Supporting information

Ordered mesoporous silica-(ZIF-8) core-shell spheres

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Experimental

Chemicals: Cetyltrimethylammonium bromide (CTABr, >98%, Sigma–Aldrich), sodium metasilicate (Na_2SiO_3, Sigma–Aldrich), and ethylacetate ($CH_3COOC_2H_5$, 99.9% Sigma–Aldrich) were used to synthesize silica spheres. Zinc nitrate hexahydrate ($ZnNO_3{\cdot}6H_2O$, >98%, Sigma-Aldrich) was used as Zn source and 2-methylimidazole ($C_4H_6N_2$, >99%, Sigma-Aldrich) was used as ligand for the synthesis of ZIF-8. Methanol (99.99%) was obtained from Sigma-Aldrich.

Mesoporous silica spheres (MSSs): The molar composition used for the preparation of MSSs was $1.5Na_2SiO_3$:1CTABr:$361H_2O$:$7.4CH_3COOC_2H_5$. For this, 3.92 g CTABr and 2 g of Na_2SiO_3 were dissolved in 70 mL of water. Then, 8 mL of ethylacetate was added under stirring for 30 s. After mixing of the reactants, the solution was kept in a closed polypropylene flask at room temperature for 5 h, and then maintained at 90 ºC for 50 h. The product obtained was filtered in distilled water and ethanol, and calcined at 600 ºC for 8 h with a heating rate of 0.5 K/min to remove the surfactant. At these conditions, MCM-41 pores of about 2.7 nm with stable silica walls between the micelles, as well as non-MCM-41 pores of about 15 nm with unstable or even missing walls due to removal of surfactant micelles were created inside the silica spheres.

Seeding process: An "In-situ" seeding process was developed as follows. Firstly, 0.1 g of MSSs was added to 3.78 g of 2-methylimidazole dissolved in 13.3 g of H_2O, and sonicated for 5 min. Secondly, another 0.1 g of silica spheres were added to a solution of 0.195 g $Zn(NO_3)_2 \cdot 6H_2O$ and 1.3 g H_2O and sonicated for another 5 min. The zinc nitrate solution was then mixed with the 2-methylimidazole solution under stirring for 5 min and the product was collected by centrifuging 3 times with DI water and dried overnight.

Regrowth of seeded MSSs: 0.47 g $Zn(NO_3)_2 \cdot 6H_2O$ was dissolved in 10 mL of MeOH and 10 mL of water. In addition, 1 g 2-methylimidazole was dissolved in 10 mL of MeOH and 0.14 g of "in situ" seeded MSSs was added. The two solutions were sonicated for 5 min and mixed under strong stirring, maintaining the agitation for 2 h. After that, the final product was collected by centrifuging with successively with DI water and MeOH several times, decanted in MeOH to separate the spheres from nano-sized ZIF-8 particles and dried overnight. This process was carried out once for MSS-Z8(1) and twice for MSS-Z8(2).

ZIF-8 crystals: ZIF-8 crystals were synthesized using the same molar ratio as that used for the regrowth of seeded MSSs, but without the addition of MSSs: 0.47 g $Zn(NO_3)_2 \cdot 6H_2O$ was dissolved in 10 mL of MeOH and 10 mL of water. In addition, 1 g 2-methylimidazole was dissolved in 10 mL of MeOH, and the two solutions were mixed and stirred for 2 h. The final product was collected by centrifuging twice with DI water and one time with MeOH, and dried overnight.

Characterization

- **Scanning electron microscopy (SEM)**

The SEM images were collected on an Inspect F scanning electron microscope (FEI).

- **Transmission electron microscopy (TEM)**

It was necessary to embed a portion of the samples in an Epofix^{TM} cold-setting embedding resin. Consequently, in volume proportion, 15 parts of embedding resin and 2 parts of hardener were mixed, while the curing time was 8 h at room temperature, so that the cross section pieces could be sliced into the desired sections thin enough to be transparent for the electron beam. The slices were cut at 30-60 nm thickness using a Leica EMUC7 ultramicrotome with a Standard Ultraknife 35º with a 3 mm diamond blade able to slice hard materials such as molecular sieves. The sliced sections were stained in aqueous solution, placed on carbon copper grids and subsequently observed at 200 kV in a JEOL-2000 FXII TEM.

- **X-ray diffraction (XRD) and low angle X-ray diffraction (LA-XRD)**

The materials were characterized by X-ray diffraction (XRD) at room temperature on a D-Max Rigaku diffractometer with a copper anode and a graphite monochromator to select Cu-$K_{\alpha 1}$ radiation (λ= 1.5418 Å). Low angle X-ray diffraction (LA-XRD) spectra were recorded on a Siemens Diffraktometer D5000, using CuKα radiation.

- **Adsorption isotherms**

Nitrogen adsorption-desorption isotherms were measured at 77 K using a *porosity analyzer* (TriStar 3000, Micromeritics Instrument Corp.). The samples were outgassed with a heating rate of 10 ºC/min until 250 ºC and maintained for 8 h. BET

specific surface areas were measured from the adsorption branches in the relative pressure range of 0.05-0.25 and the pore size distributions were calculated using the Barrett-Joyner-Halenda (BJH) model from the adsorption branches. Argon adsorption-desorption isotherms were measured in Micrometrics ASAP 2020 equipment to obtain the microporous size distribution using the Horvath-Kawazoe model.

- **Thermogravimetry (TG) and differential thermal analysis (DTA)**

TG and DTA measurements were performed simultaneously on Mettler Toledo TGA/DTA 1 Start system equipment. Samples (10 mg) placed in 70 μL alumina pans were heated in air flow (64 cm^3(STP)/min) up to 700 °C for calculating the percentage of ZIF-8 and MSSs in the samples, and in N_2 flow (64 cm^3(STP)/min) up to 450 °C for the n-decane and water adsorption experiments. Both were performed at a heating rate of 10 ^oC/min.

Supplementary Figures

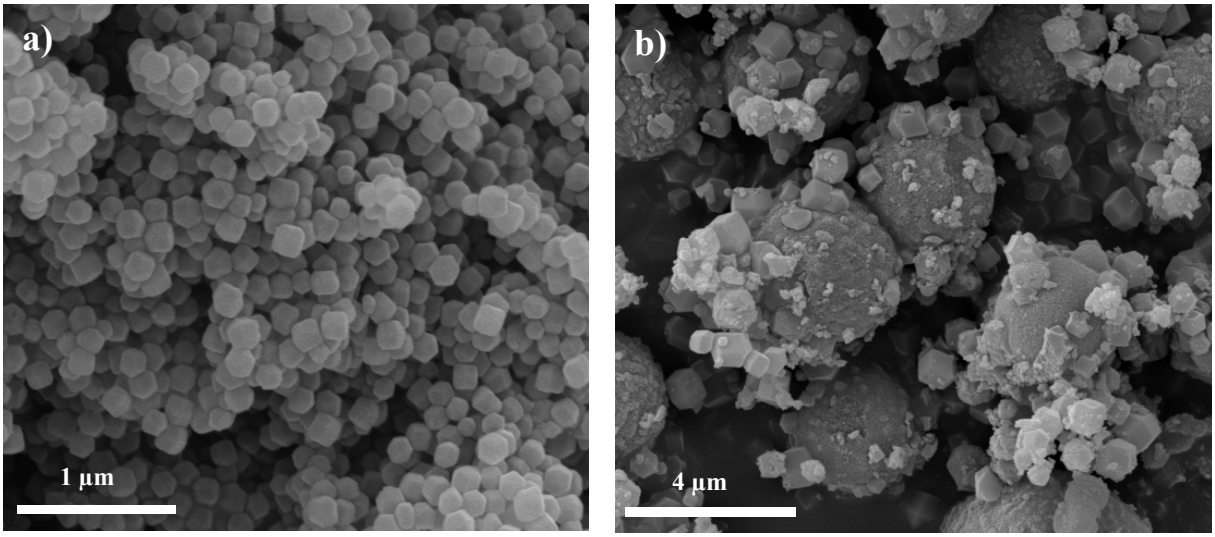

Fig. S1. SEM images of: a) ZIF-8 crystals, b) MSS-Z8(1) without seeding process.

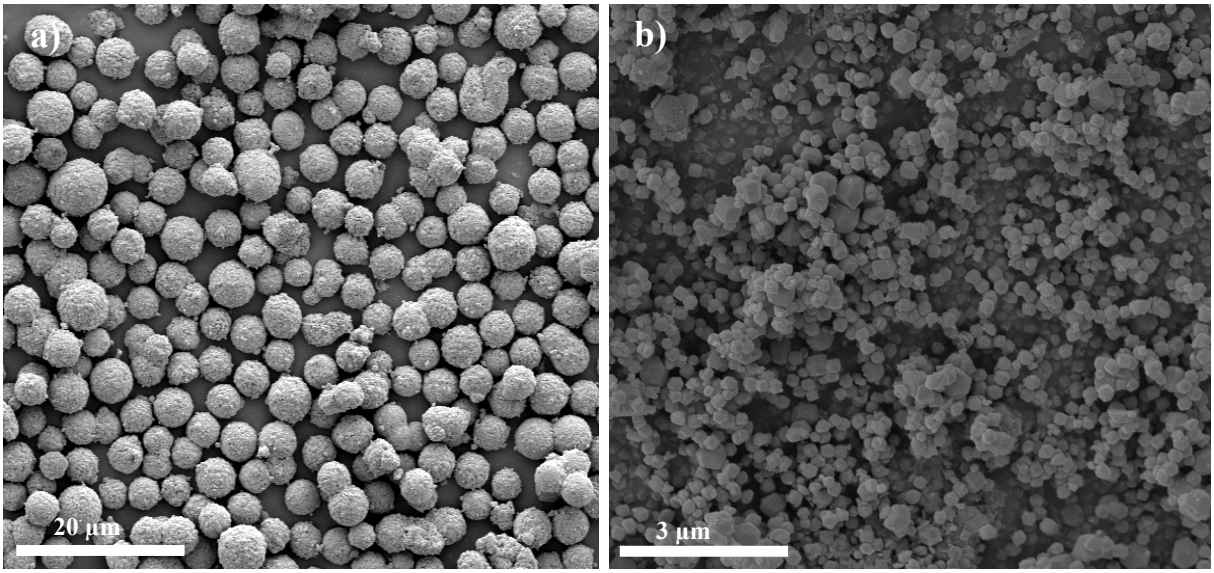

Fig. S2. SEM images of MSS-Z8(1) after decantation: a) bottom solution, b) supernatant solution. ZIF-8 crystals formed outside the spheres (supernatant solution) represent 22 wt% of the sample.

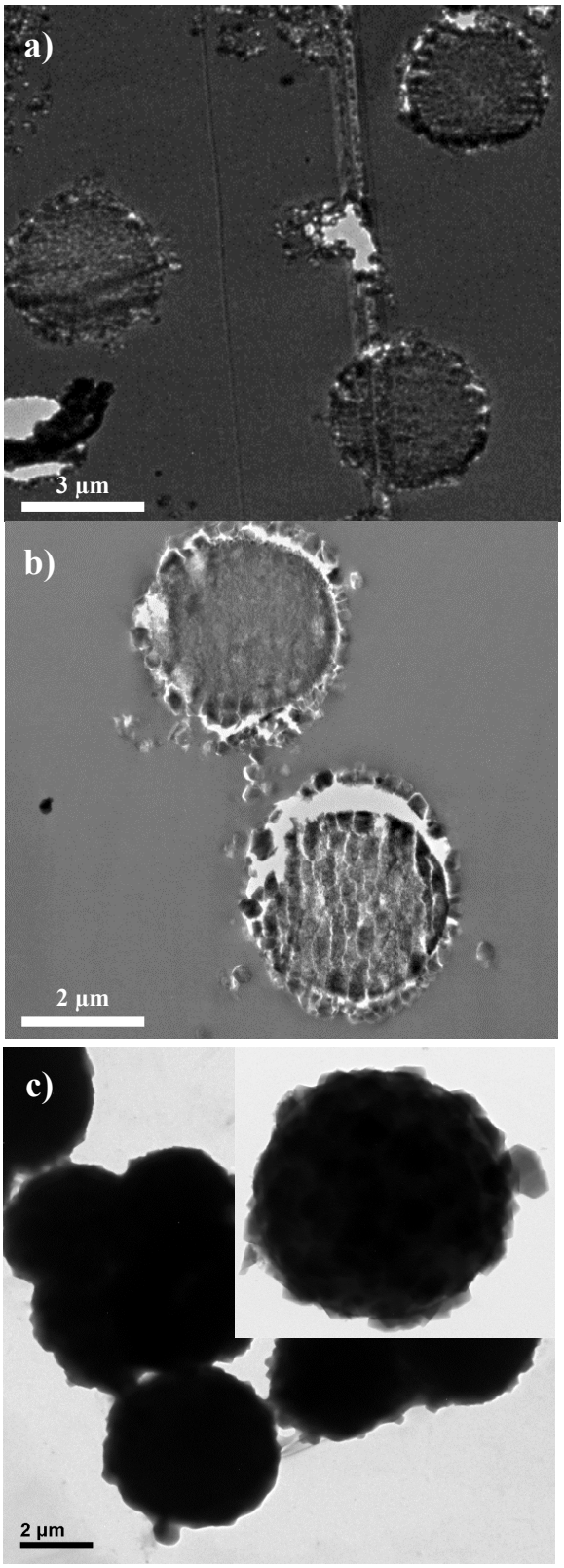

Fig. S3. TEM images of MSS-Z8(1) before decantation: a, b) embedded in epoxy resin and cut with ultramicrotome, c) powder dispersion. ZIF-8 layer is separated from the silica sphere, due to the preparation process, in which a Standard Ultraknife 35º with a 3 mm diamond blade is used to prepare the slice of 30-60 nm thickness.

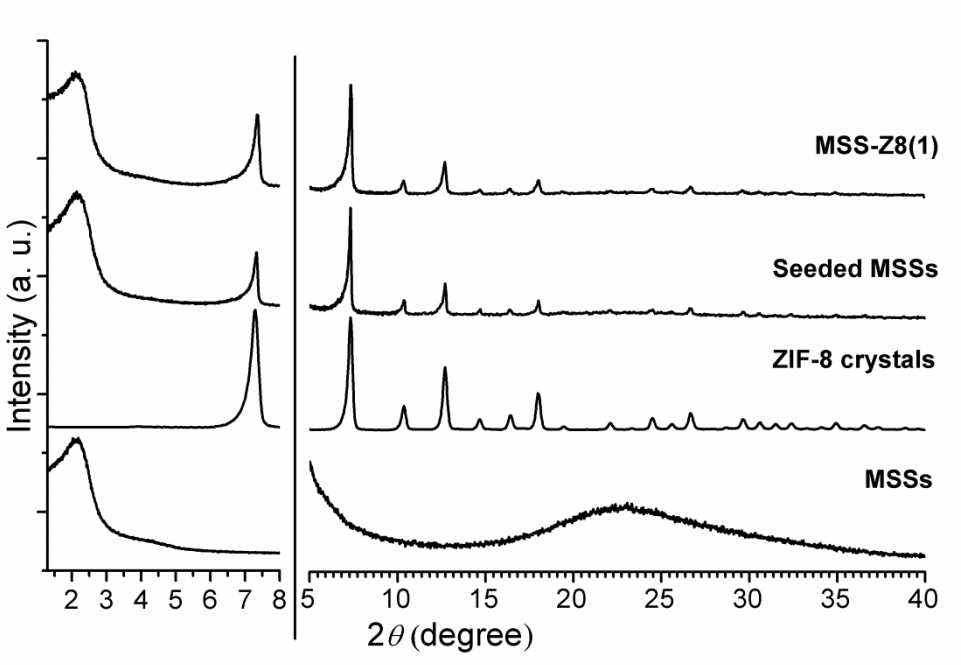

Fig. S4. LA-XRD (left) and XRD (right) patterns of MSSs, ZIF-8 crystals (see experimental for synthesis procedure), seeded MSSs and MSS–Z8(1).

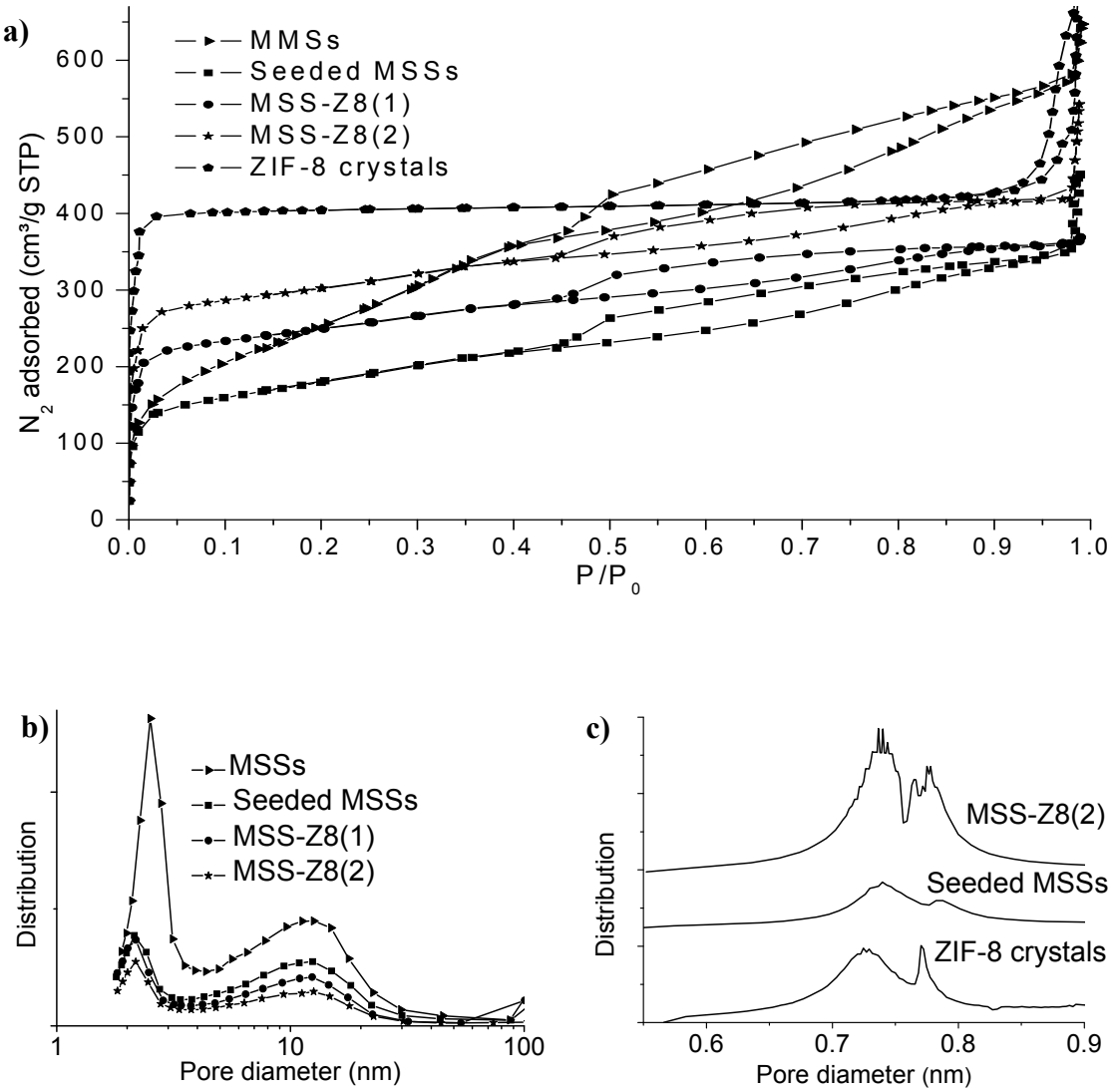

Fig. S5. a) Nitrogen sorption isotherms of MSSs, seeded MSSs, MSS-Z8(1), MSS-Z8(2) and ZIF-8 crystals, b) pore size distribution curves of MSSs, seeded MSSs, MSS-Z8(1) and MSS-Z8(2), by BJH method using N_2, c) pore size distribution curves of MSSs, seeded MSSs and MSS-Z8(2), by HK method using Ar.

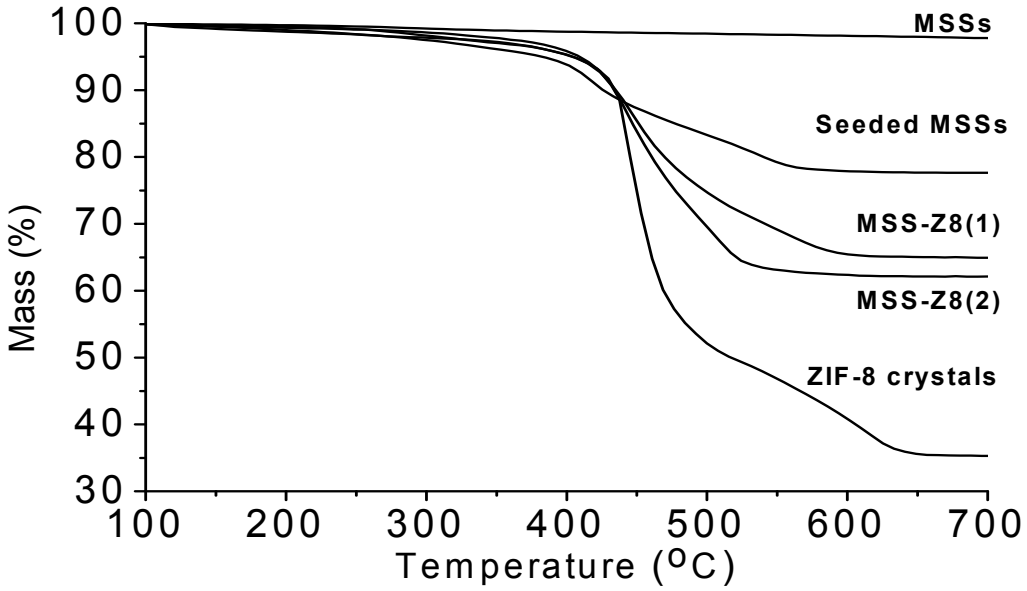

Fig. S6. TGA curves of the as-synthesized samples.