

## Electronic Supplementary Information

### Soft-templating Method to Synthesize Crystallize Mesoporous $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> Film

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#### Experimental details

##### 1. The synthesis of poly(ethylene oxide)-b-poly(butyl acrylate) (PEO-b-PtBA, molecular weight is about 17,000)

The procedure was mainly referred and modified from the reported papers [1,2]. The first step was the preparation of PEO-Br initiator. The experimental details are as follows: 10.0 g of MeO-PEO-OH (molecular weight is about 5,000) was dissolved in 100 mL of toluene, elevated the temperature to 140°C, refluxed for 3h to remove the trace water in MeO-PEO-OH. Toluene was removed under vacuum at 90°C for 3 h. 125 mL of anhydrous CH<sub>2</sub>Cl<sub>2</sub> was added to dissolve the solid, followed by 0.55 mL of anhydrous triethylamine addition. Then, 1.5 mL of 2-bromoisobutyryl bromide in 30 mL of CH<sub>2</sub>Cl<sub>2</sub> was added into the MeO-PEO-OH solution, and the solution was kept for 2h under ice-water bath, The reaction was continued for 20 h under N<sub>2</sub> atmosphere. Thereafter, 2 mL of milli-Q water was added into the reaction solution under vigorous stirring for 0.5 h, and the solution was transferred to a 250 mL separation funnel, washed with 4 mL of 1 M HCl solution for three times, 4 mL of 1 M NaOH for three times and then 4 mL of milli-Q water

for twice. The organic phase was dried over anhydrous  $\text{MgSO}_4$ .  $\text{MgSO}_4$  was removed by filtration, and the solid was obtained after  $\text{CH}_2\text{Cl}_2$  evaporation. Recrystallization was carried out twice in ethanol to remove impurity. Then the solid was dissolved in  $\text{CH}_2\text{Cl}_2$  and passed through an alumina oxide column. The solid precipitated in diethylether and was dried. The obtained solid was the purified PEO-Br initiator.

The amphiphilic di-block polymer PEO-*b*-PtBA was synthesized by atom transfer radical polymerization of the tert-butyl acrylate (tBA) monomer. In a 15 mL two neck flask equipped with a magnetic stirrer, 1 g PEO-Br initiator, 71 mg Cu(I)Br, 2 mL anisole, 0.1 g pentamethyldiethylenetriamine (PMDETA) and 2.5 g tBA were added. The flask was put into liquid nitrogen and degassed into nitrogen for three times. Then, the reaction was carried out at 90°C for 24 h. Then, the viscous liquid was dissolved in  $\text{CH}_2\text{Cl}_2$ , and passed through alumina column to remove CuBr. Finally, the purification of PEO-*b*-PtBA was carried out using dialysis to remove small molecules. The purified PEO-*b*-PtBA white solid was obtained after freeze-drying.

The  $^1\text{H}$  NMR ( $\delta_{\text{ppm}}$ ,  $\text{CDCl}_3$ ) spectrum (**Fig.1**) was used to confirm the formation of PEO-*b*-PtBA and molecule weight evaluation.  $^1\text{H}$  NMR ( $\delta_{\text{ppm}}$ ,  $\text{CDCl}_3$ ): 3.63-3.65 (PEO), 1.36-1.48 (PtBA, broad peak). Here, we proposed the PEO part had 440 H, then the number of H in PtBA part was about 1128.44. Each tBA monomer had 12 H, so the total number of repeated tBA monomer unit would be about 94. The molecular weight of tBA was about 128, then the total molecular weight of PtBA part was about 12,032. The total molecular weight of PEO-*b*-PtBA was about 17,000.

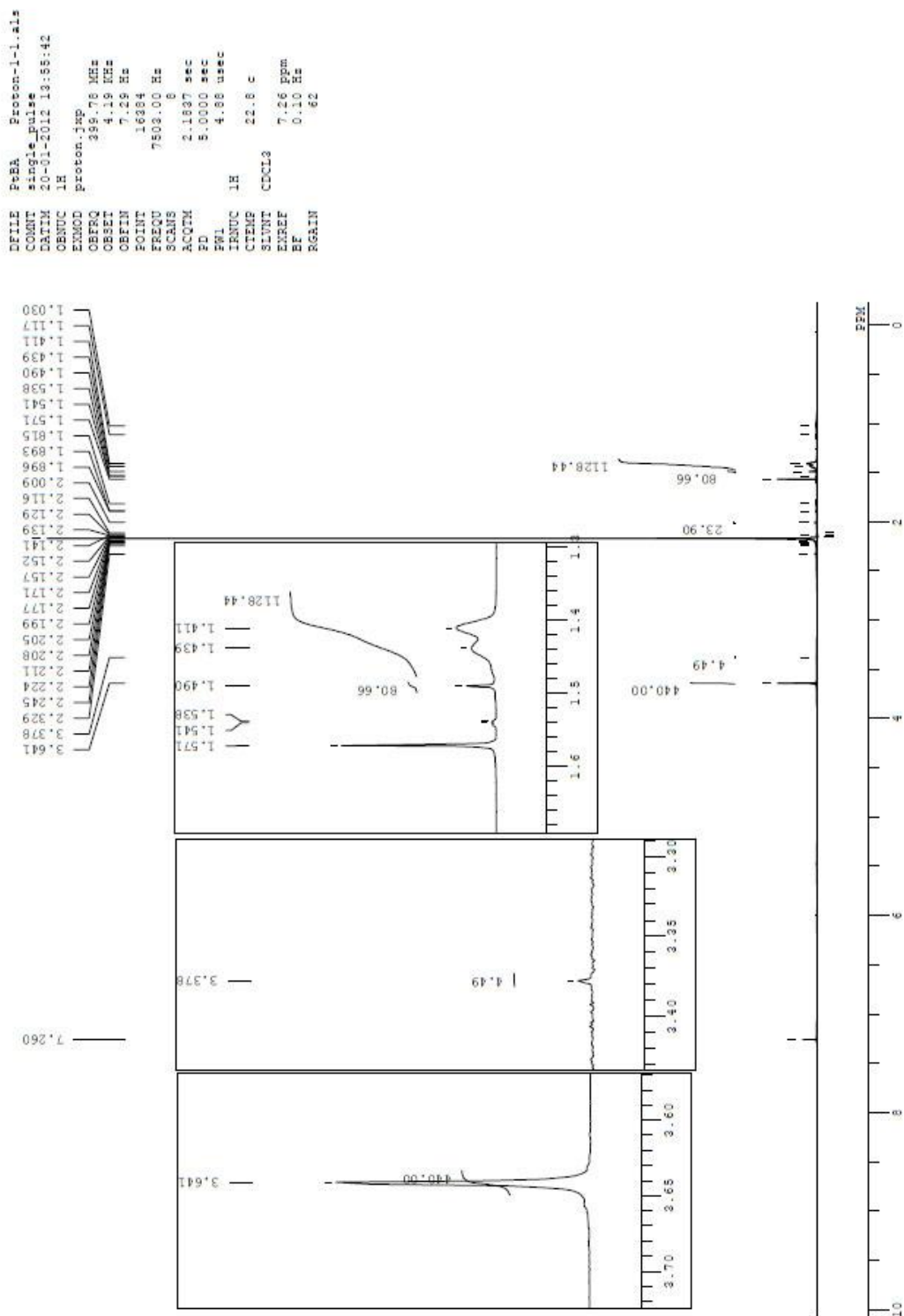
## 2. The synthesis of mesoporous silica film

The mesoporous silica film was prepared from two precursor solutions and the main difference between them was the solvents. One precursor solution used tetrahydrofuran (THF) as a solvent, and the other used ethanol (EtOH). At first, the details on precursor preparation using THF as the solvent were described. 1.0 mL THF, 3.8 mL tetraethoxysilane (TEOS) and 0.92 g HCl solution (pH = 2) were mixed and stirred for 1 h. 0.36 g PEO-*b*-PtBA was dissolved into 3 mL THF. Then, the two solutions were mixed and stirred for 15 min.

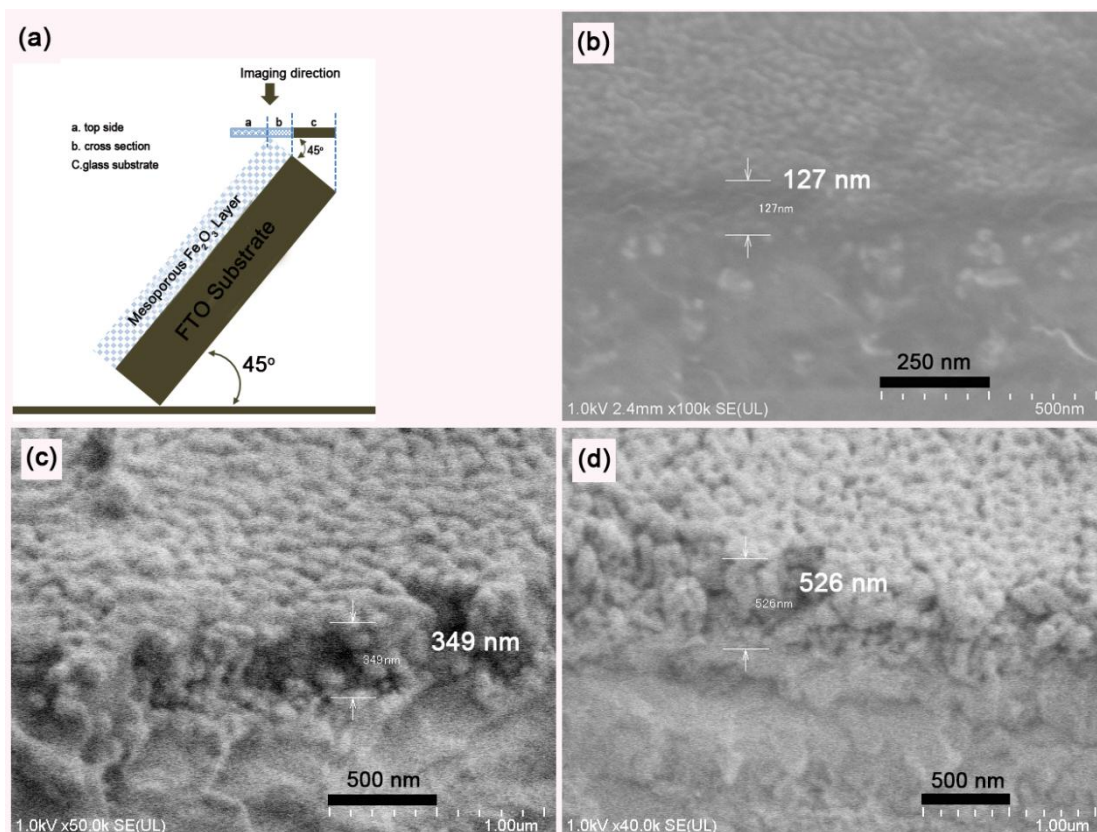
Thereafter, the solution was statically kept for one day aging. Secondly, the details on precursor preparation using EtOH as the solvent were described. 1.5 mL EtOH, 5.7 mL TEOS and 1.38 g HCl solution (pH = 2) were mixed and stirred for 1 h. 0.53 g PEO-*b*-PtBA was dissolved into 4.5 mL EtOH. Then, the two solutions were mixed and stirred for 15 min. Thereafter, the solution was statically kept for one day aging. The mesoporous silica films were prepared by dip-coating (84 mm/min) onto cleaned glass slides. The films were dried at 80 °C for 12 h and then the films were heated in deionized water at 95 °C one day. After drying, the films were calcined in air at 500 °C for 1 h to remove the di-block polymers.

### 3. Characterization

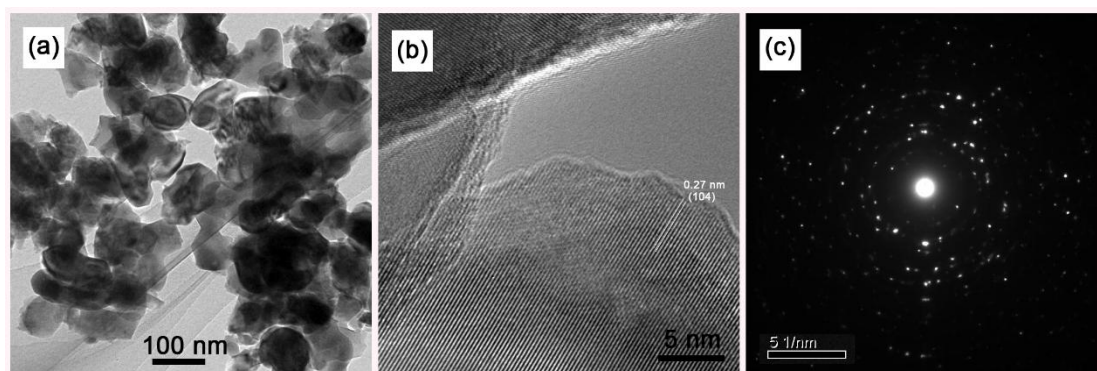
X-ray diffraction (XRD) patterns of as-synthesized nanoporous films were recorded with Rigaku X-ray diffract meter/RINT2500HLR<sup>+</sup> using Cu K $\alpha$  radiation (40kV and 80mA) and the scanning rate was 5 °/min. Scanning electron microscopic (SEM) images were recorded with a Hitachi SU-4300 or SU-8000 field emission electron microscope (FE-SEM). The cleaved nanoporous  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> film with the FTO substrate was fixed by carbon tape and directly used for observations by SU-8000. The cleaved mesoporous silica film with the glass substrate was fixed by carbon tape and SEM measurements were done by SU-4300 after depositing of a thin Pt/Pd layer using a magnetron ion-sputter apparatus. Surface morphology of as-synthesized nanoporous  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> films was also observed by atomic force microscope (AFM) (SII Nano navi 2). Transmission electron microscopic (TEM) images were taken by a JEM-ARM200F with a spherical aberration corrector at an accelerating voltage of 200 kV. Samples were prepared by the following procedures: the film was firstly scraped off from the FTO substrate and then directly dispersed on a Cu grid for TEM observation. The film of M-Fe-1 cannot be well scraped off for TEM sample preparation due to the thin thickness of the film. Electrochemical experiments were carried out in a conventional three-electrode electrochemical cell with a Pt counter electrode and a saturated Ag/AgCl reference electrode and the solution is 0.1 M Na<sub>2</sub>SO<sub>4</sub>. A 500 W Xe lamp (USHIO SX-UI500XQ) was used as a light source.



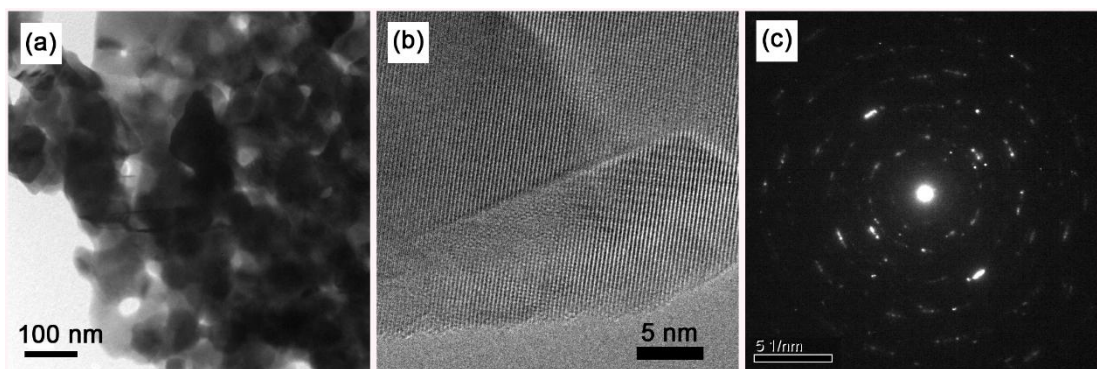
**Fig.1.** The  $^1\text{H}$  NMR ( $\delta_{\text{ppm}}$ ,  $\text{CDCl}_3$ ) spectrum of as-synthesized PEO-b-PtBA.



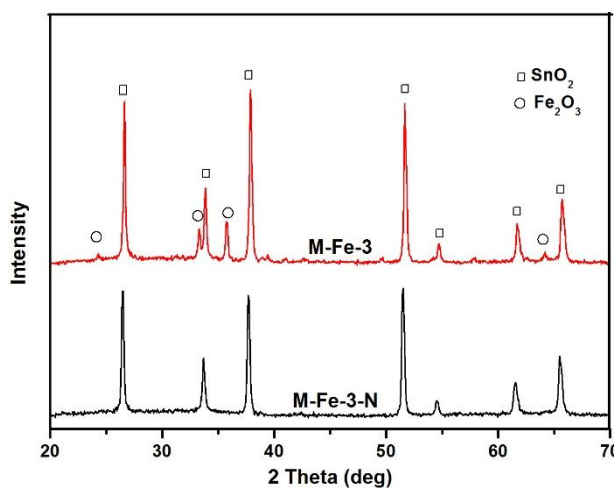
**Fig. 2.** (a) The schematic illustration of SEM imaging and the thickness of nanoporous  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> film should be the length of (b part) multiply  $\sqrt{2}$ ; cross section SEM images of M-Fe-1 (b), M-Fe-2 (c) and M-Fe-3 (d).



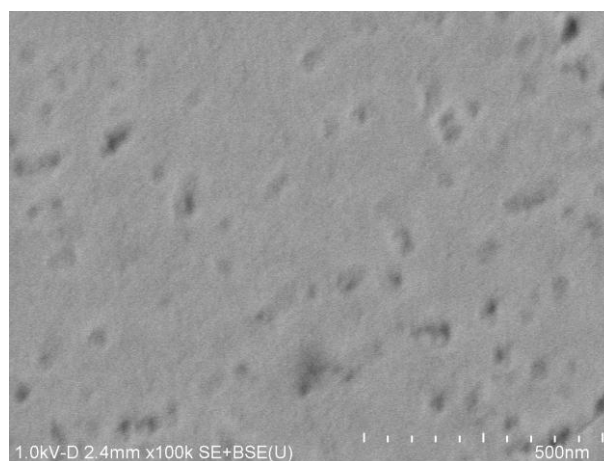
**Fig. 3.** The low magnification (a) and (b) high resolution TEM images of M-Fe-2, and (c) selected area diffraction pattern of M-Fe-2.



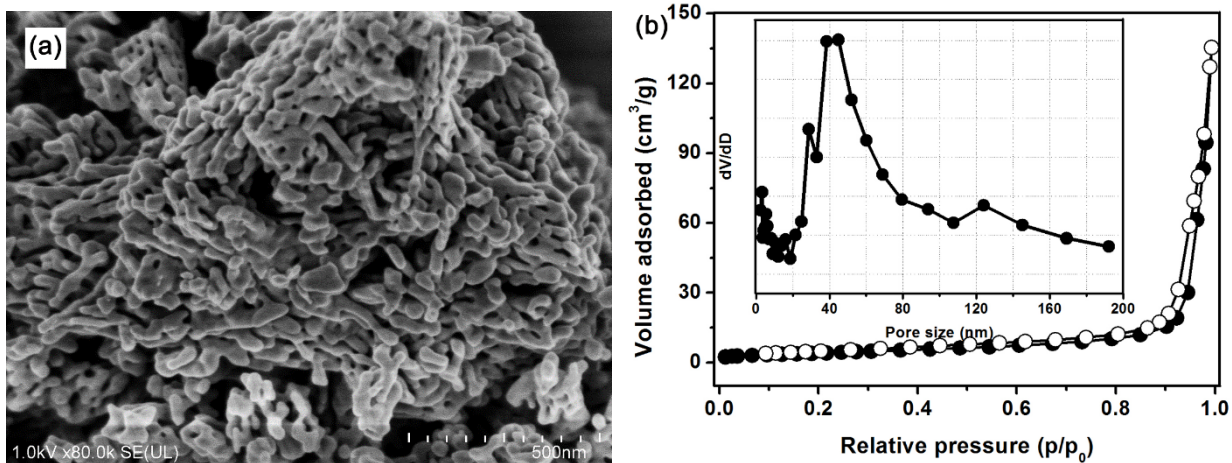
**Fig. 4.** The low magnification (a) and (b) high resolution TEM images of M-Fe-3, and (c) selected area diffraction pattern of M-Fe-3.



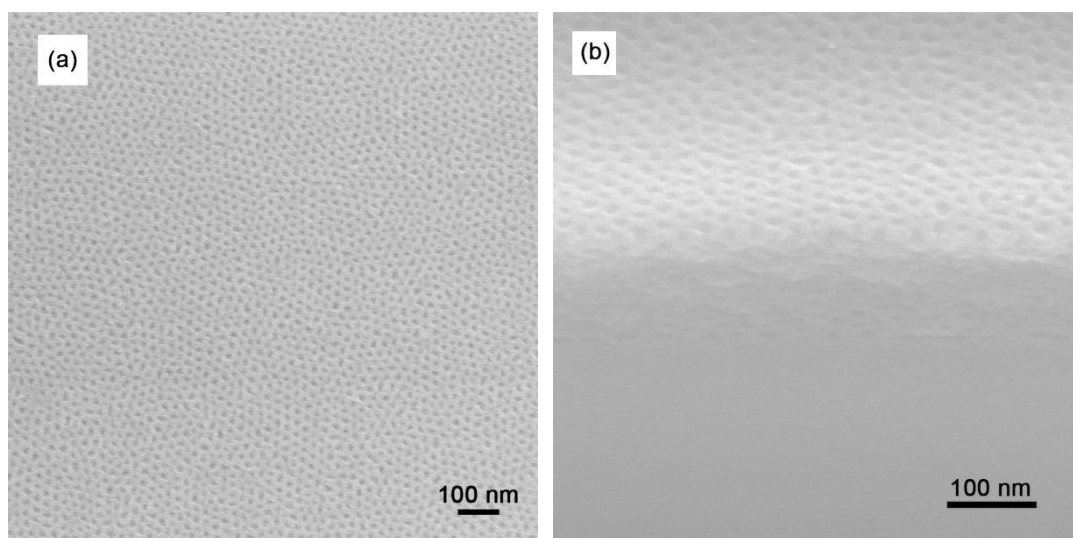
**Fig. 5.** XRD patterns of M-Fe-3-N (after 250 °C heat treatment) and M-Fe-3 (after 700 °C calcination for complete removal of polymer template and crystallization).



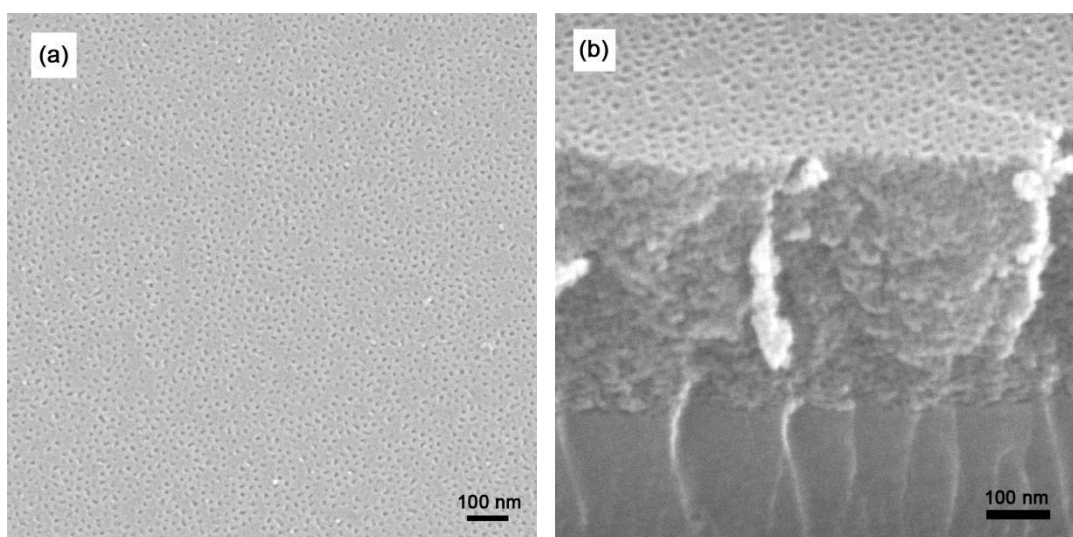
**Fig. 6.** SEM image of M-Fe-3-N (after 250 °C heat treatment).



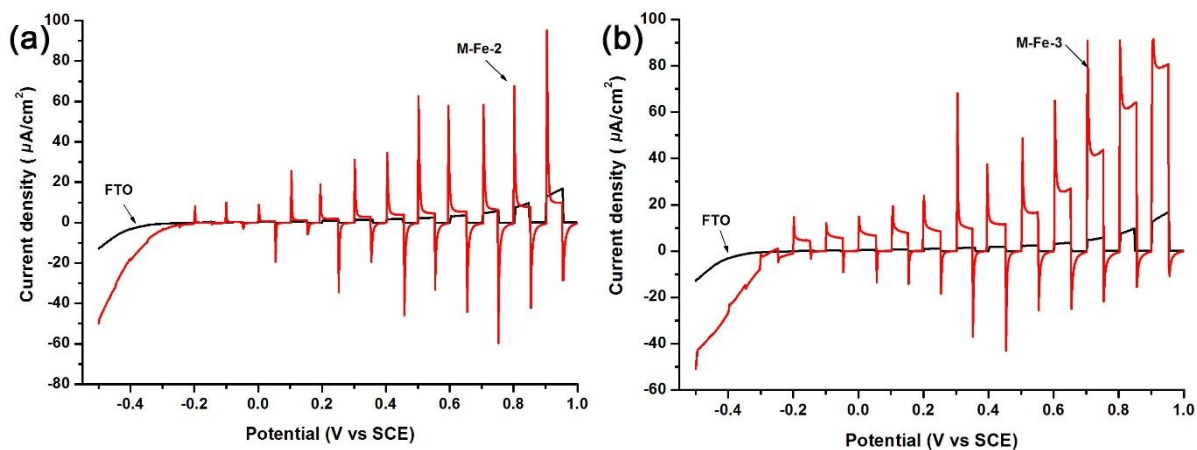
**Fig.7.** (a) SEM image and (b)  $\text{N}_2$  sorption isotherm (pore size distribution (inset)) of crystalline mesoporous  $\alpha$ - $\text{Fe}_2\text{O}_3$  powder.



**Fig.8.** SEM images of M-Si-THF. (a) top-side and (b) cross-section view.



**Fig.9.** SEM images of M-Si-EtOH. (a) top-side and (b) cross-section view.



**Fig. 10.** Photochemical performance of M-Fe-2 (a), M-Fe-3 (b) and the results of bare FTO substrate was also enclosed for reference.

## References

- [1] J. Z. Du, S. P. Armes, *J. Am. Chem. Soc.*, 2005, **127**, 12800-1.
- [2] S. J. Hou, E. L. Chaikof, D. Taton, Y. Gnanou, *Macromolecules*, 2003, **36**, 3874-81.