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Water intrusion-extrusion experiments in ZIF-8: Impacts of the shape and particle size on the energetic performances

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1. Experimental Section

1.1. Chemical reactants and solvents

The following chemicals were used as received without further purification: zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 99.9%, Sigma-Aldrich), 2-methylimidazole (HMeIm, 99%, abcr), hexadecyltrimethyl ammonium bromide (CTAB, 98%, Fluka), *N,N*-dimethylformamide (DMF, 99.8%, Sigma-Aldrich), ammonium hydroxide solution (NH_4OH, 33% aqueous solution, Riedel-de Haën) and methanol (MeOH, 99.8%, Sigma-Aldrich).

1.2. Synthesis of ZIF-8 nanospheres (NS-ZIF-8)

The *ZIF-8 nanospheres* were synthesized according to a procedure similar to that described in litterature.[1] 44.3 g (539.4 mmol) of HMeIm and 1.6 g (5.4 mmol) of $Zn(NO_3)_2 \cdot 6H_2O$ were dissolved in 150 and 66.7 g of deionized water, respectively. Afterwards, zinc nitrate and HMeIm solutions were quickly mixed together under stirring. The final synthesis solution had the following molar composition 1 Zn : 100 HMeIm : 2233 H_2O. The mixture was then stirred at room temperature for 24 h. The product was collected by centrifugation and washed 6 times with MeOH. The resulting ZIF-8 sample was dried at room temperature overnight.

1.3. Synthesis of rhombic dodecahedron ZIF-8 nanoparticles (NRD-ZIF-8)

The *rhombic dodecahedron ZIF-8 nanoparticles* were synthesized according to a procedure similar to that described in reference.[2] 2.659 g (8.937 mmol) of $Zn(NO_3)_2 \cdot 6H_2O$ were first dissolved in 121.35 g of DMF and then mixed with 1.996 g (5.474 mmol) of CTAB under stirring for 5 min at room temperature. Then, 4.508 g (54.902 mmol) of HMeIm were dissolved in 121 g of DMF. The zinc nitrate and 2-methylimidazole solutions were mixed and stirred for 5 min at room temperature. The final molar composition was 1 Zn : 6.14 HMeIm : 0.61 CTAB : 371 DMF : 18.4 H_2O. The resulting synthesis suspension was transferred into Teflon®-lined autoclaves for hydro-solvothermal treatment at 120 °C for 6 h. Then, the particles were collected by centrifugation, washed 6 times with MeOH at room temperature. The resulting ZIF-8 sample was dried at room temperature overnight.

1.4. Synthesis of ZIF-8 nanocubes (NC-ZIF-8)

The *ZIF-8 nanocubes* were synthesized according to a procedure previously published.[2] 0.907 g (3.02 mmol) of $Zn(NO_3)_2 \cdot 6H_2O$ was first dissolved in 91.5 g of deionized water and mixed with 0.0562 g (0.154 mmol) of CTAB under stirring for 5 min at room temperature. Then, 13.48 g (164.25 mmol) of HMeIm were dissolved in 150 g of deionized water. After that, the zinc nitrate and 2-methylimidazole solutions were mixed and stirred for 5 min at room temperature. The final molar composition was 1 Zn : 54.3 HMeIm : 0.05 CTAB : 4437 H_2O. The resulting synthesis solution was transferred into Teflon®-lined autoclaves for hydrothermal synthesis at 120 °C for 6 h. After synthesis, the particles were collected by centrifugation, washed 3 times with MeOH at room temperature, then 3 times with DMF at 120 °C, and finally again 3 times with MeOH at room temperature. The resulting ZIF-8 sample was dried at room temperature overnight.

1.5. Synthesis of rhombic dodecahedron ZIF-8 microparticles (MRD-ZIF-8)

The *rhombic dodecahedron ZIF-8 microparticles* were synthesized according to a procedure similar to that described in litterature.[3] 0.87 g (2.925 mmol) of $Zn(NO_3)_2 \cdot 6H_2O$ was first dissolved in 91.5 g of deionized water. Then, 13.62 g (165.875 mmol) of HMeIm were dissolved in 30 g of deionized water. After that, the zinc nitrate and 2-methylimidazole solutions were mixed and stirred for 5 min at room temperature. The final mixture had the following molar composition 1 Zn : 56.72 HMeIm : 4560 H_2O and was transferred into Teflon®-lined autoclaves for hydrothermal treatment at 120 °C for 6 h. The particles were collected by centrifugation and washed 6 times with MeOH at room temperature. The resulting ZIF-8 sample was dried at room temperature overnight.

1.6. Synthesis of ZIF-8 microcubes with truncated edges (MCTE-ZIF-8)

The *ZIF-8 microcubes with truncated edges* were synthesized according to the procedure published by He *et al.*[4] 0.99 g of HMeIm and 1.79 g of $Zn(NO_3)_2 \cdot 6H_2O$ were dissolved in 9.93 g of NH_4OH solution and in 9.72 g of deionized water, respectively. After that, the two solutions were mixed together under stirring. The final synthesis solution had the following molar composition 1 Zn : 2 HMeIm : 32 NH_4OH : 157 H_2O. The solution which quickly turned into milk-like suspension was stirred for 10 min at room temperature to complete the crystallization. The product was

collected by centrifugation and washed with deionized water four times until the final product reaches pH value of 7, then 4 more washings with MeOH took place. The resulting ZIF-8 sample was dried at room temperature overnight.

2. Characterization techniques

2.1. Powder X-ray Diffraction

X-ray diffraction patterns of the different samples were recorded in a Debye-Scherrer geometry on a STOE STADI-P diffractometer equipped with a curved germanium (111), primary monochromator, and a linear position-sensitive detector (6° in 2θ) using Cu $K\alpha_1$ radiation (λ = 1.5406 Å). Measurements were achieved for 2θ angle values in the 5-50 range, step 0.04° in 2θ.

2.2. Scanning Electron Microscopy

The size and the shape of the crystals were determined by scanning electron microscopy (SEM) using a Philips XL 30 FEG microscope.

2.3. Particle Size Distribution

The particle size distribution of ZIF-8 crystals was determined by manual measurements from the SEM micrographs.

2.4. Nitrogen Adsorption-Desorption Measurements

Nitrogen adsorption-desorption isotherms were performed at 77 K using a Micromeritics ASAP 2420 apparatus. Prior to the adsorption measurements, the samples were outgassed at 200 °C overnight under vacuum. The specific surface areas (S_{BET} and S_L) and microporous volume (V_μ), before and after water intrusion-extrusion experiments, were calculated using the BET, in the $0.0003 \leq p/p° \leq 0.006$ range, Langmuir (in the same range as BET surface) and *t*-plot methods, respectively.

2.5. Thermogravimetric Analyses

Thermogravimetric (TG) analyses were carried out on a TG Mettler Toledo STARe apparatus, under air flow, with a heating rate of 2 °C min^{-1} from 30 to 900 °C.

2.6. Water intrusion-extrusion experiments under high pressure

The intrusion-extrusion experiments of water in ZIF-8 samples were performed at room temperature using a modified mercury porosimeter (Micromeritics Model Autopore IV) as described in our previous works.[5] ZIF-8 (*i.e.*, NRD-ZIF-8, NS-ZIF-8, NC-ZIF-8, MRD-ZIF-8, and MCTE-ZIF-8) powders were directly introduced in the cell. The values of the intrusion (P_{int}) and

extrusion (P_{ext}) pressures correspond to that of the half volume total variation. The start intrusion pressure ($P_{1\ int}$) corresponds to the start of intrusion step and the final extrusion pressure ($P_{2\ ext}$) corresponds to the end of extrusion step when the water molecules are completely expelled from the porosity. Pressure is expressed in megapascals (MPa) and volume variation in milliliters per gram of sample (mL g^{-1}).

3. Particle Size Distribution

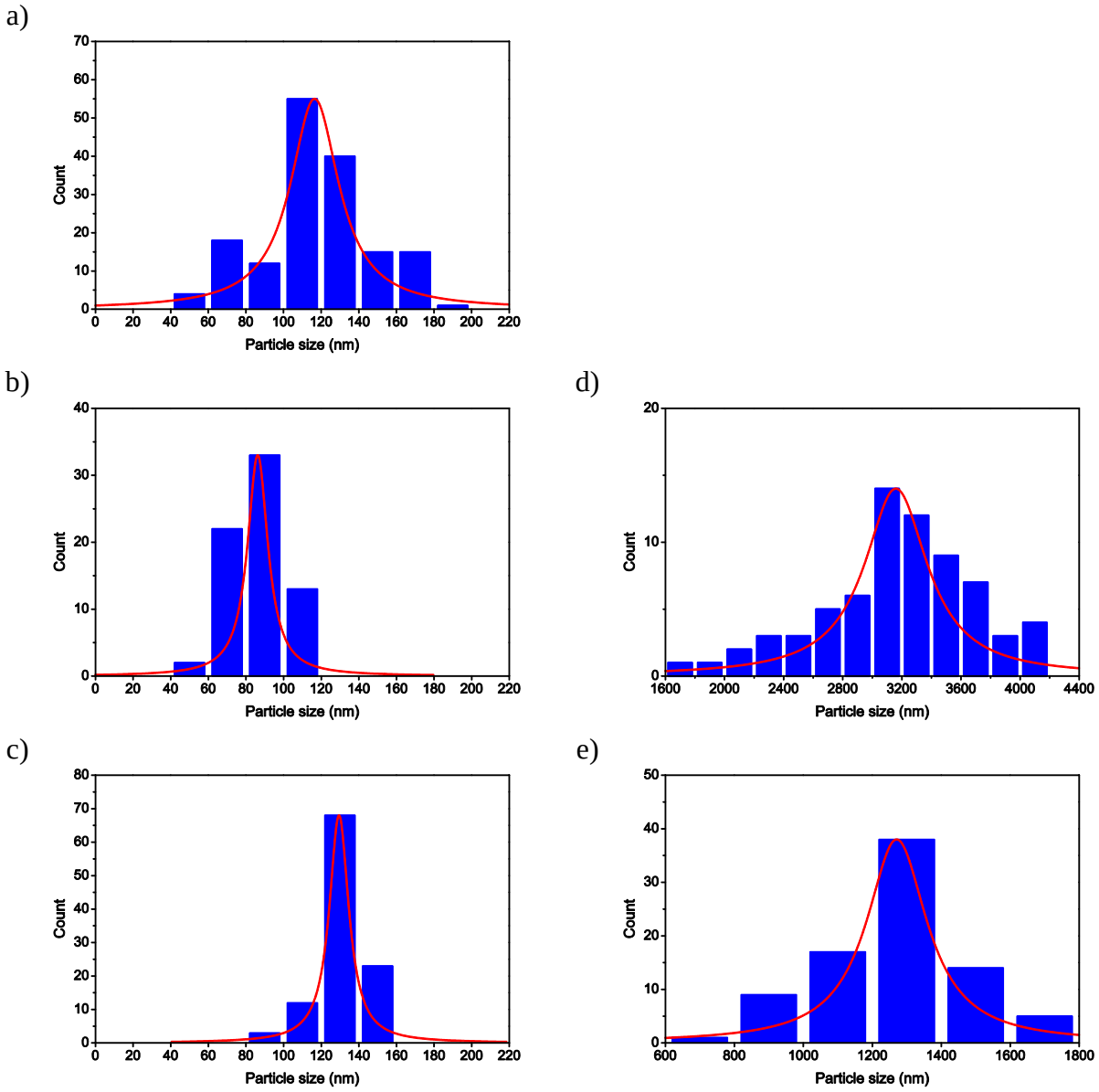


Fig. S1 Histograms of particle size distribution (PSD) for (a) nanometer-sized spherical crystals (NS-ZIF-8 sample), (b) nanometer-sized rhombic dodecahedron crystals (NRD-ZIF-8 sample), (c) nanometer-sized cubic crystals (NC-ZIF-8 sample), (d) micrometer-sized rhombic dodecahedron crystals (MRD-ZIF-8 sample) and (e) micrometer-sized cubic crystals with truncated edges (MCTE-ZIF-8 sample). Additional Lorentzian fit is also given for each PSD.

4. Stability of ZIF-8 framework upon high pressure intrusion-extrusion of water

4.1. X-Ray Diffraction

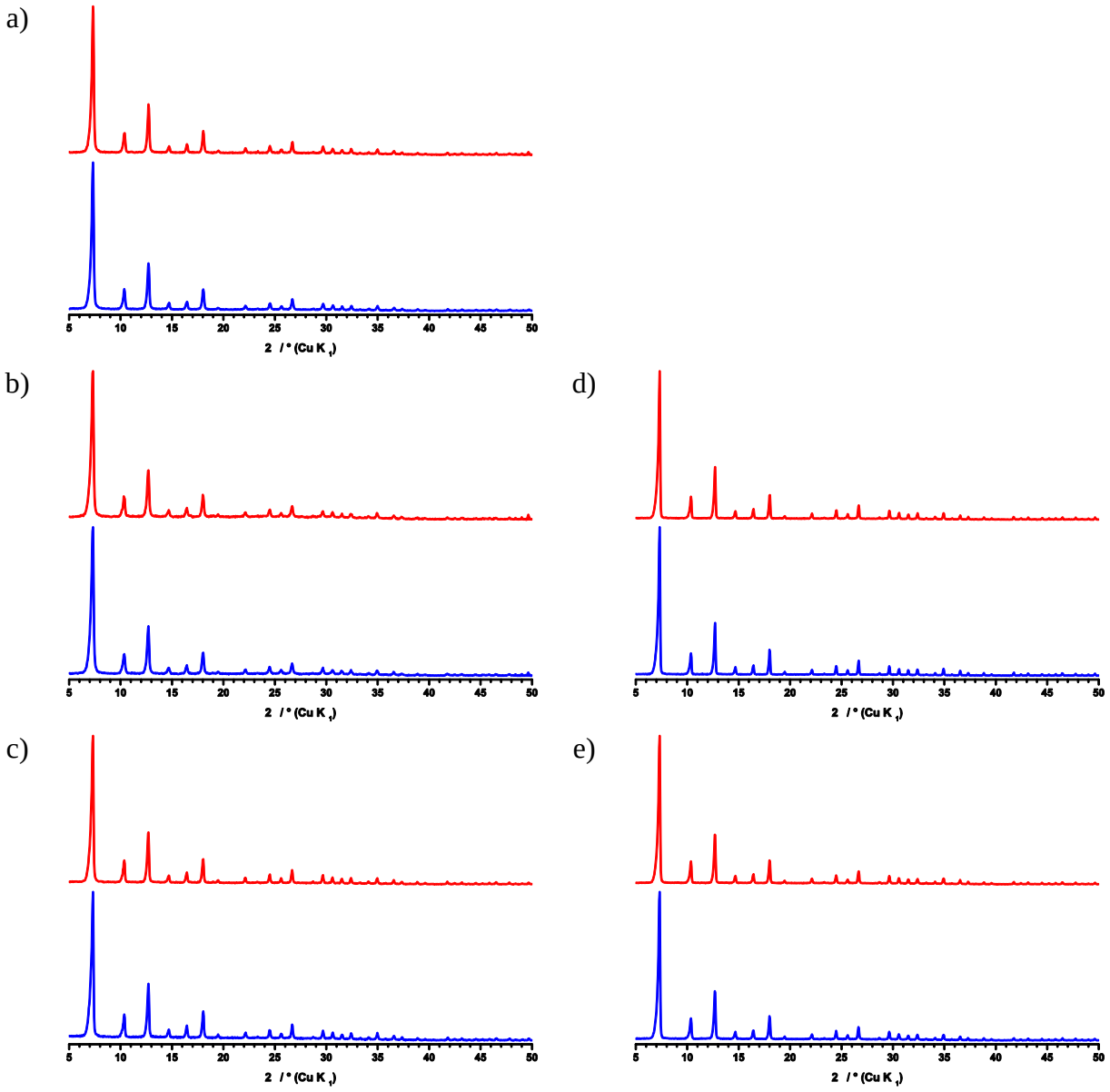
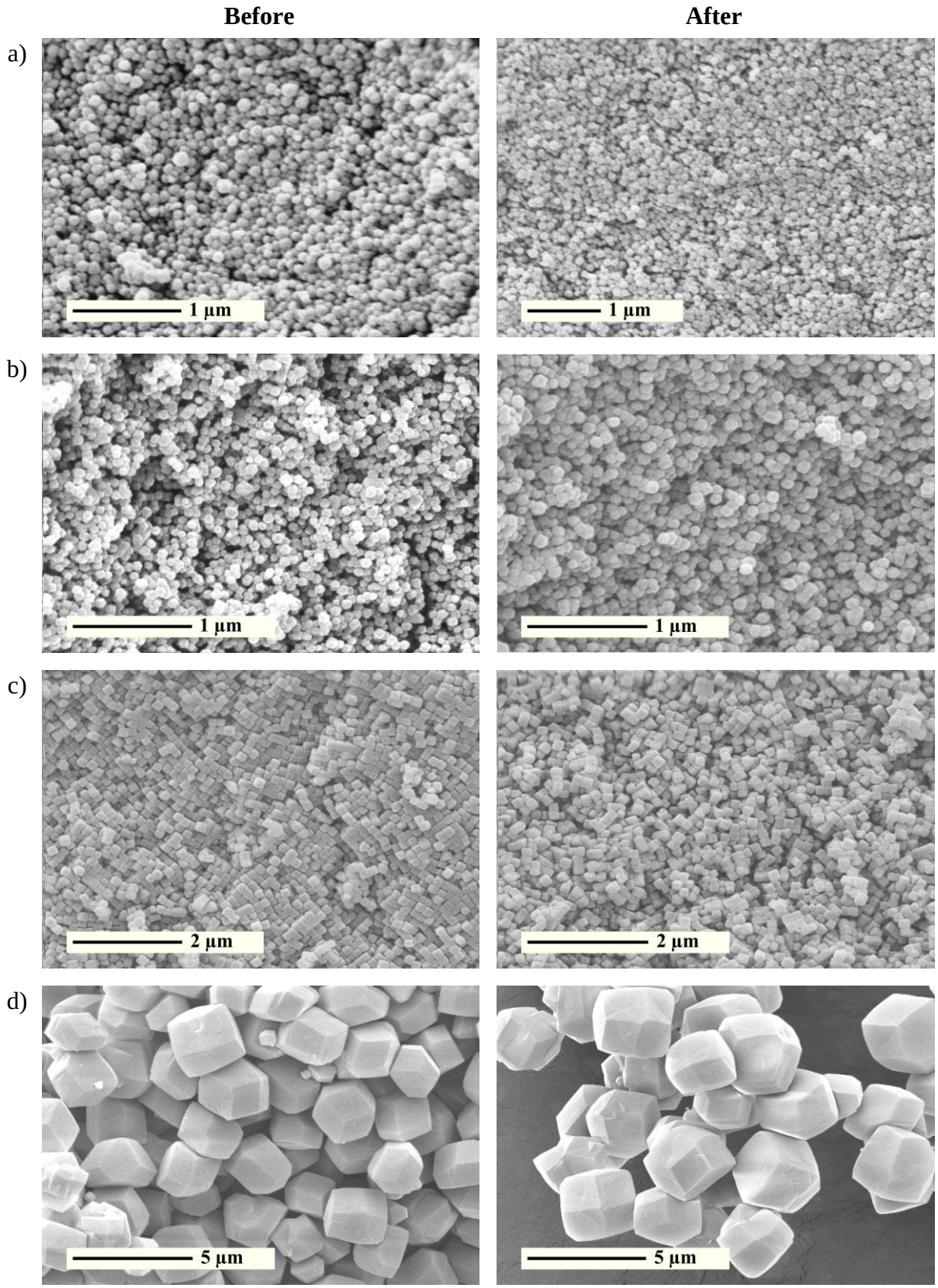


Fig. S2 X-ray diffraction patterns before (blue) and after (red) three water intrusion-extrusion cycles of (a) nanometer-sized spherical crystals (NS-ZIF-8 sample), (b) nanometer-sized rhombic dodecahedron crystals (NRD-ZIF-8 sample), (c) nanometer-sized cubic crystals (NC-ZIF-8 sample), (d) micrometer-sized rhombic dodecahedron crystals (MRD-ZIF-8 sample) and (e) micrometer-sized cubic crystals with truncated edges (MCTE-ZIF-8 sample).

4.2. Scanning Electron Microscopy



e)

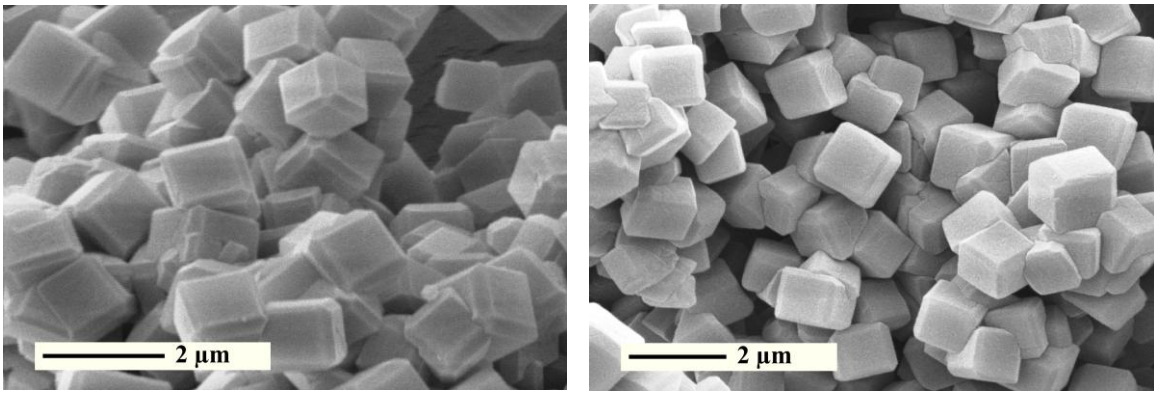


Fig. S3 SEM micrographs before (left) and after (right) three water intrusion-extrusion cycles of (a) nanometer-sized spherical crystals (NS-ZIF-8 sample), (b) nanometer-sized rhombic dodecahedron crystals (NRD-ZIF-8 sample), (c) nanometer-sized cubic crystals (NC-ZIF-8 sample), (d) micrometer-sized rhombic dodecahedron crystals (MRD-ZIF-8 sample) and (e) micrometer-sized cubic crystals with truncated edges (MCTE-ZIF-8 sample).

4.3. N_2 Adsorption-Desorption Measurements

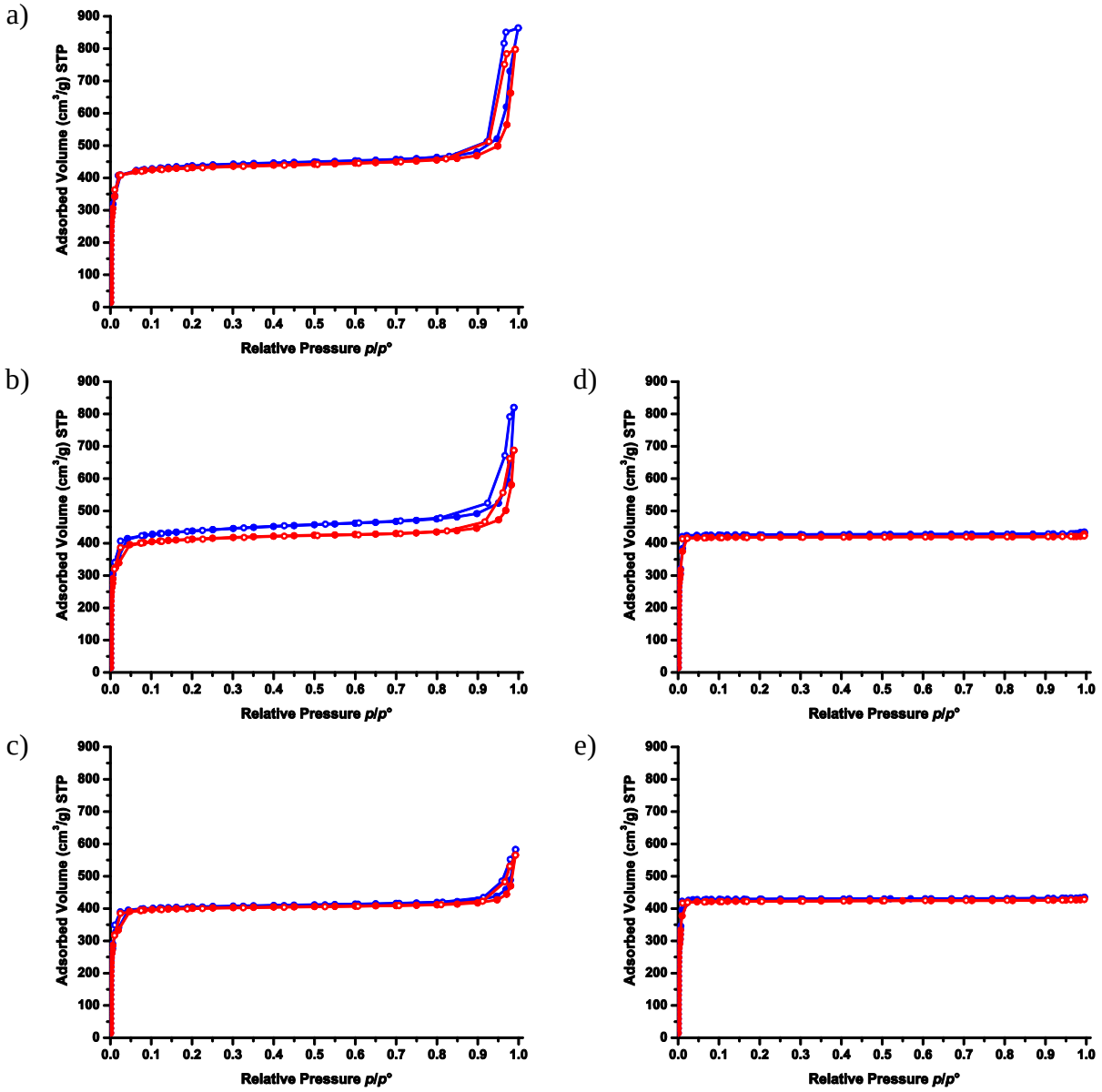


Fig. S4 N_2 adsorption-desorption isotherms at 77 K before (blue) and after (red) three water intrusion-extrusion cycles of (a) nanometer-sized spherical crystals (NS-ZIF-8 sample), (b) nanometer-sized rhombic dodecahedron crystals (NRD-ZIF-8 sample), (c) nanometer-sized cubic crystals (NC-ZIF-8 sample), (d) micrometer-sized rhombic dodecahedron crystals (MRD-ZIF-8 sample) and (e) micrometer-sized cubic crystals with truncated edges (MCTE-ZIF-8 sample). (Filled symbols: adsorption, open symbols: desorption)

Table S1 N_2 adsorption-desorption data before and after three intrusion-extrusion cycles of the nanometer-sized spherical crystals (NS-ZIF-8 sample), nanometer-sized rhombic dodecahedron crystals (NRD-ZIF-8 sample), nanometer-sized cubic crystals (NC-ZIF-8 sample), micrometer-sized rhombic dodecahedron crystals (MRD-ZIF-8 sample) and micrometer-sized cubic crystals with truncated edges (MCTE-ZIF-8 sample).

Samples	Non-intruded samples			Intruded samples		
	V_μ (cm^3/g)	S_{BET} (m^2/g)	S_L (m^2/g)	V_μ (cm^3/g)	S_{BET} (m^2/g)	S_L (m^2/g)
NS-ZIF-8	0.66	1359	1360	0.65	1346	1336
NRD-ZIF-8	0.66	1330	1337	0.64	1265	1273
NC-ZIF-8	0.64	1261	1269	0.64	1246	1253
MRD-ZIF-8	0.66	1390	1374	0.65	1344	1350
MCTE-ZIF-8	0.66	1405	1407	0.65	1360	1366

4.4. Thermogravimetric Analyses

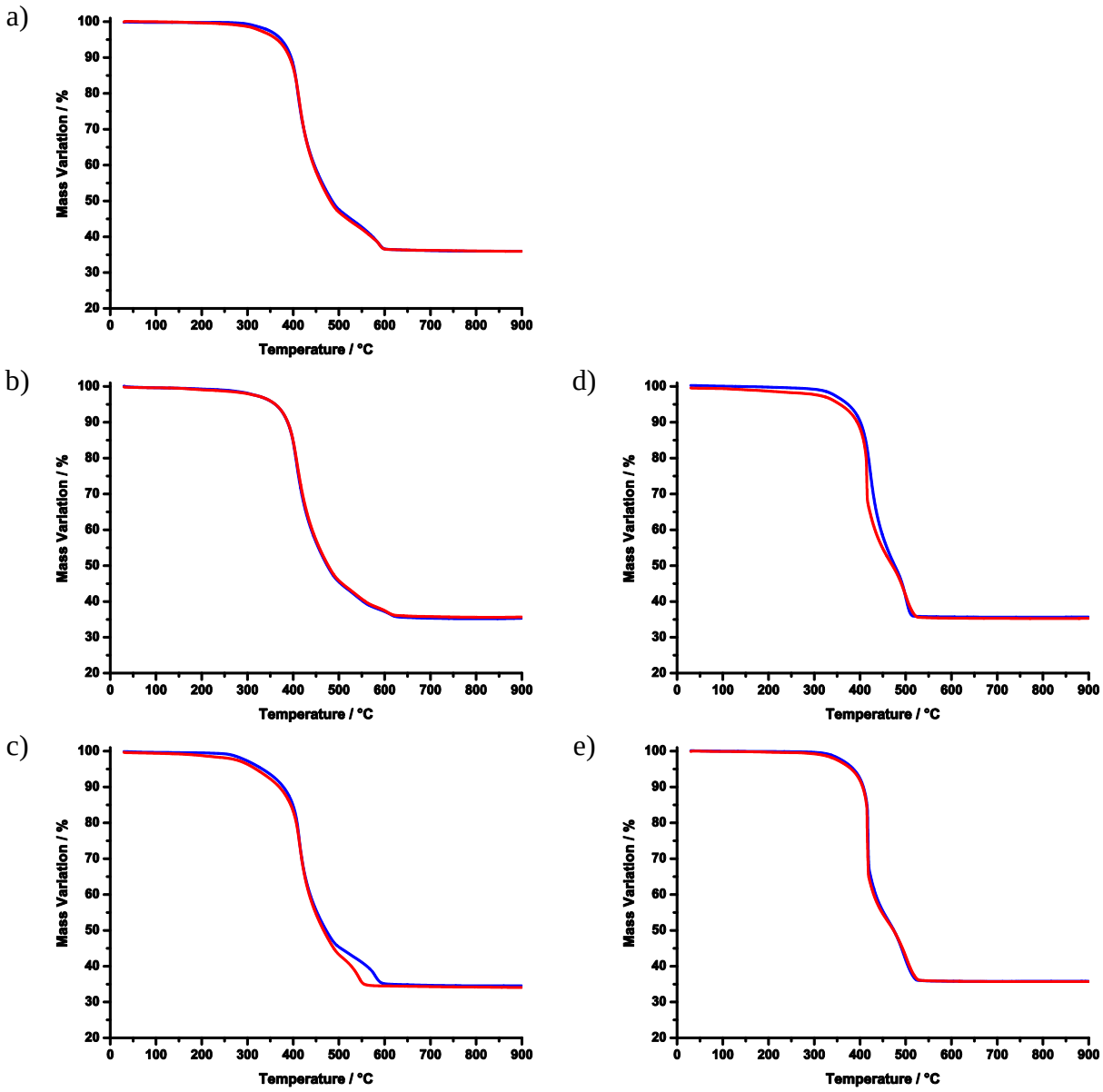


Fig. S5 TG curves before (blue) and after (red) three water intrusion-extrusion cycles of (a) nanometer-sized spherical crystals (NS-ZIF-8 sample), (b) nanometer-sized rhombic dodecahedron crystals (NRD-ZIF-8 sample), (c) nanometer-sized cubic crystals (NC-ZIF-8 sample), (d) micrometer-sized rhombic dodecahedron crystals (MRD-ZIF-8 sample) and (e) micrometer-sized cubic crystals with truncated edges (MCTE-ZIF-8 sample).

5. References

1 S. Tanaka, K. Kida, M. Okita, Y. Ito and Y. Miyake, *Chem. Lett.*, 2012, **41**, 1337.

2 Z. Li and H. C. Zeng, *Chem. Mater.*, 2013, **25**, 1761.

3 Y. Pan, D. Heryadi, F. Zhou, L. Zhao, G. Lestari, H. Su and Z. Lai, *CrystEngComm*, 2011, **13**, 6937.

4 M. He, J. Yao, Q. Liu, K. Wang, F. Chen and H. Wang, *Microporous Mesoporous Mater.*, 2014, **184**, 55.

5 G. Ortiz, H. Nouali, C. Marichal, G. Chaplais and J. Patarin, *Phys. Chem. Chem. Phys.*, 2013, **15**, 4888.