## **Supporting Information**

# Liquid Intrusion into Zeolitic Imidazolate Framework-7 Nanocrystals: Exposing the Roles of Phase Transition and Gate Opening to Enable Energy Absorption Applications

Yueting Sun,<sup>†</sup> Yibing Li,<sup>‡</sup> and Jin-Chong Tan<sup>\*,†</sup>

<sup>†</sup>Multifunctional Materials & Composites (MMC) Laboratory, Department of Engineering Science, University of Oxford, Parks Road, Oxford OX1 3PJ, United Kingdom <sup>‡</sup>State Key Laboratory of Automotive Safety and Energy, Tsinghua University, Beijing, 100084, P.R. China

\*Correspondence to: jin-chong.tan@eng.ox.ac.uk

#### **Experimental Methods**

#### 1. Materials synthesis

#### 1.1 Nano-sized ZIF-7 crystals

Nano-sized ZIF-7 was synthesized by adopting a reported method.<sup>1</sup> All chemicals were commercially available and used as received, including zinc nitrate hexahydrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 98%, Acros Organics), benzimidazole (HbIm, 98%, Acros Organics) and *N*, *N*-dimethylformamide (DMF, extra pure, Fisher Chemical). In a typical synthesis, 2.35 g Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (7.9 mmol) and 5.85 g HbIm (49.5 mmol) were firstly dissolved in 750 mL DMF (9.7 mol), with a molar ratio of 1 Zn: 6.3 HbIm: 1226 DMF. The resultant solution was kept stirring at room temperature for 2 h, followed by 22 h without stirring. The suspended precipitates were separated from solvent through a centrifuge (12,000 rpm for 45 mins) and then washed three times with DMF. Finally, the product was dried at room temperature overnight, which is ZIF-7-I. ZIF-7-II was obtained by heating ZIF-7-I in air at 200 °C for 12 h. ZIF-7-III was obtained by immersing ZIF-7-II in water for one week.

#### 1.2 Micron-sized ZIF-7 crystals

Micron-sized ZIF-7 was synthesized using a reported method.<sup>2</sup> While the same chemicals to those of §1.1 were used to synthesize micron-sized ZIF-7, the ratio of reactants and reaction temperature used were different. In a typical synthesis, 0.76 g Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (2.6 mmol) and 0.61 g HbIm (5.1 mmol) were firstly dissolved in 40 mL DMF (0.5 mol), and then the resultant solution was kept at 100 °C for 72h without stirring. The molar ratio was 1 Zn: 2 HbIm: 200 DMF. The ZIF-7-I powders were separated by centrifugation, washed with DMF for 3 times, and then dried at room temperature overnight. The phase transition can be achieved in the same way as the nanosized ZIF-7: ZIF-7-II was the product of heating ZIF-7-I at 200 °C for 12 h, and ZIF-7-III could be obtained by immersion of ZIF-7-II in water for one week.

#### 2. Materials characterization

#### 2.1 Powder X-ray diffraction (PXRD)

X-ray diffraction patterns were recorded on the Rigaku Miniflex 600 using CuK $\alpha$  radiation (15 mA and 40 kV) at a scan rate of 2°/min with a step size of 0.01° in 2 $\theta$ .

#### 2.2 Scanning electron microscopy (SEM)

The morphology of the as-synthesized crystals was determined employing the Zeiss Merlin field emission scanning electron microscope (FEGSEM), operating at 1-3 keV.

#### 2.3 Pressure-induced liquid intrusion test

The combination of 25 mg ZIF-7 powder and 0.1 mL liquid was sealed in a stainless steel chamber with precisely fitted sealing rings (see Figure S2). The intrusion tests were then conducted on the Instron 5582 universal testing machine, which can compress the pistons into the chamber and thus apply controlled mechanical pressure onto the liquid inside. The length and volume of the specimen were  $\sim$ 4.0 mm and  $\sim$ 0.11 mL respectively, with a cross-sectional area of the piston  $A = 28.26 \text{ mm}^2$ . In this study, the displacement rate (speed) of the piston was set as 0.5 mm/min. When the pressure had reached 106 MPa (3 kN), the movement of the piston was reversed but maintaining the same speed. The force F and displacement d were recorded by the Instron machine for analysis. In the P- $\Delta V$  curves, the nominal pressure P is defined as P = F/A, and the specific volume change  $\Delta V$  is defined as  $\Delta V = (A \cdot d)/m$ , with *m* being the mass of the ZIF-7 sample (25 mg here). The intrusion pressure  $P_{in}$  is taken as the pressure with the lowest gradient  $\Delta P / \Delta V$ , which equals 57 MPa for water intrusion into ZIF-7-II. The length of the intrusion plateau indicates the effective pore volume of ZIF-7 accessible to liquid molecules. Energy dissipation by liquid intrusions were calculated by integrating the areas enclosed by the loading and unloading curves on the P- $\Delta V$  plots. When salt or alcohol solutions were used as liquid phase, the solutions of certain concentrations were prepared first, and then combined with ZIF-7 powder in the stainless steel chamber.

#### 2.4 Fourier-transform infrared (FT-IR) spectroscopy

Fourier-transform infrared attenuated total reflection (FTIR-ATR) spectra were collected using the Nicolet iS10 FT-IR spectrometer (Thermo Fisher Scientific). Spectra were obtained by accumulating 16 scans over the range of 650-4000 cm<sup>-1</sup>. The background spectrum was collected before analyzing each sample at ambient atmosphere.

#### 2.5 Raman spectroscopy

The Raman measurements were performed with a Bruker MultiRAM Raman with sample compartment D418, equipped with a Nd-YAG-Laser (1064 nm) and a LN-Ge diode as detector. The laser power used for sample excitation was 50 mW, and 64 scans were accumulated at a resolution of 1 cm<sup>-1</sup>.

#### 2.6 Atomic force microscopy (AFM)

The morphologies of the ZIF-7 nanocrystals were characterized by AFM imaging using the Veeco Dimension 3100 instrument operating under the tapping mode. A silicon probe, Scout 350 (NuNano) was employed, which consists of a Si cantilever with a conical tip at its end. The cantilever was 125  $\mu$ m long, 30  $\mu$ m wide and 4.5  $\mu$ m thick. Its resonance frequency was 350 kHz and spring constant was 42 N/m.

#### 2.7 Gas sorption measurements

 $N_2$  physisorption isotherms at 77 K of ZIF-7-II were measured using an Autosorb iQ (Quantachrome). In order to eliminate undesired sorption during storage, both nano-sized crystals and micron-sized crystals were further degassed at 150 °C overnight before the measurements.



Figure S1. SEM image of the as-synthesized ZIF-7 nanocrystals with a mean diameter of  $\sim$ 30 nm.



**Figure S2.** FT-IR spectra of ZIF-7, including three phases and two different crystal sizes (micron- vs. nano-sized). For clarification, FT-IR spectra shown in (a) were further magnified in the range of (b) 650-1800 cm<sup>-1</sup> and (c) 1800-4000 cm<sup>-1</sup>. Arrows in (b) and (c) indicate the FT-IR peaks corresponding to DMF in ZIF-7-I, which are absent in ZIF-7-II. Dash lines in (b) show the shift of IR peaks upon the phase transition from ZIF-7-II to ZIF-7-III.



**Figure S3.** Raman spectra of ZIF-7, including three phases and two different crystal sizes. For clarification, Raman spectra shown in (a) were further magnified into sub-graphs from (b) to (j). Raman bands are assigned according to Ref. 24. v: stretching;  $\delta$ : in-plane bending;  $\tau$ : torsion. Bz: benzene ring; Im: imidazole ring.



**Figure S4**. (a) SEM image of as-synthesized micron-sized ZIF-7 crystals with a mean diameter of ~3  $\mu$ m. (b) XRD patterns of the three phases of ZIF-7 micron-sized crystals, including those after water intrusion study (marked with 'WI'). The experimental XRD pattern of ZIF-7-II was obtained from ref.24 (in main manuscript). (c) *P*- $\Delta V$  curves showing the absence of any water intrusion phenomena into the three phases of ZIF-7 micron-sized crystals. Note that the curves have been shifted horizontally for clarity.



**Figure S5**. Cross sections of the experimental setup for liquid intrusion experiments. The piston and pressure chamber were made from stainless steels.



**Figure S6**. XRD patterns of the nano- and micron- sized crystals of ZIF-7-II, in comparison with the reported experimental and simulated spectra in ref. 24 (main manuscript). It is clear that the simulated spectrum of ZIF-7-II is of poor quality, which cannot fully capture the experimental pattern in ref. 24. Our experimental data agree well with the experimental spectrum in ref. 24. Due to the small crystal size, there is a broadening of the Bragg peaks from nano-crystals.



**Figure S7**. (a)  $P-\Delta V$  curves showing the water intrusion behavior into ZIF-7-II nanocrystals derived from ZIF-7-I starting material, after being subjected to different heat treatments. (b) XRD patterns of the corresponding ZIF-7-II nanocrystals subjected to different heat treatments, showing only minor structural changes.



**Figure S8.** FT-IR spectra of the ZIF-7-II nanocrystals obtained by different heating treatments on as-synthesized ZIF-7-I. For clarification, FT-IR spectra shown in (a) were further magnified in the range of (b) 650-1800 cm<sup>-1</sup> and (c) 1800-4000 cm<sup>-1</sup>. The three spectra are almost identical in general. The small hump around 1675 cm<sup>-1</sup> (arrow in (b)) suggests that some residual DMF may be retained in the framework if 153 °C 3h is adopted as the heating condition.



**Figure S9.** Raman spectra of the ZIF-7-II nanocrystals obtained by different heating treatments on as-synthesized ZIF-7-I. For clarification, Raman spectra shown in (a) were further magnified into sub-graphs from (b) to (j). The three spectra are almost identical in general, except for the most intensive heating condition, 330 °C 36h, which seems to cause some minor differences in the lattice mode (50-150 cm<sup>-1</sup>) compared with the lower temperatures.



**Figure S10.** XRD pattern of the material obtained by a heating treatment of 480 °C 12h on the as-synthesized ZIF-7-I nanocrystals, showing structural decomposition into zinc oxide (ZnO).



**Figure S11**. *P*- $\Delta V$  curves of silicone oil intrusion into ZIF-7-II, including two consecutive loading cycles. The 1<sup>st</sup> cycle adopted the same testing method as the water intrusion test, while the 2<sup>nd</sup> cycle attempted a higher pressure exceeding 200 MPa. No intrusion plateau can be detected, thereby confirming that the plateau observed in the water intrusion test results from the penetration of water molecules, rather than the structural breathing induced by mechanical pressure.



**Figure S12**. P- $\Delta V$  curves of water intrusion (2 cycles) into ZIF-7-II and ZIF-8. Inset shows that the intrusion pressure of ZIF-7-II and ZIF-8 are 57 MPa and 25 MPa, respectively.



**Figure S13**. (a) P- $\Delta V$  curves of water intrusion into recycled ZIF-7-II after water intrusion (obtained by heating at 120 °C under vacuum overnight). (b) XRD patterns of the fresh and recycled ZIF 7-II samples, before and after water intrusion. No phase transition is detected throughout the water intrusion and recycling process.



**Figure S14**. Space filled unit cell structures of ZIF-7-I, II, and III. The size of the channel aperture has been estimated in the CrystalMaker software<sup>3</sup> using the largest probe sphere that can penetrate the window opening, indicated in red. The analysis assumes a rigid framework structure, corresponding to the gate 'closed' configuration. Note that there is no solvent accessible volume present in the layered structure of ZIF-7-III.



**Figure S15**. P- $\Delta V$  curves of re-intrusion tests on ZIF-7-II nanocrystals after a relaxation for 24h and 84h respectively, in comparison with the result of a fresh sample. No intrusion plateau can be detected for the re-intrusion tests (inset), this means that the cavities of ZIF-7-II remain occupied by the water molecules without outward diffusion during the long relaxation time.



**Figure S16.** AFM images of ZIF-7 nanocrystals (three phases) before and after water intrusion (WI). (a) ZIF-7-I, (b) ZIF-7-II, (c) ZIF-7-III, (d) ZIF-7-I\_WI, (e) ZIF-7-II\_WI, (f) ZIF-7-III\_WI. No significant difference can be detected between the fresh samples and water-intruded samples. The aggregation of nanocrystals is evident for almost all the samples except for the as-synthesized ZIF-7-I, which can be attributed to the inevitable drying (e.g., after water intrusion or immersion) or heating (e.g., to obtain ZIF-7-II) during sample preparation.



**Figure S17.** FT-IR spectra of the ZIF-7 nanocrystals (three phases) before and after water intrusion. For clarification, FT-IR spectra shown in (a) were further magnified in the range of (b) 650-1800 cm<sup>-1</sup> and (c) 1800-4000 cm<sup>-1</sup>. No significant difference can be detected between the fresh samples and intruded samples.



**Figure S18.** Raman spectra of the ZIF-7 nanocrystals (three phases) before and after water intrusion. For clarification, Raman spectra shown in (a) were further magnified into sub-graphs from (b) to (j). No significant differences can be detected between the fresh samples and the intruded samples.



Figure S19. N<sub>2</sub> physisorption of ZIF-7-II, with a comparison between micron-sized and nanosized crystals. Solid points represent adsorption and open points represent desorption. The corresponding external surface areas are  $18 \text{ m}^2/\text{g}$  for the micron-sized crystals and  $70 \text{ m}^2/\text{g}$  for the nano-sized crystals. This indicates that N<sub>2</sub> was mainly physisorbed on the external surface, in agreement with testing results in Ref. 21.

### References

(1) Li, Y. S.; Liang, F. Y.; Bux, H.; Feldhoff, A.; Yang, W. S.; Caro, J. Molecular Sieve Membrane: Supported Metal–Organic Framework with High Hydrogen Selectivity. *Angew. Chem.* **2010**, *122*, 558-561.

(2) Aguado, S.; Bergeret, G.; Titus, M. P.; Moizan, V.; Nieto-Draghi, C.; Bats, N.; Farrusseng, D. Guest-Induced Gate-Opening of a Zeolite Imidazolate Framework. *New J. Chem.* **2011**, *35*, 546-550.

(3) Crystalmaker Software Ver.10 (Www.Crystalmaker.Com).