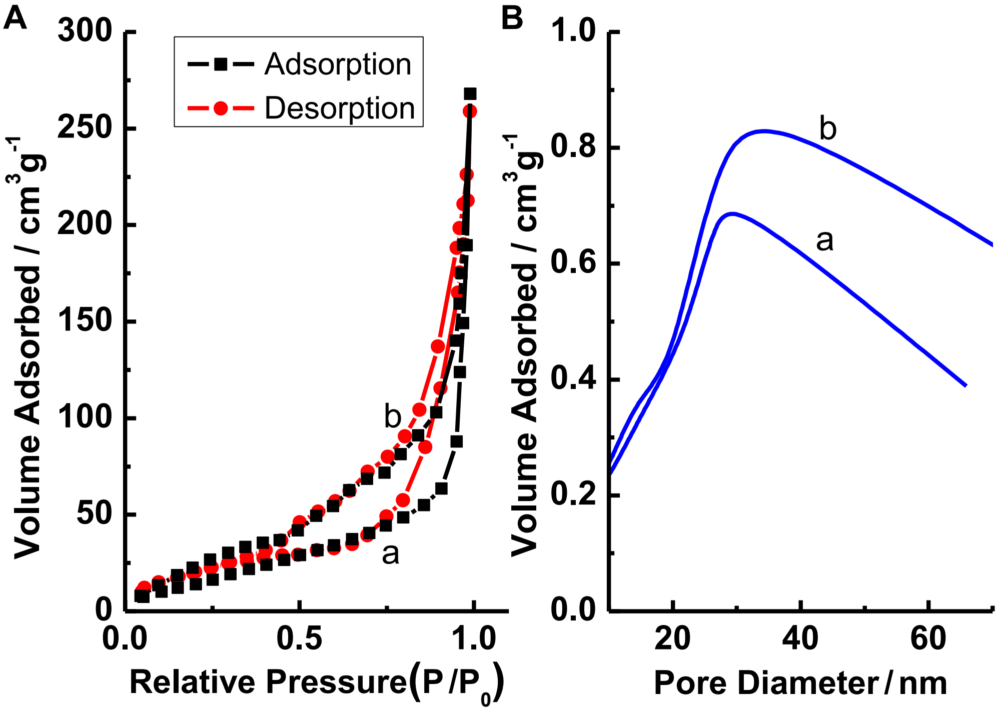

Fig. S6 N_2 adsorption-desorption isotherms (A) and mesopore size distribution curves (B) of Mn_3O_4-2 (a) and Mn_3O_4-3 (b).

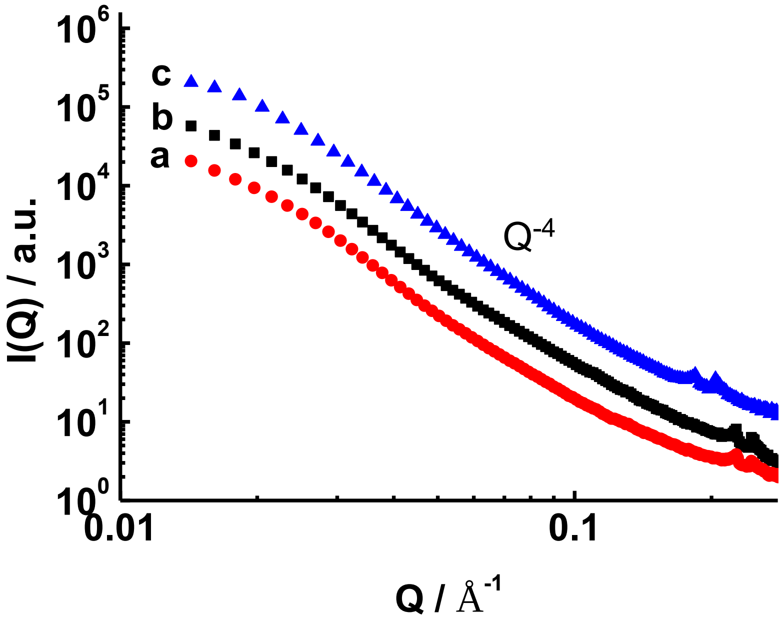

Fig. S7 SAXS curves of the Mn-MOFs synthesized in [bmim]PF_6-water mixture (a), [hmim]PF_6-water mixture (b), and [omim]PF_6-water mixture (c). The SAXS profiles display powerlaw scattering of Q^{-4} in the low-Q region ($0.01<Q<0.08$ $Å^{-1}$), corresponding to the asymptotic scattering behavior of larger pores or mesopores.[4] In the low-Q region of $0.01<Q<0.04$ $Å^{-1}$, the intensity drops as $I(Q) \propto Q^{-D}$, D being the mass fractal dimension of the network structure. A smooth surface with D_s value of 2 leads to a power law of Q^{-4} (the Porod law), while a rough surface with $D_s=2\text{-}3$ causes a less steep intensity decay. Crossover between the mass and surface fractal regions occurs at the scattering vector (Q_c), corresponding to the reciprocal of the gyration radius R_g of the constituent pores ($Q_c^{-1}=R_g$). The pore diameters of three Mn-MOFs synthesized in [bmim]PF_6-water mixture, [hmim]PF_6-water mixture and [omim]PF_6-water mixture were thus determined to be 20.6, 24.6 and 29.6 nm from the crossovers at 0.025, 0.021 and 0.018 $Å^{-1}$, respectively.

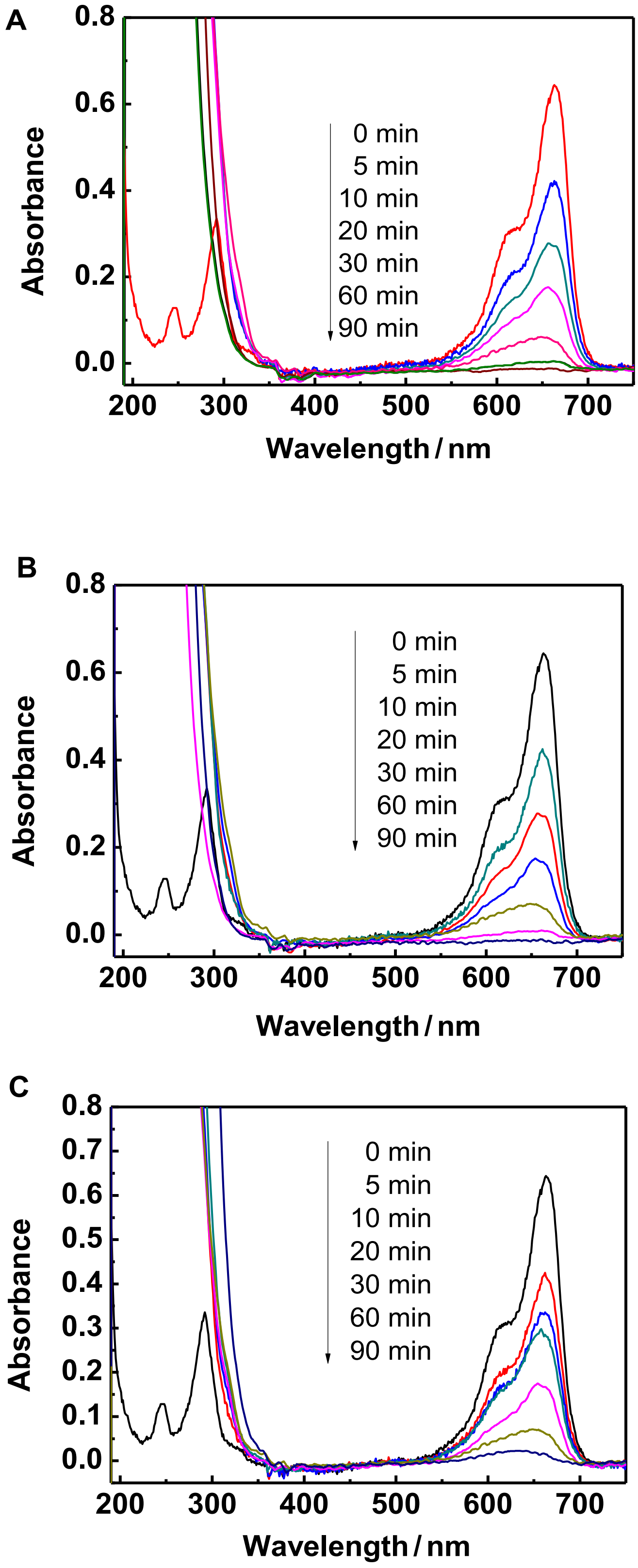

Fig. S8. Absorption spectra of a mixture of MB (100 mg /L, 20 mL), Mn_3O_4 (0.02 g, A: Mn_3O_4-2; B: Mn_3O_4-2; C: Mn_3O_4-3) and H_2O_2 (15 mL, 30 wt%) that was heated at 75 °C for different time intervals.

References

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