

Supporting Information

Repetitive in situ recycling of degraded metal-organic frameworks within nanocapsules.

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Section 1. Materials and Characterization Methods

Azobisisobutyronitrile (AIBN) was purified by recrystallization in ethanol. All other chemicals were obtained from commercial sources and used without further purification.

Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D2 PHASER and Bruker D8 ADVANCE X-ray diffractometers with Cu K α radiation ($\lambda = 1.54184 \text{ \AA}$) at a scan rate of 0.02° per second at room temperature. The 2θ range is from $5 - 30^\circ$.

Single crystal X-ray diffraction (SCXD) data were collected on a Bruker D8 Venture diffractometer equipped with an Apex II CCD detector and an I μ S micro-focus CuK α X-ray source ($\lambda = 1.54178 \text{ nm}$). A piece of blue rod-shaped crystal with dimensions $0.05 \times 0.015 \times 0.08 \text{ mm}$ was mounted onto a Kapton micromount with Fluorolube and placed in a cold N $_2$ stream (150 K). A monoclinic unit cell with $a = 3.4664 (3)$, $b = 9.8407 (8)$, $c = 17.1098 (15)$ and $\beta = 93.178 (4)$ was derived from the least-square refinement of 2259 reflections in the range of $4.493 < \theta < 48.507$. Examination of systematic absences indicated that the crystal crystallized in P n.

Due to the small size of the crystal, the diffraction was very weak. Few diffraction spots were observed beyond 1.05 \AA . Therefore, the X-ray data was collected to 1.05 \AA . After integration of the data, empirical absorption correction was applied.

The structure was solved by direct methods which located all the Cu atoms and most of the O atoms. Remaining non-hydrogen atoms were generated via subsequent difference Fourier syntheses. Anisotropic refinement of the non-hydrogen atoms was not successful likely due to weak diffraction. Therefore, all the atoms except Cu were refined isotropically.

Thermogravimetric analyses (TGA) were performed on a Perkin Elmer TGA 8000 from $35 \text{ }^\circ\text{C}$ to $700 \text{ }^\circ\text{C}$ with a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$ in O $_2$ atmosphere.

Transmission electron microscopy (TEM) was conducted on a JEM-1400Plus TEM (120kV) or a JEM 2100 plus (200 kV). Briefly, 10 μ L methanol dispersed sample was deposited on a TEM grid. After 30 s, excessive solution was wicked away with pieces of filter paper. After wicking off, the grid was dried for 15 minutes at 70 °C.

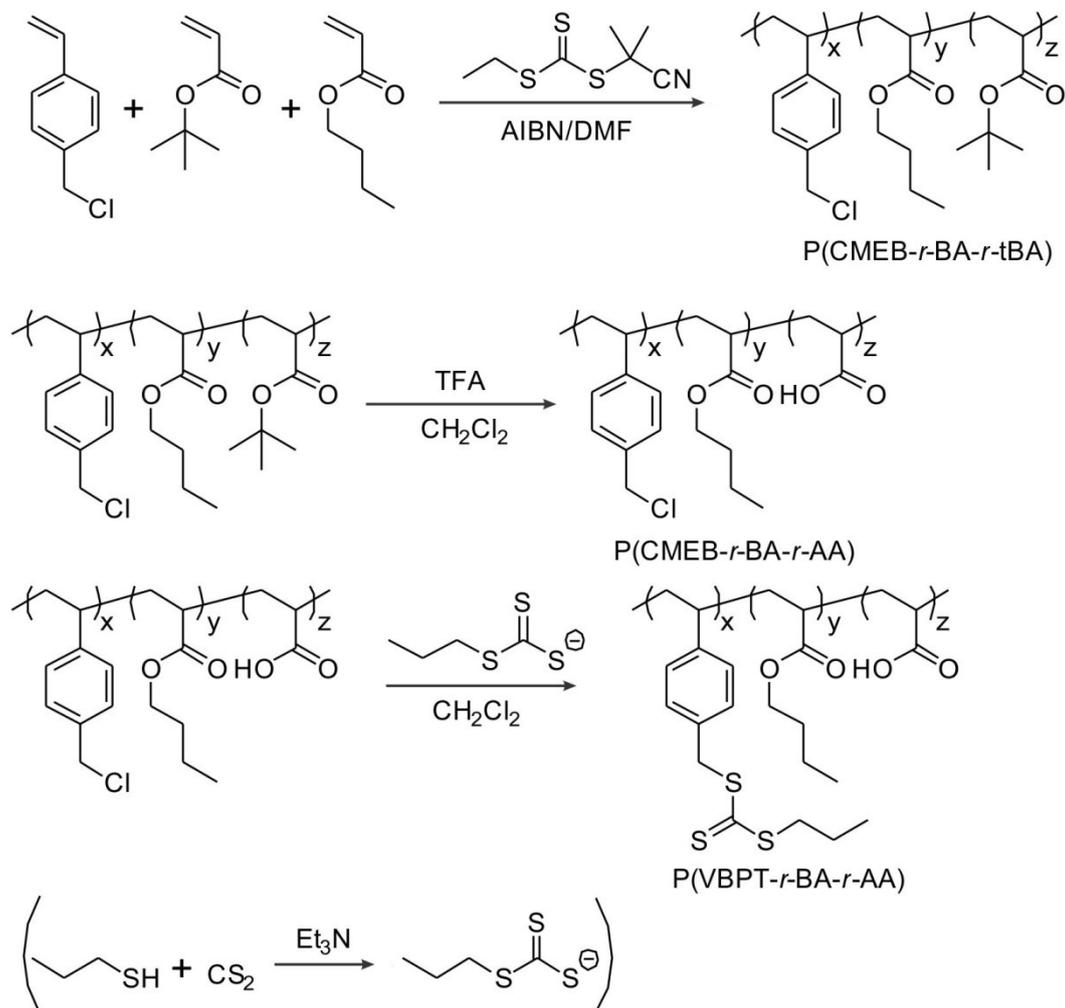
Scanning electron microscopy (SEM) images were obtained using a JSM-7800F Prime scanning electron microscopy. The samples were sputtered with Pt prior to imaging.

Physisorption analyses were performed on a QUADRASORB SI, or a Quantachrome iQ or a BELSORP-maxII; water vapor uptake measurements were conducted on a BELSORP-aqua3 or a BELSORP-maxII. Before gas adsorption-desorption measurement, all samples were activated under vacuum at 120 °C for 10 h. Pore size distribution was calculated based on the N₂ adsorption isotherms using non-local density functional theory (NLDFT).

ICP-OES experiment was carried out on an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES Icap7400), with the wavelength -Cu (327 nm). For each ICP sample, ~5 mg MOF powder was added into a centrifuge tube with 10 mL deionized (DI) water and then sonicated to get well dispersed. After 10 s, 60 s, 120 s, 240 s, and 360 s the solution was filtered through a 0.45 μ m PVDF microporous membrane to remove suspended particles prior to testing.

Section 2. Experimental Details

Synthesis of random copolymer (RCP) P(VBPT-*r*-BA-*r*-AA)



Scheme S1. Synthetic route of P(VBPT-*r*-BA-*r*-AA)

2.77 mL 1-(chloromethyl)-4-ethenylbenzene (CMEB), 3.54 mL *n*-butyl acrylate (BA), 0.71 mL 2-*tert*-butyl acrylate (tBA), 0.23 mL 2-cyano-2-propyl ethyl trithiocarbonate, and 27.8 mg AIBN were added into a Schlenk tube with 7 mL DMF. The solution was degassed through 3 cycles of freeze-pump-thaw. The Schlenk tube was then placed in a 70 °C oven overnight to start RAFT polymerization.^[1]

After polymerization, the polymer was precipitated with methanol and collected by centrifugation. Then the polymer was redissolved in acetone and precipitated again with methanol.

This process was repeated for at least 3 times to obtain P(CMEB-*r*-BA-*r*-tBA). The ratio among three monomers is 5:5:1 (CMEB:BA:tBA) according to the ¹H NMR results.

P(CMEB-*r*-BA-*r*-tBA) was then dissolved in a mixture of DCM and TFA for 2 h to allow tert-butyl group to hydrolyze. Then the polymer, P(CMEB-*r*-BA-*r*-AA), was precipitated in methanol for three times and dried under vacuum.

To synthesize P(VBPT-*r*-BA-*r*-AA) (VBPT represents S-(4-vinyl)benzyl S'-propyltrithiocarbonate), P(CMEB-*r*-BA-*r*-AA) was redissolved in DCM. To the solution was added 1.8 mL 1-propanethiol, 1.2 mL carbon disulfide and 1.49 g trimethylamine. The solution was kept stirring for 1 h. The product, P(VBPT-*r*-BA-*r*-AA), was precipitated with methanol and redissolved in acetone. This process was repeated 3 times to remove small molecular impurities. The final product was dried in a vacuum chamber at room temperature overnight.

Synthesis of HKUST-1

12.2 g of Cu(NO₃)₂·3H₂O and 2.9 g of benzene-1,3,5-tricarboxylic acid (H₃BTC) was dissolved in 25 mL of dimethylsulfoxide (DMSO). The solution was heated in a 65 °C oven for 30 min. The solution was then injected into a 250 mL of methanol solution containing 2.5 g of polyvinylpyrrolidone (PVP) under vigorously stirring at 55 °C. The solution was kept stirring for 90 min. The blue product was harvested by centrifuging and washed twice with methanol and finally redispersed in methanol for further use.

Synthesis of HKUST-1@xPS

~1g HKUST-1 suspension in methanol was collected by centrifugation and re-dispersed in 15 mL of dichloromethane (DCM) containing 250 mg P(VBPT-*r*-BA-*r*-AA). The mixture was capped

in a small vial and sonicated until fully dispersed. After 12 h of incubation, the particles were washed twice with toluene then dispersed in 15 mL toluene in a Schlenk tube. 4.5 mL styrene, 1.125 mL divinylbenzene (DVB), and 15 mg azobisisobutyronitrile (AIBN) were then added to the solution. After three-time freeze-pump-thaw cycles, dissolved O₂ was removed. Then the Schlenk tube was sealed and placed in an oil bath at 75 °C and stirred for 1.5 h. The reaction was stopped by cooling to room temperature and the catalyst and excess monomers were removed by washing with DCM (3 times).

Synthesis of CuBTC coordination complex (1)

The synthesis conditions of the new CuBTC coordination complex came from the imitation of HKUST-1@xPS degradation process. 1.1254 g of Cu(NO₃)₂·3H₂O, 0.16 g NaOH and 0.664 g of H₃BTC was mixed in 10 ml of methanol to form a paste and then added into a Teflon-lined stainless-steel autoclave. The mixture was then heated in a 100 °C oven overnight to form small blue rod-shaped crystals of **1**.

Degradation of HKUST-1 and HKUST-1@xPS

HKUST-1 or HKUST-1@xPS sample (~15.0 mg) was put on a glass slide and loaded into a Teflon-lined stainless-steel hydrothermal reactor containing ~ 1ml water. The glass slide was elevated above the water level without touching. The reactor was placed in a 150 °C oven overnight. After cooling to room temperature, the sample was taken out, collected, and denoted as HKUST-1-DE or HKUST-1@xPS-DE, respectively.

Synthesis of ZIF-8

175.0 mg $\text{Zn}(\text{CH}_3\text{COO})_2$ and 263.0 mg 2-methylimidazole (MIM) were separately dissolved in 20.0 mL methanol. Then, the two solutions were mixed and stirred for 5 min. The mixture was aged at room temperature for 12 h. White solid started to form during this stage. Next the white solid was collected and rinsed by methanol for three times. The resulting material ZIF-8 was suspended in methanol for future use.

Synthesis of ZIF-8@MS

A methanol suspension containing ~30.0-50.0 mg ZIF-8 was mixed with another solution containing 33.0 mL of H_2O , 21.0 mL of methanol, and 0.25 g of MIM. The mixture was then sonicated for 3 min, followed by injecting 0.55 mL (25 wt%) of hexadecyltrimethylammonium chloride (CTAC) aqueous solution and stirring for 15 min. Then 0.40 mL of tetraethyl orthosilicate (TEOS) was added into this mixture dropwise within 3 min. The resultant mixture was stirred for another 1 h. The final products were harvested by centrifuging and washing three times with 40.0 mL of methanol each time, and later dried under vacuum overnight.

Synthesis of ZIF-8@xPS

~600 mg ZIF-8 suspension in methanol was collected by centrifugation and re-dispersed in 15.0 mL of DCM containing 150.0 mg P(VBPT-*r*-BA-*r*-AA). The mixture was capped in a small vial and sonicated until well dispersed. After 12 h of incubation, the particles were washed twice with toluene then re-dispersed in 15.0 mL toluene in a Schlenk tube. Then 4.5 mL styrene, 1.125 ml

DVB, and 15.0 mg AIBN were added to the solution. After three-time freeze-pump-thaw cycles, dissolved O₂ was removed. Then the Schlenk tube was sealed and placed in an oil bath at 75 °C and stirred for 1.5 h. The reaction was stopped by cooling to room temperature and the catalyst and excess monomers were removed by washing with DCM (3 times).

Preparation of hollow mesoporous silica

5.0 mg ZIF-8@MS was treated with 1 ml acetic acid in a 1.5 ml centrifuge tube. The mixture was then sonicated for 2 min. The final products were harvested by centrifuging and washing three times with 1 mL of methanol each time, and later dried under vacuum overnight.

Degradation of ZIF-8, ZIF-8@xPS and ZIF-8@MS

40.0 mg of ZIF-8, ZIF-8@xPS or ZIF-8@MS were dispersed into 3.0 ml of methanol solution. Then ZIF-8, ZIF-8@xPS or ZIF-8@MS solutions were put on to a glass slide to allow methanol evaporate in the fume hood. Next, the glass slide was placed in a stainless-steel chamber containing an acetic acid solution (acetic acid (AA):ethylene glycol (EG) = 3:1) for 10~15 min. After degradation, the samples were dried under vacuum overnight at 85 °C to remove residual acid in the samples. After cooling to room temperature, the samples were taken out, collected, and denoted as ZIF-8-DE, ZIF-8@xPS-DE and ZIF-8@MS-DE, respectively.

Vapor assisted reconstruction (VAR) of HKUST-1

HKUST-1-DE or HKUST-1@xPS-DE (~15 mg) was placed on a glass slide and loaded into a Teflon-lined stainless-steel autoclave containing ~ 1ml ethanol (EtOH)/trifluoroacetic acid (TFA)

mixture (ethanol:TFA = 95:5). The glass slide was suspended above the solvent layer without touching. The reactor was placed in a 100 °C oven overnight. After cooling, the samples were taken out, collected, and denoted as HKUST-1-RE and HKUST-1@xPS-RE, respectively.

Vapor assisted reconstruction of ZIF-8

ZIF-8-DE, ZIF-8@xPS-DE or ZIF-8@MS-DE (~30-50 mg) was placed on a glass slide and loaded into a Teflon-lined stainless-steel hydrothermal reactor containing ~ 3.0 ml MeOH. The glass slide was suspended above the solvent layer without touching. The reactor was placed in a 70 °C oven for 24h. After cooling, the samples were taken out, collected, and denoted as ZIF-8-RE, ZIF-8@xPS-RE and ZIF-8@MS-RE, respectively.

HKUST-1 recycling protocol

A homemade stainless-steel hydrothermal reactor (Figure S1) was used for HKUST-1 recycling. HKUST-1@xPS (~30 mg) was placed on a glass slide and loaded into the reactor. The glass slide was positioned on a stainless-steel stand with ~5 mm gap away from the bottom. Within this gap, a few pieces of filter paper were loaded to which solvents can be added. Material recycling process can be divided into two stages. For the degradation stage, water was added to the filter paper. The reactor was placed in a 120 °C oven for 6 h. For reconstruction, EtOH/TFA mixture (ethanol:TFA = 95:5) was added to the filter paper. The reactor was then placed in a 100 °C oven for 6 h. This degradation-reconstruction cycle was repeated for up to 5 times to give HKUST-1@xPS-DE_n and HKUST-1@xPS-RE_n.

ZIF-8 recycling protocol

For the degradation stage, ZIF-8@MS (~40 mg) was placed on a glass slide and loaded into the glass container with liquid of AA/EG mixture (AA:EG = 3:1) for 10~15 min. The glass slide was positioned on a stainless-steel stand with ~1 cm gap away from the bottom. For reconstruction, the glass slide was loaded into a homemade stainless-steel hydrothermal reactor. The glass slide was positioned on a stainless-steel stand with ~1 cm gap away from the bottom. Within this gap, a few pieces of filter paper were loaded to which solvents can be added. Methanol was added to the filter paper. The reactor was then placed in a 70 °C oven for 24 h. This degradation-reconstruction cycle was repeated for up to 10 times to give ZIF-8@MS-DE_n and ZIF-8@MS-RE_n.

Section 3. Molecular Dynamics Simulation

To construct simulation cells, firstly, we prepared a polymer slab model that mimics the crosslinked PS capsule on the MOF surface. With two monomers which are styrene and 1,4-divinylbenzene, random copolymers (RCP) were generated using the Materials Studio 7.0.^[2] Each RCP chain has 90 styrenes and 10 1,4-divinylbenzenes with random distribution. We prepared a cubic box of 30 nm×30 nm×30 nm containing 32 RCPs. Then, with a closed boundary condition in z-direction while applying periodic boundary conditions in x and y orientations, RCPs were relaxed by performing molecular dynamics runs (MD) using the LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator)^[3] with a canonical ensemble (NVT) at a fixed temperature of 423.15 K. During relaxation, box sizes were adjusted so that the final dimensions of each box became 11.5nm×11.5nm×6nm. Then, vacuum spaces were added on both the top and bottom sides of the polymer slab in z-direction. Finally, the vacuum space on the bottom (which is regarded as the inner part of polymer capsule) of polymer slab was filled with Cu²⁺ or BTC³⁻ ion. The final dimension of the simulation cell was 11.5 nm×11.5 nm×45 nm.

Forcefield parameters for polymers were employed from the consistent-valence forcefield.^[4] Cu²⁺ and BTC³⁻ ions were modeled using the Amber force field.^[5] Atomic charges were obtained using the Rappe-Goddard charge equilibration method (QEq).^[6] In our calculations, the van der Waals and Coulombic interactions were subject to a 14 Å cutoff.

To obtain the equilibrated configuration of ions within the inside of polymer slab, we performed relaxation MD runs over 200 ps with a timestep of 1 fs, while confining the maximum z coordinates of both ions below the polymer slab. Next, the MD production runs were performed during 10 ns in the NVT ensemble at 423.15 K. For the reference case which is without PS capsule, we performed the MD production runs after removing the polymer slab, but using the same equilibrated configuration of ions as the initial configurations.

Section 4. Supplementary Figures

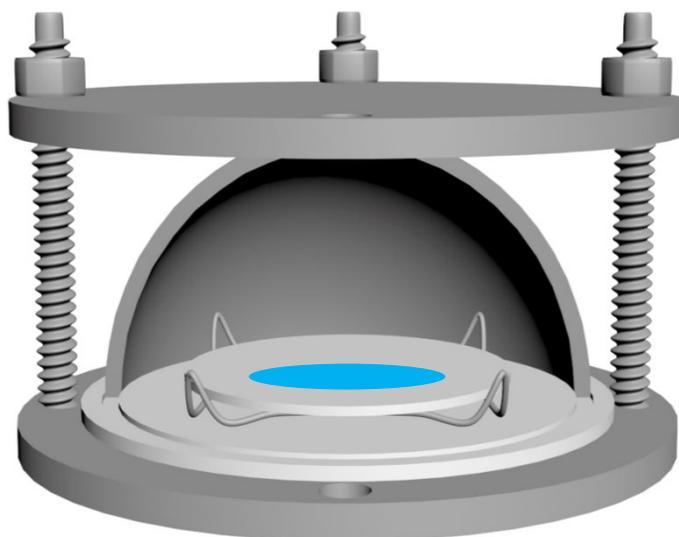


Fig. S1 Homemade stainless-steel hydrothermal reactor

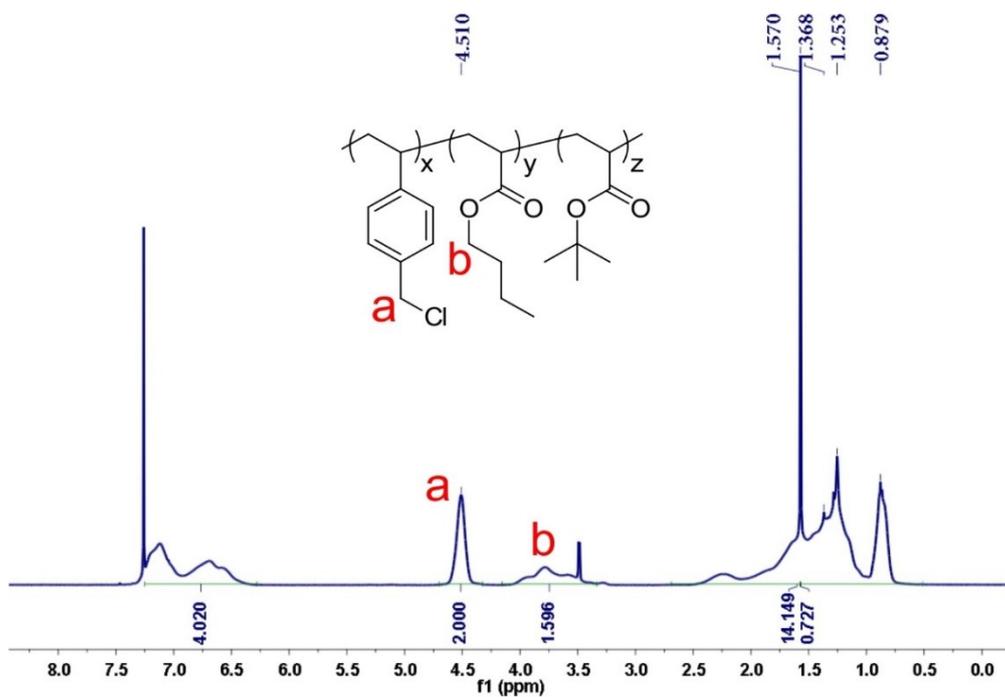


Fig. S2 ^1H NMR spectrum of P(CMEB-*r*-BA-*r*-tBA).

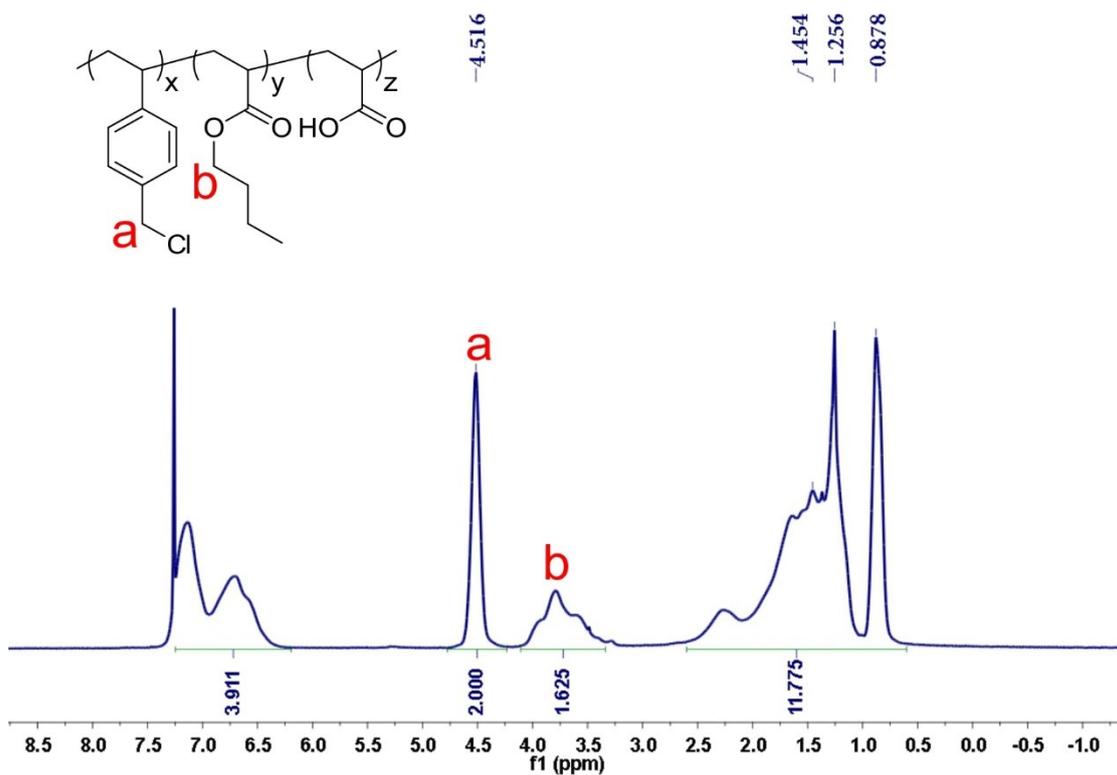


Fig. S3 ^1H NMR spectrum of P(CMEB-*r*-BA-*r*-AA).

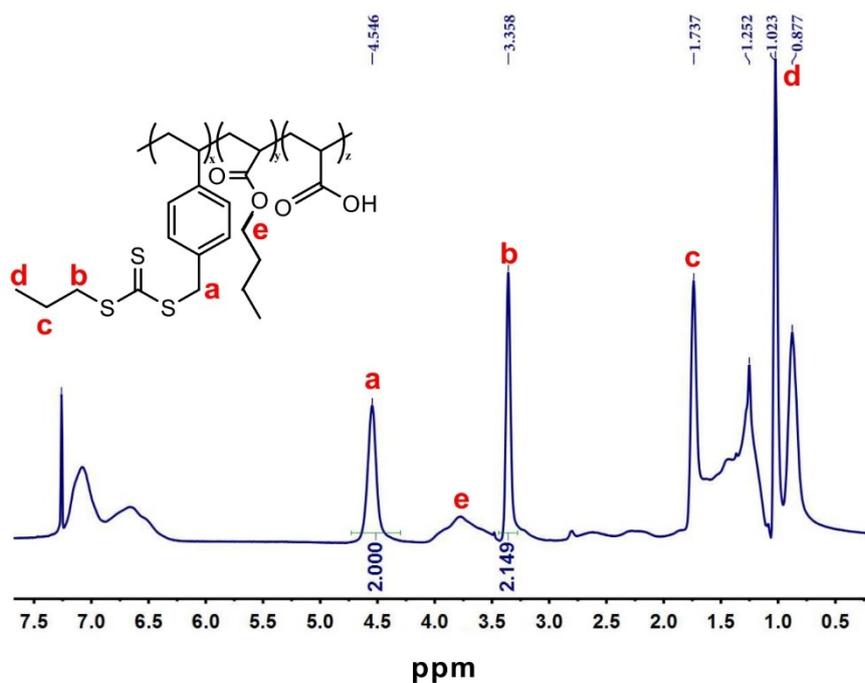


Fig. S4 ^1H NMR spectrum of P(VBPT-*r*-BA-*r*-AA).

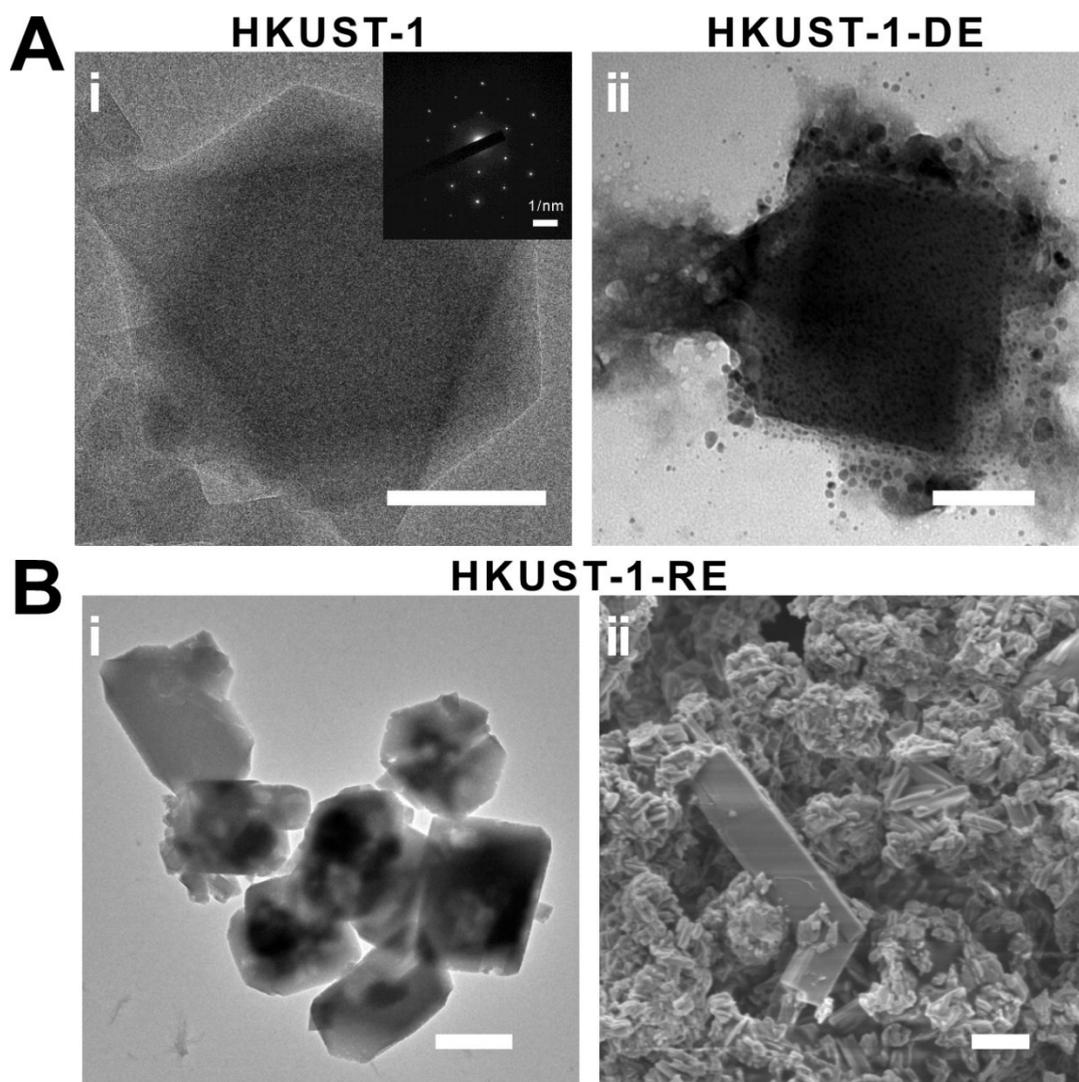


Fig. S5 (A) TEM images of HKUST-1 and HKUST-1-DE. (B) TEM image and (C) SEM image of HKUST-1-RE. The scale bars are 100 nm for A and Bi, 500 nm for Bii.

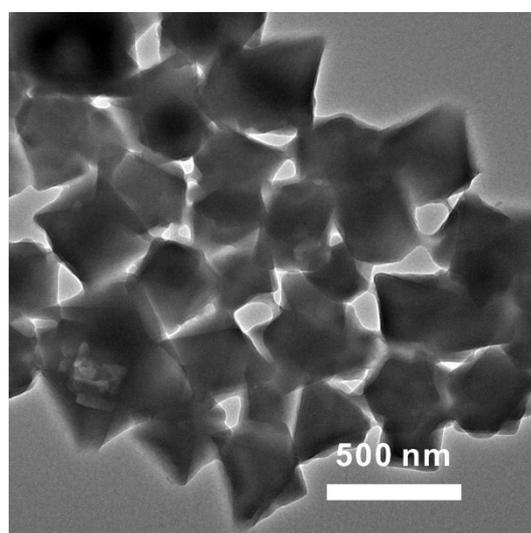


Fig. S6 TEM image of HKUST-1@xPS

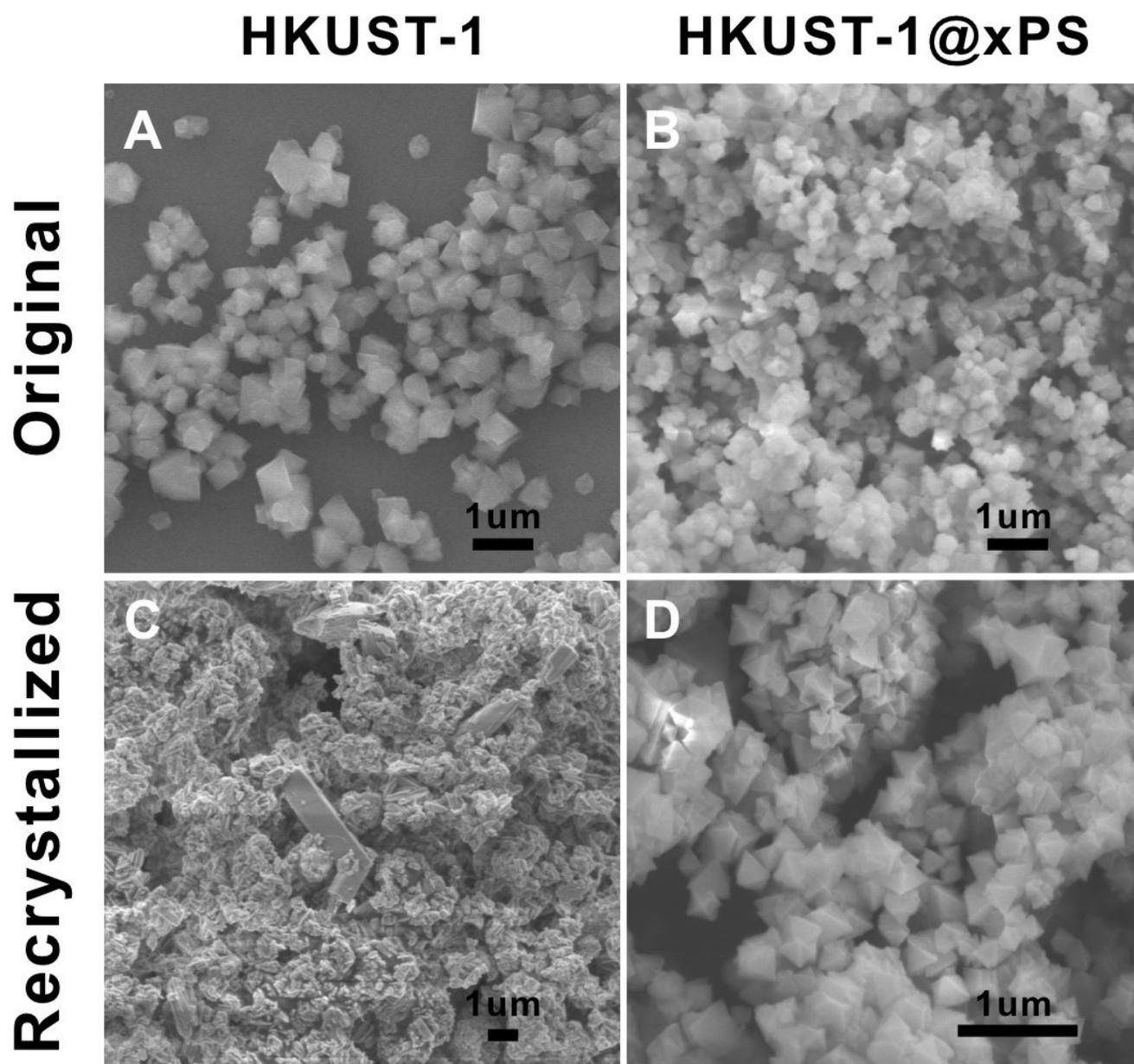


Fig. S7 SEM images of HKUST-1 (A), HKUST-1@xPS (B), HKUST-1-RE (C), and HKUST-1@xPS-RE (D).

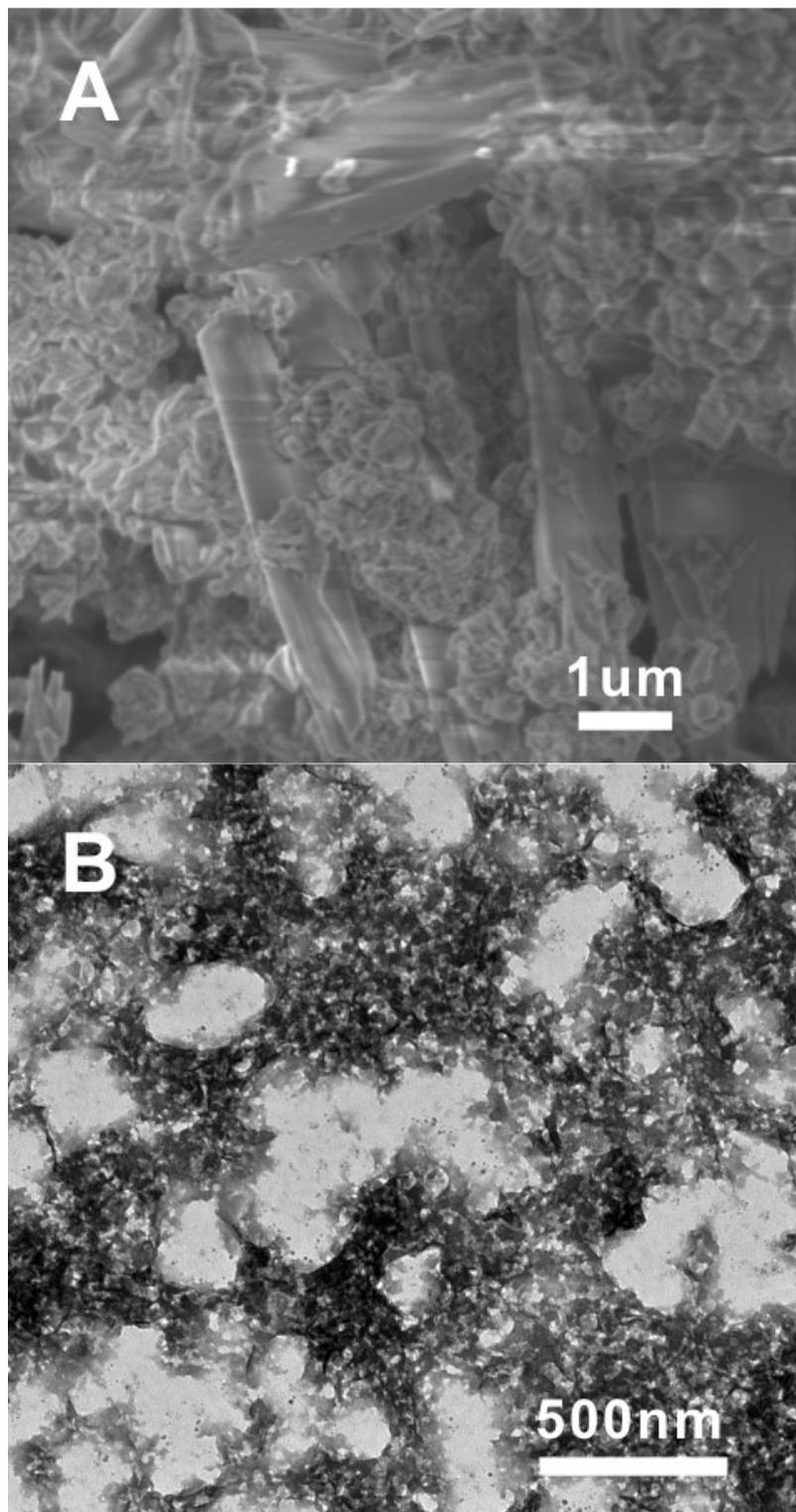


Fig. S8 SEM image (A) and TEM image (B) of HKUST-1-DE.

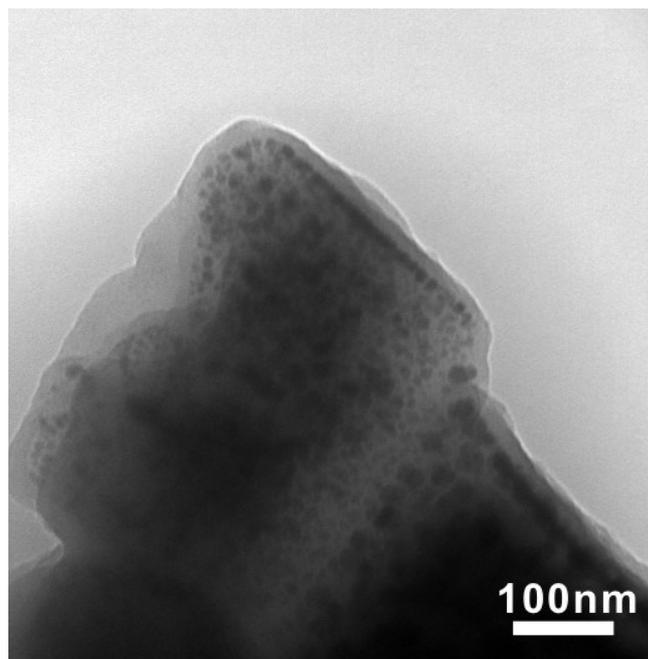


Fig. S9 TEM image of HKUST-1@xPS-DE

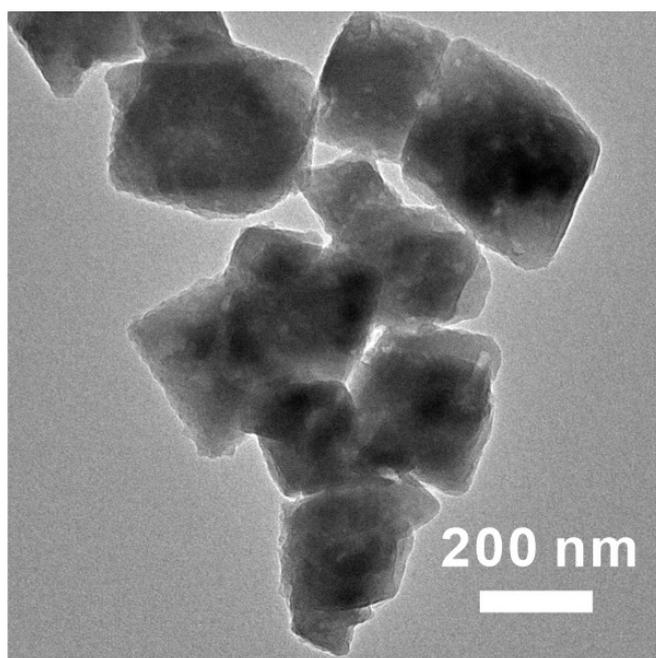


Fig. S10 TEM image of HKUST-1@xPS-RE

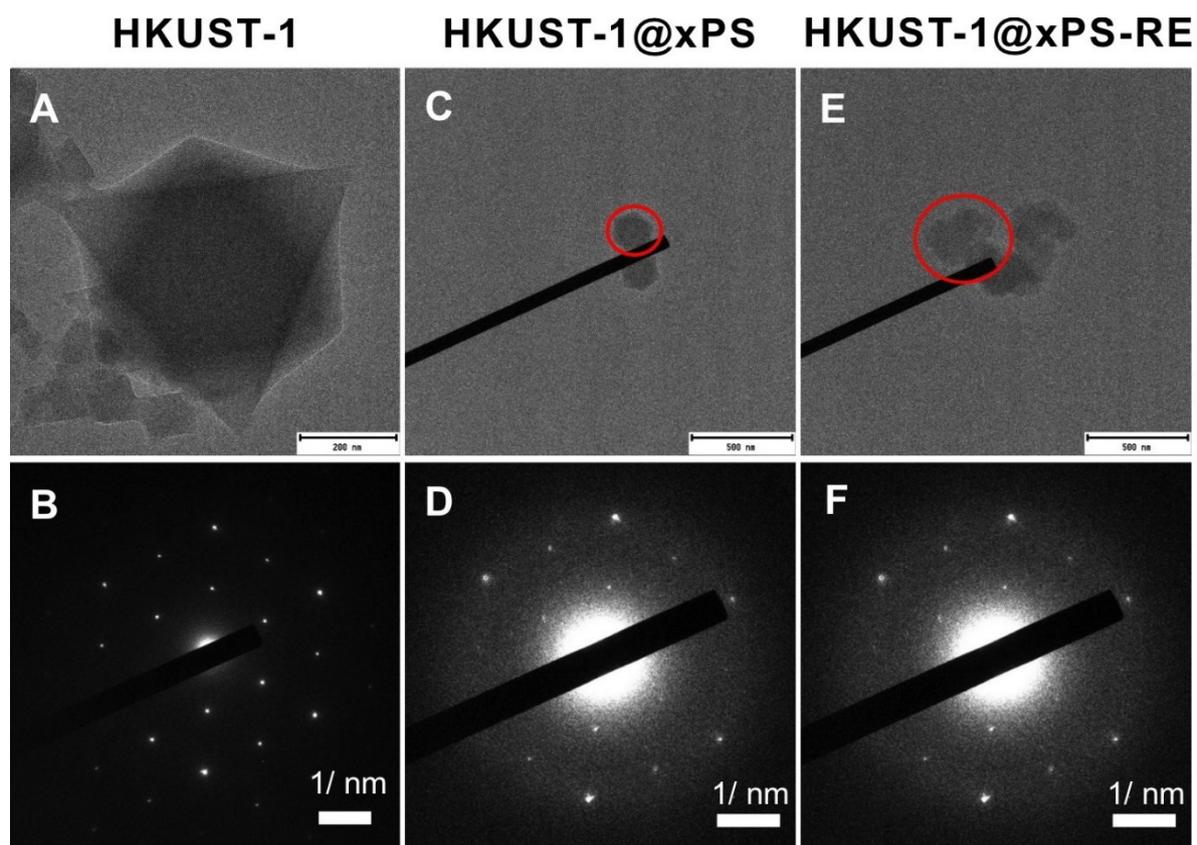


Fig. S11 TEM image (A) and selected area electron diffraction (SAED) pattern (B) of an HKUST-1 particle. TEM image (C) and SAED pattern (D) of an HKUST-1@xPS particle. TEM image (E) and SAED pattern (F) of an HKUST-1@xPS-RE particle.

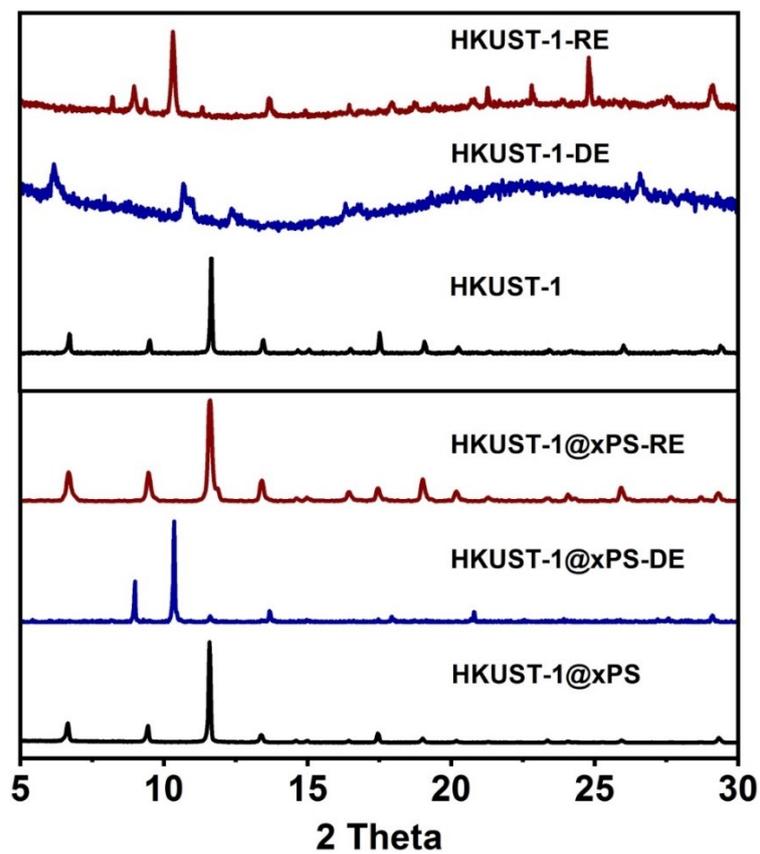


Fig. S12 PXRD patterns of the HKUST-1 and HKUST-1@xPS during the degradation-reconstruction cycle.

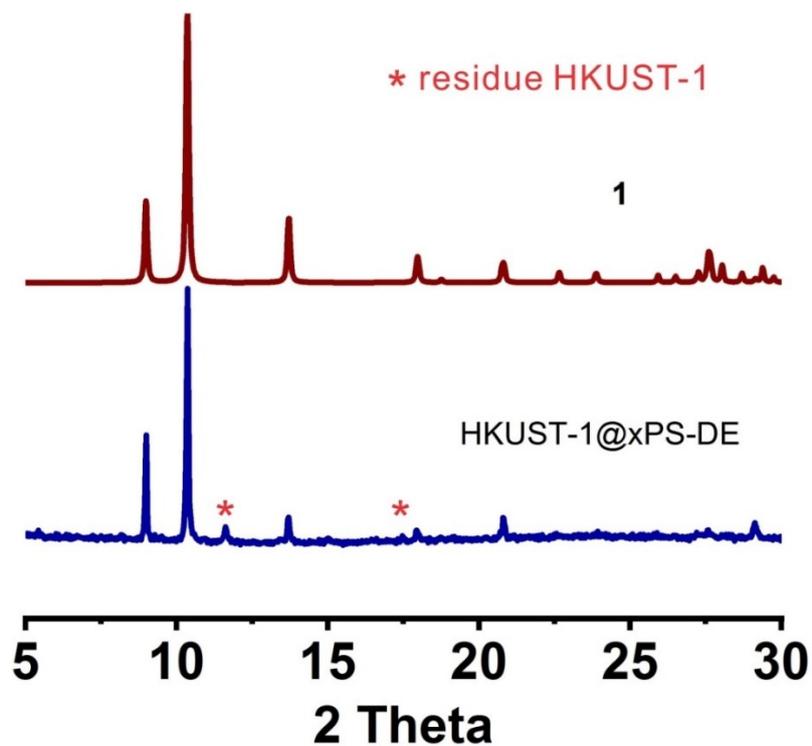


Fig. S13 PXRD patterns of complex 1 and HKUST-1@xPS-DE.

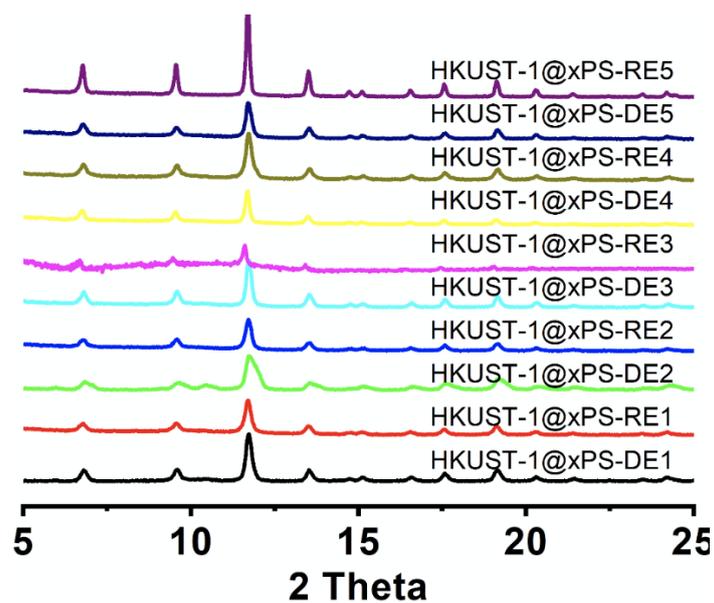


Fig. S14 PXR D patterns of HKUST-1@xPS-DE_n and HKUST-1@xPS-RE_n.

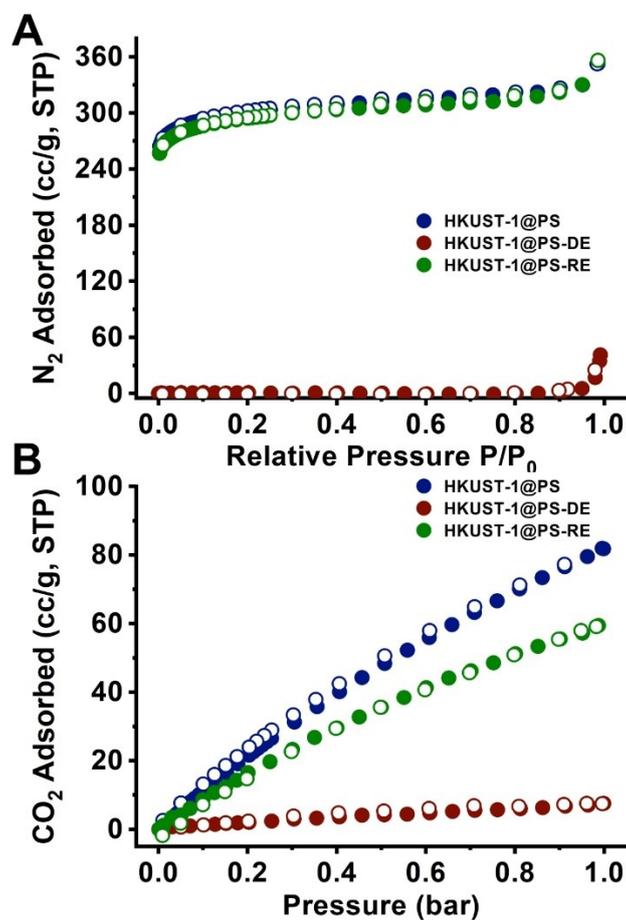


Fig. S15 (A) N₂ uptake isotherms of HKUST-1@xPS, HKUST-1@xPS-DE and HKUST-1@xPS-RE at 77 K. (B) CO₂ uptake isotherms of HKUST-1@xPS, HKUST-1@xPS-DE and HKUST-1@xPS-RE at 298 K. The closed and open symbols represent adsorption and desorption respectively.

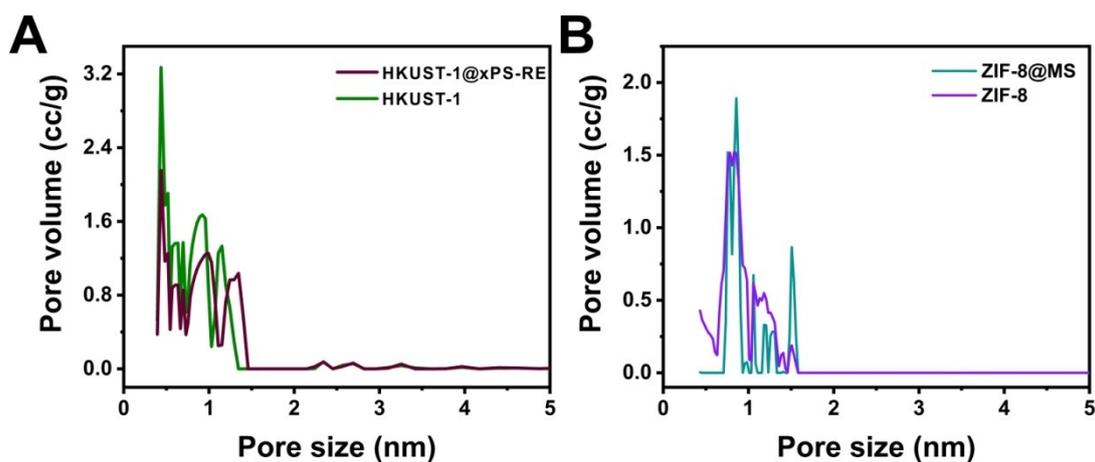


Fig. S16 pore size distribution of (A) HKUST-1 and HKUST-1@xPS-RE, (B) ZIF-8 and ZIF-8@MS

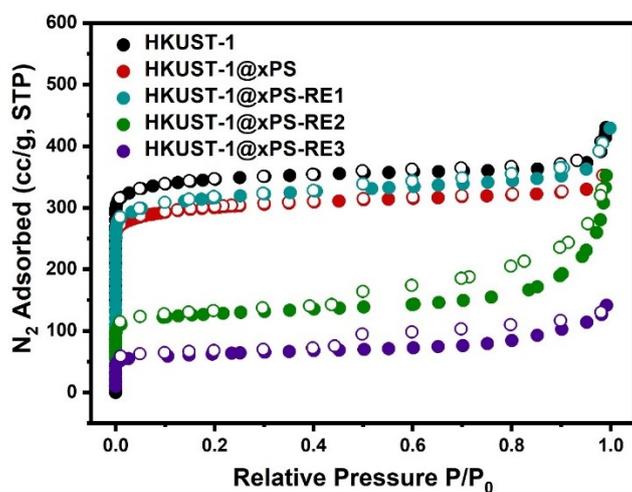


Fig. S17 N₂ uptake isotherms of HKUST-1, HKUST-1@xPS, HKUST-1@xPS-RE1, HKUST-1@xPS-RE2 and HKUST-1@xPS-RE3 at 77 K. The degradation process was carried out at 150 °C for 12 h to achieve complete degradation of HKUST-1.

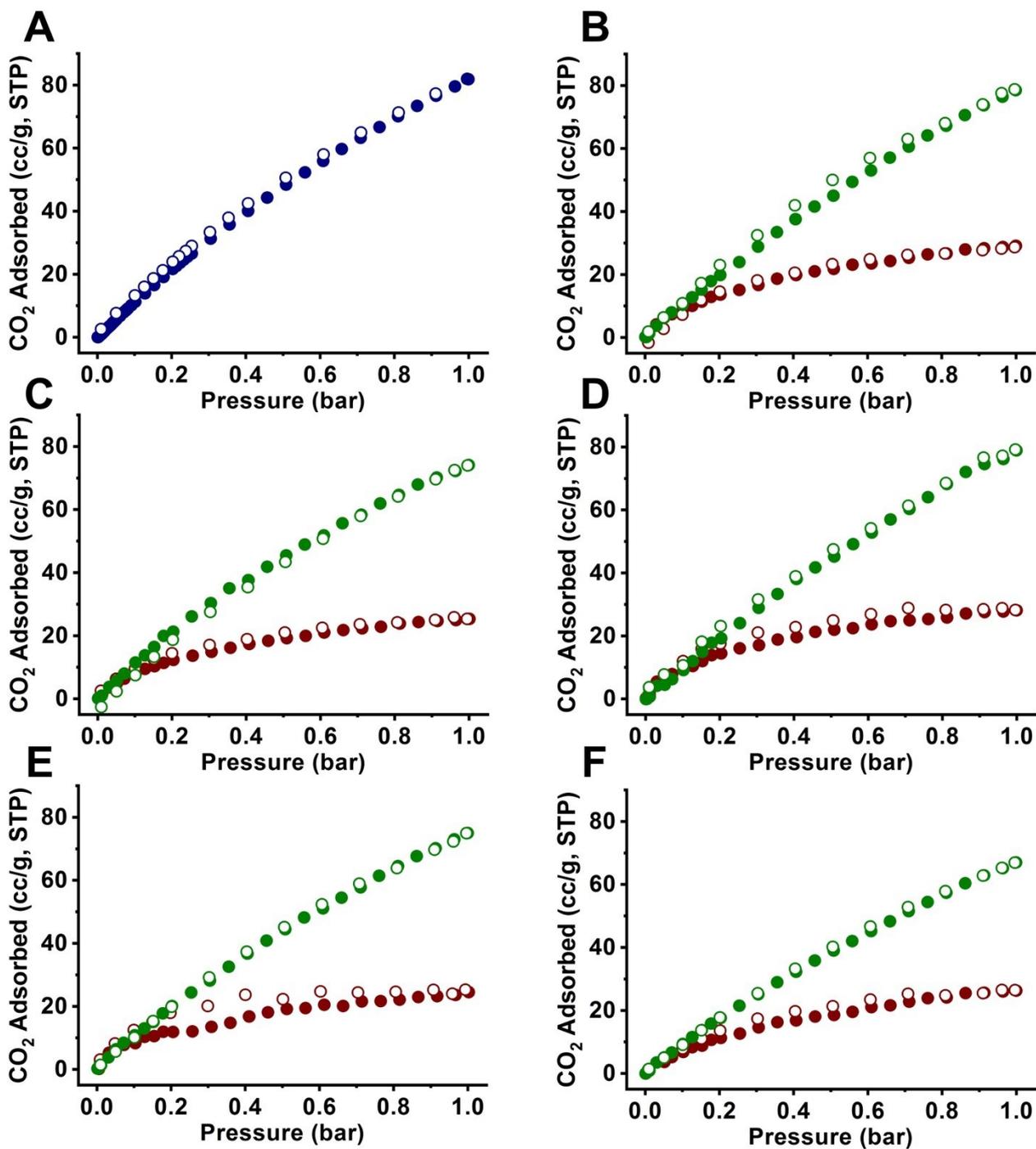


Fig. S18 CO₂ uptake isotherms of HKUST-1@xPS (A), HKUST-1@xPS-DE1 (B, red), HKUST-1@xPS-RE1 (B, green), HKUST-1@xPS-DE2 (C, red), HKUST-1@xPS-RE2 (C, green), HKUST-1@xPS-DE3 (D, red), HKUST-1@xPS-RE3 (D, green), HKUST-1@xPS-DE4 (E, red), HKUST-1@xPS-RE4 (E, green), HKUST-1@xPS-DE5 (F, red), and HKUST-1@xPS-RE5 (F, green).

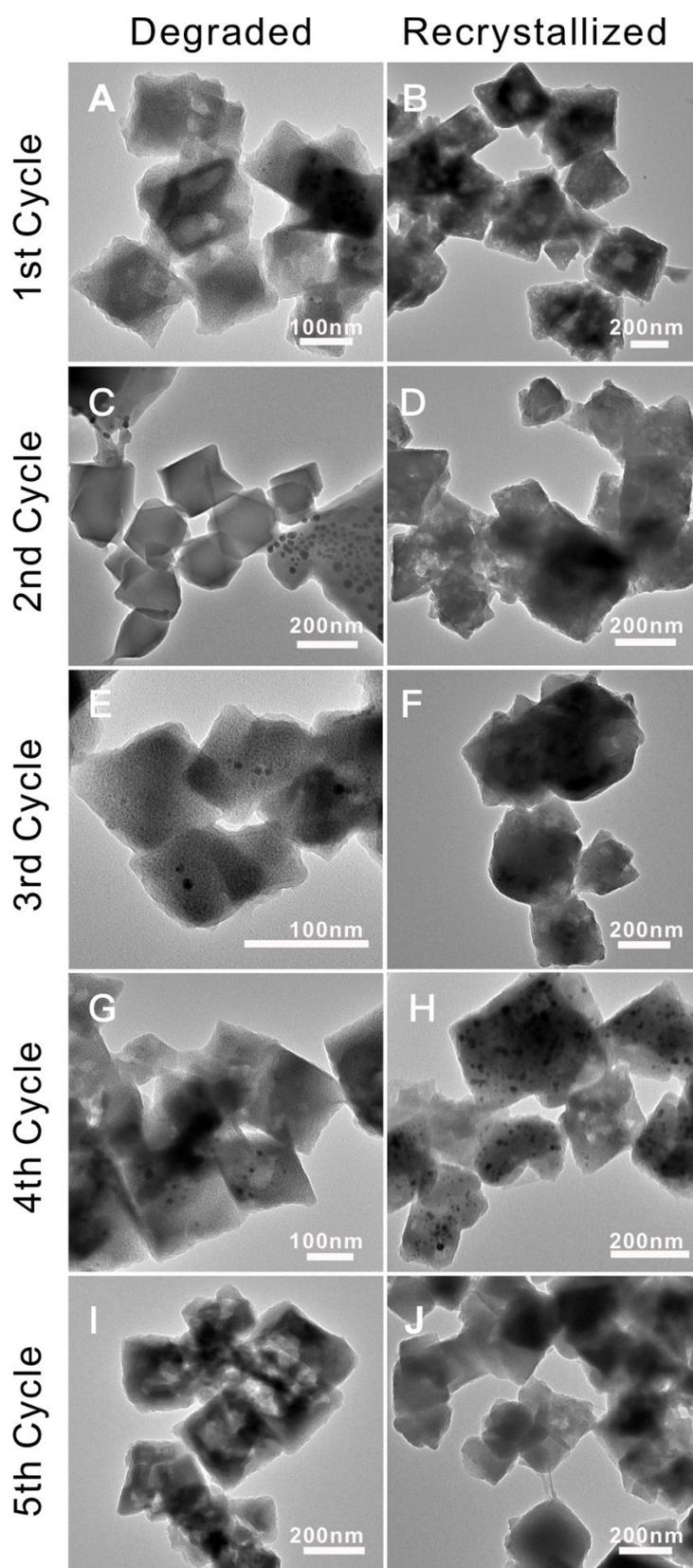


Fig. S19 TEM images of HKUST-1@xPS-DEn (A, C, E, G, I) and HKUST-1@xPS-REn (B, D, F, H, J).

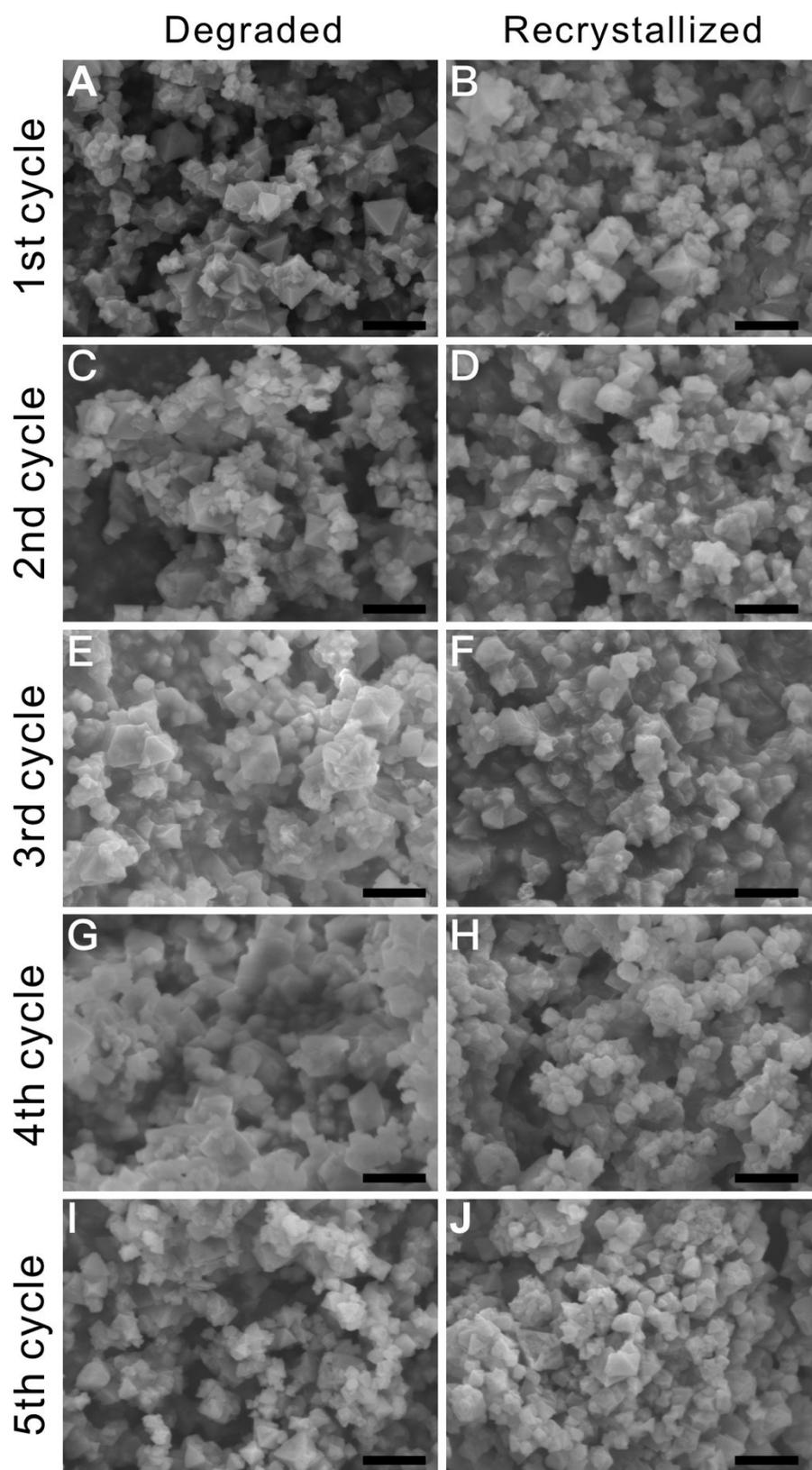


Fig. S20 SEM images of HKUST-1@xPS-DEn (A, C, E, G, I) and HKUST-1@xPS-REn (B, D, F, H, J). Scale bars = 1 μ m

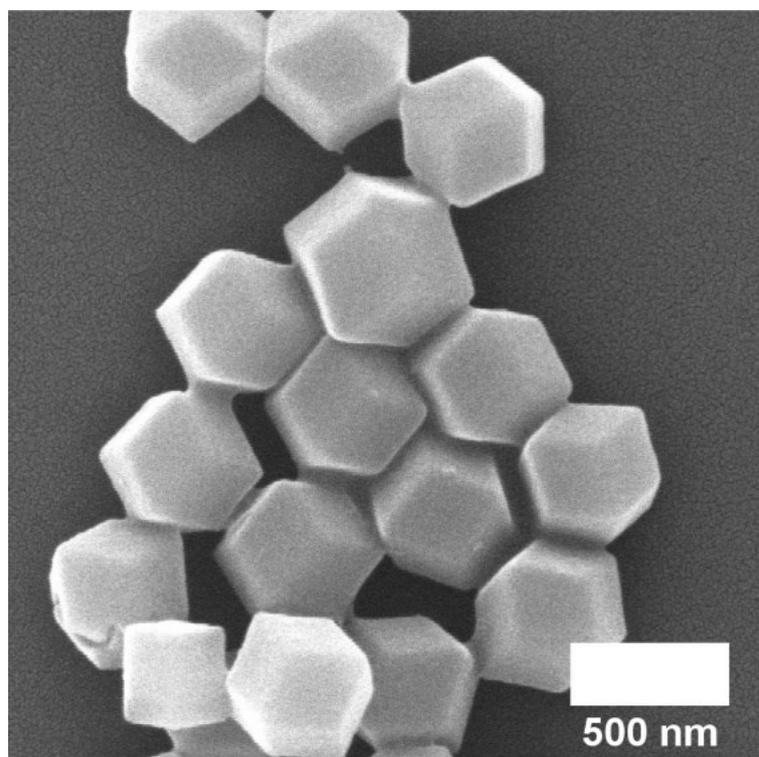


Fig. S21 SEM image of ZIF-8

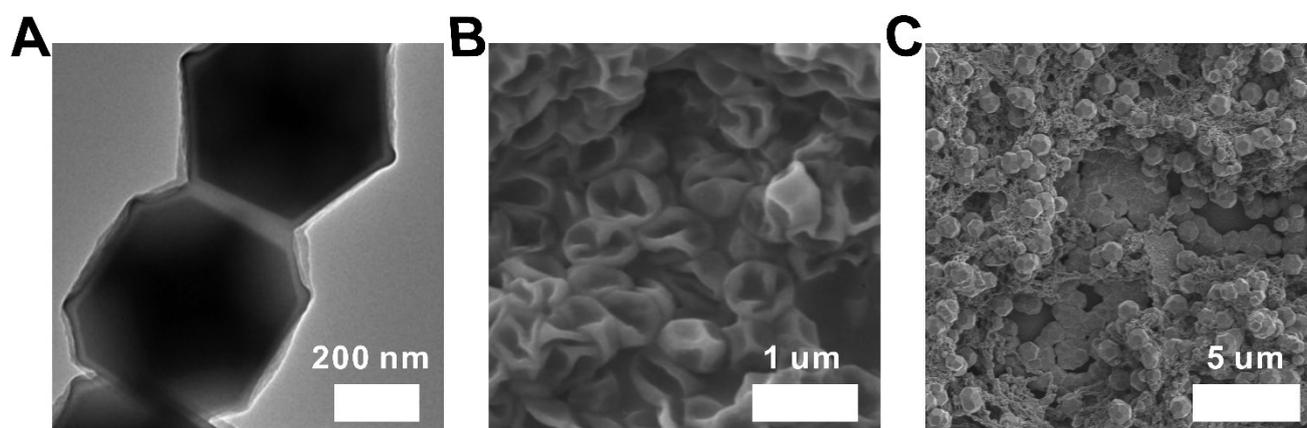


Fig. S22 (A) TEM image of ZIF-8@xPS. SEM image of ZIF-8@xPS-DE (B) and ZIF-8@xPS-RE (C).

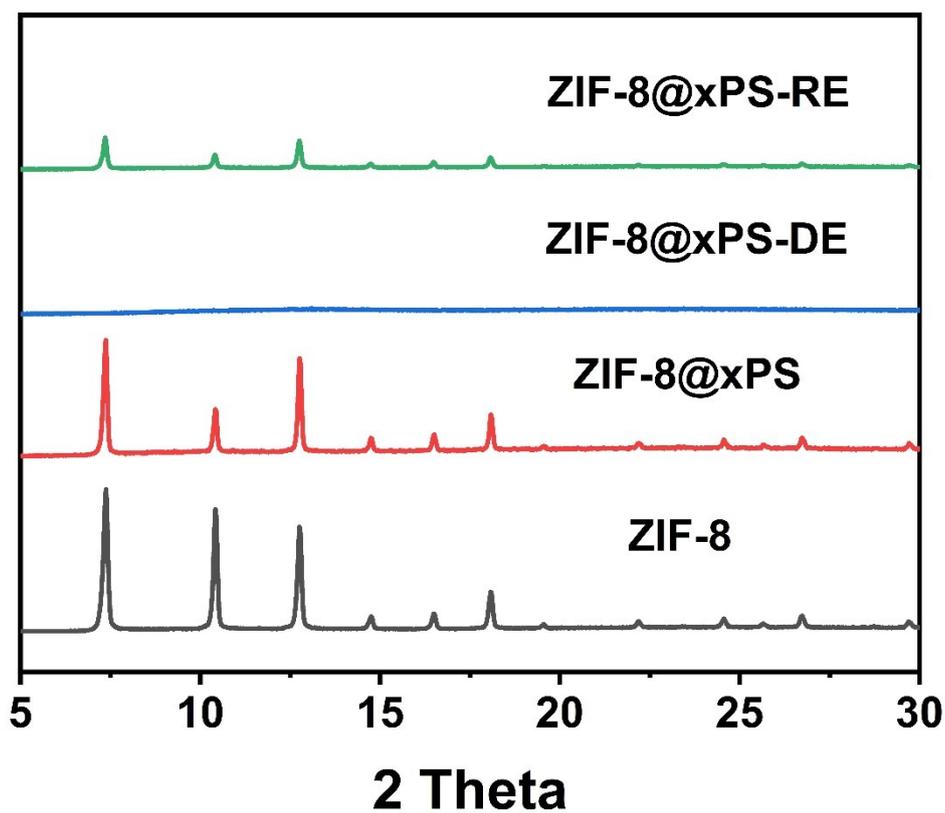


Fig. S23 PXRD patterns of the ZIF-8 and ZIF-8@xPS during the degradation-reconstruction process.

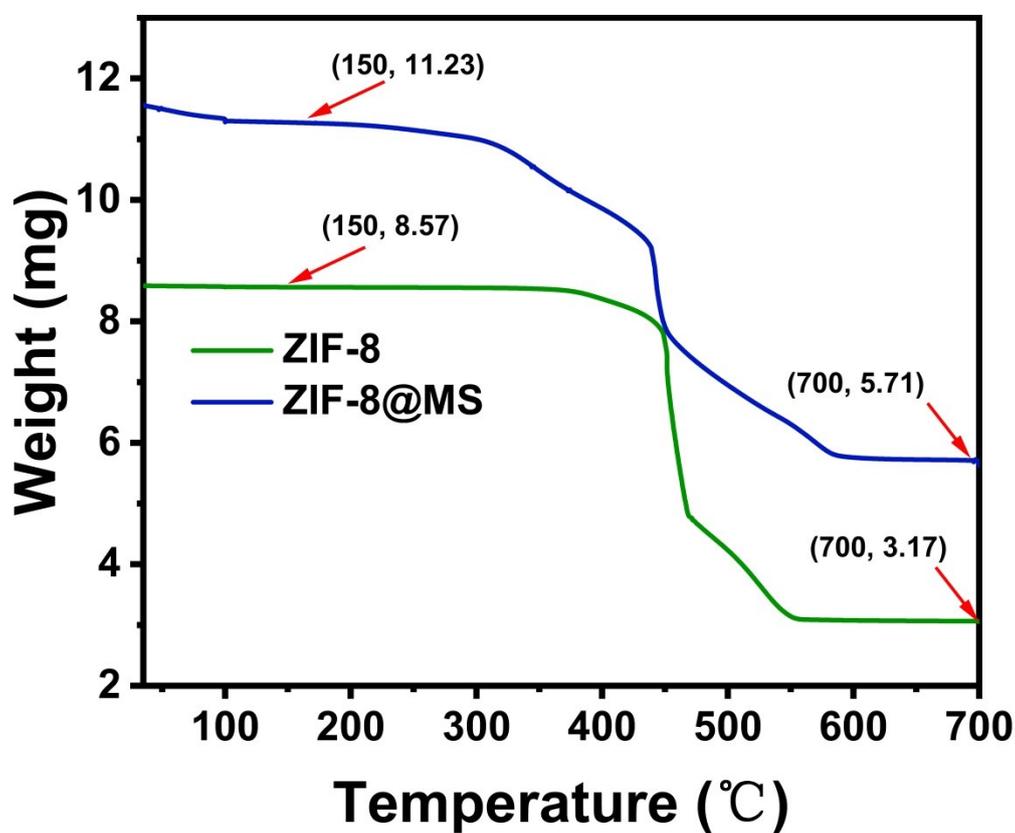


Fig. S24 TGA profiles of pre-dried ZIF-8 and ZIF-8@MS under O₂ atmosphere.

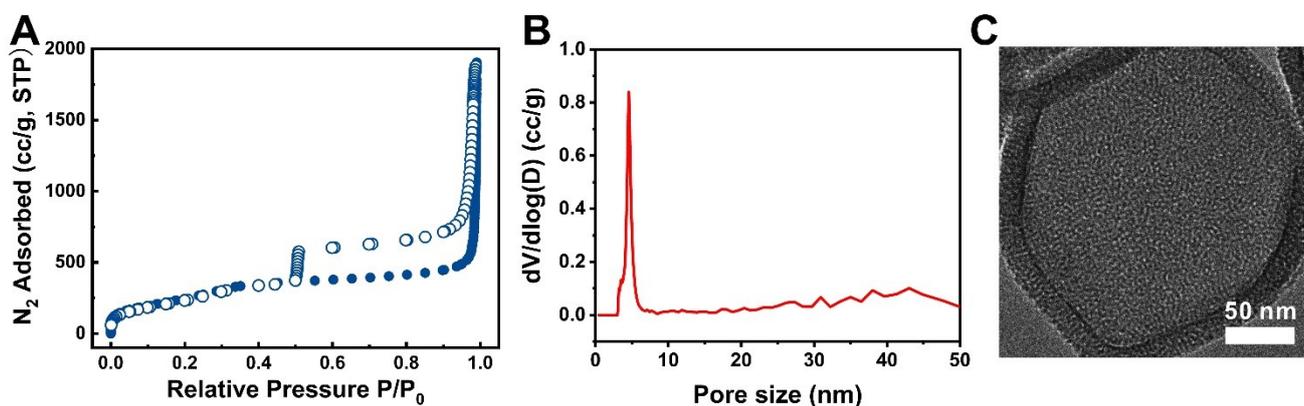


Fig. S25 N_2 adsorption isotherm (A) and pore size distribution diagram (B) of hollow silica at 77 K. (C) TEM image of hollow silica.

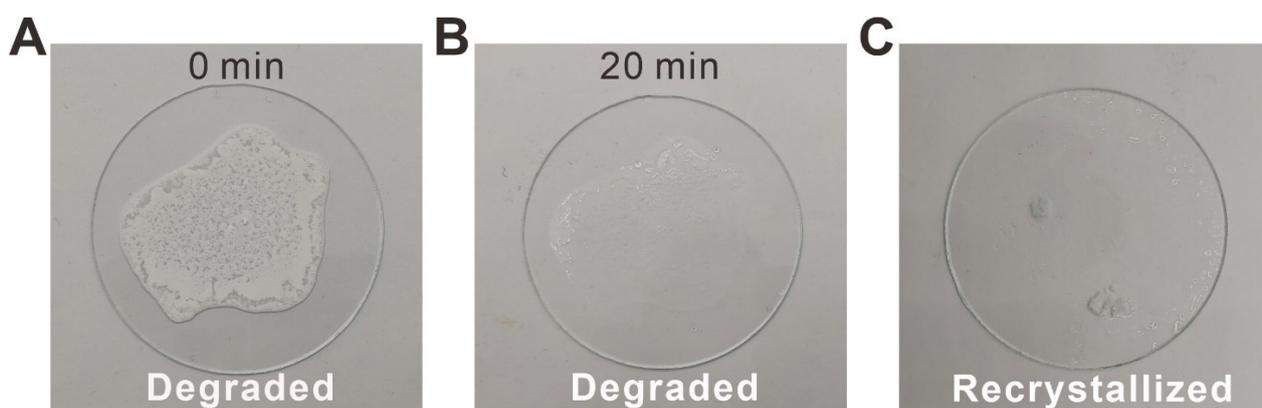


Fig. S26 Photographs of ZIF-8 after exposing to acetic acid vapor for 0 (A) and 20 minutes (B); (C) Photograph of ZIF-8 sample in B after VAR treatment for 24 h.

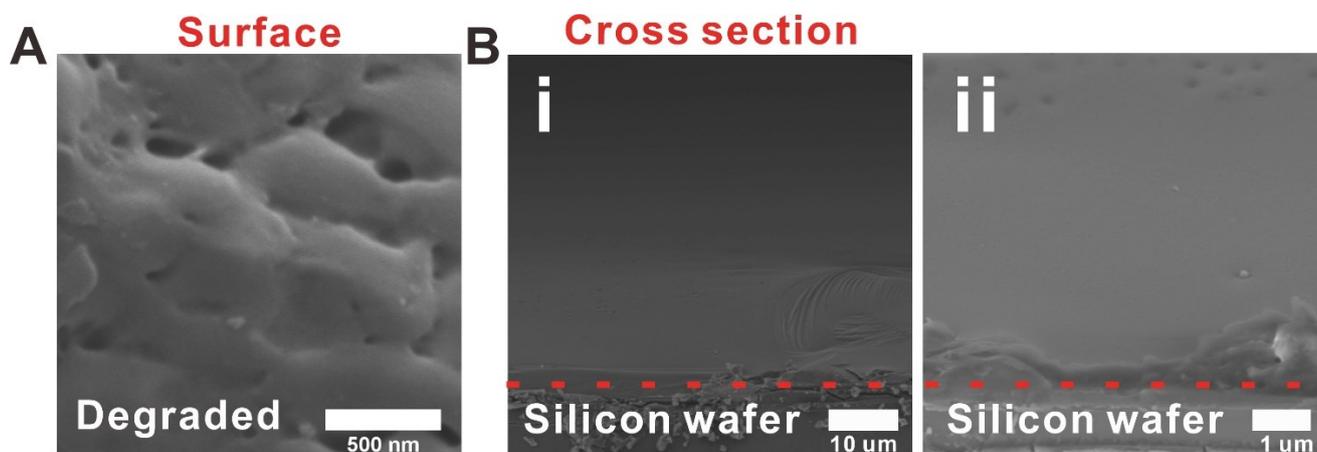


Fig. S27 SEM images of the surface (A) and cross section (B) of ZIF-8-DE

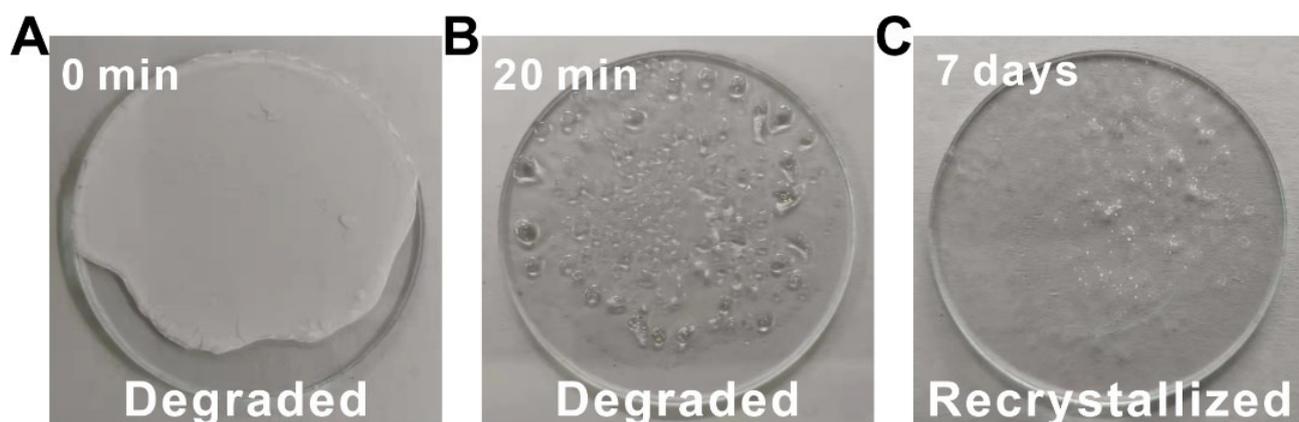


Fig. S28 Photograph of ZIF-8 after exposing to acetic acid vapor for 0 (A) and 20 minutes (B); (C) Photograph of ZIF-8 sample in B after VAR treatment for 7 days.

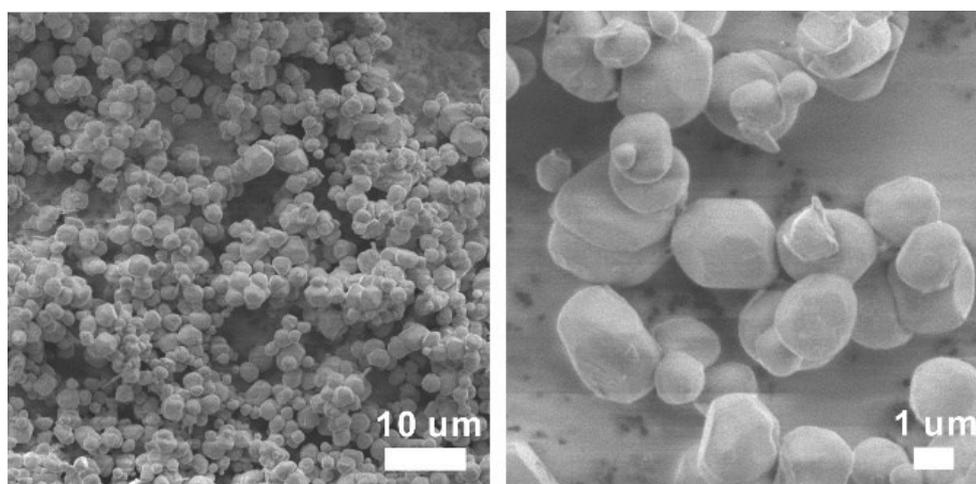


Fig. S29 SEM images of the white speckles from the sample in Fig. S28C.

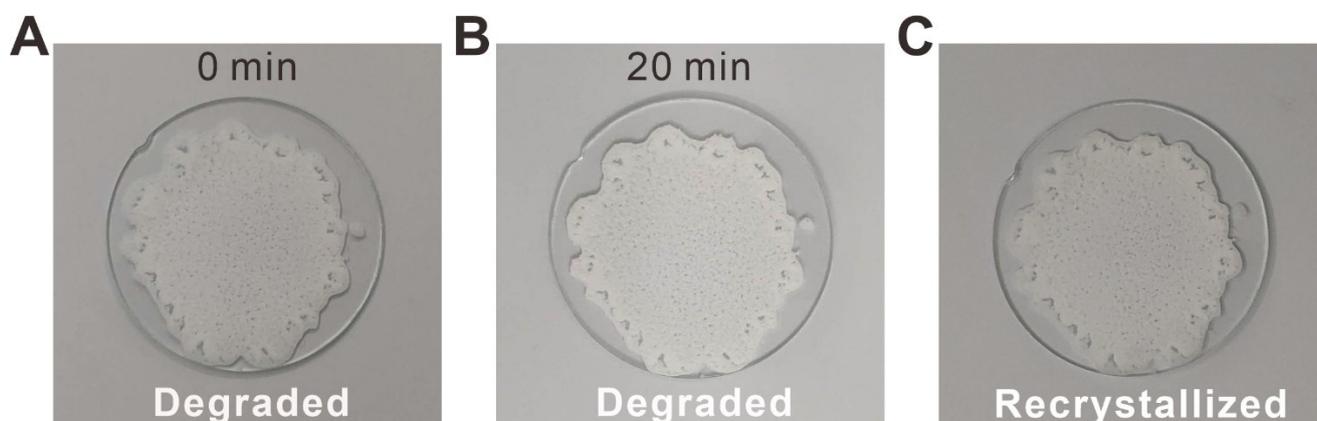


Fig. S30 Photograph of ZIF-8@MS after exposing to acetic acid vapor for 0 (A) and 20 minutes (B); (C) Photograph of ZIF-8@MS sample in B after VAR for 24 h.

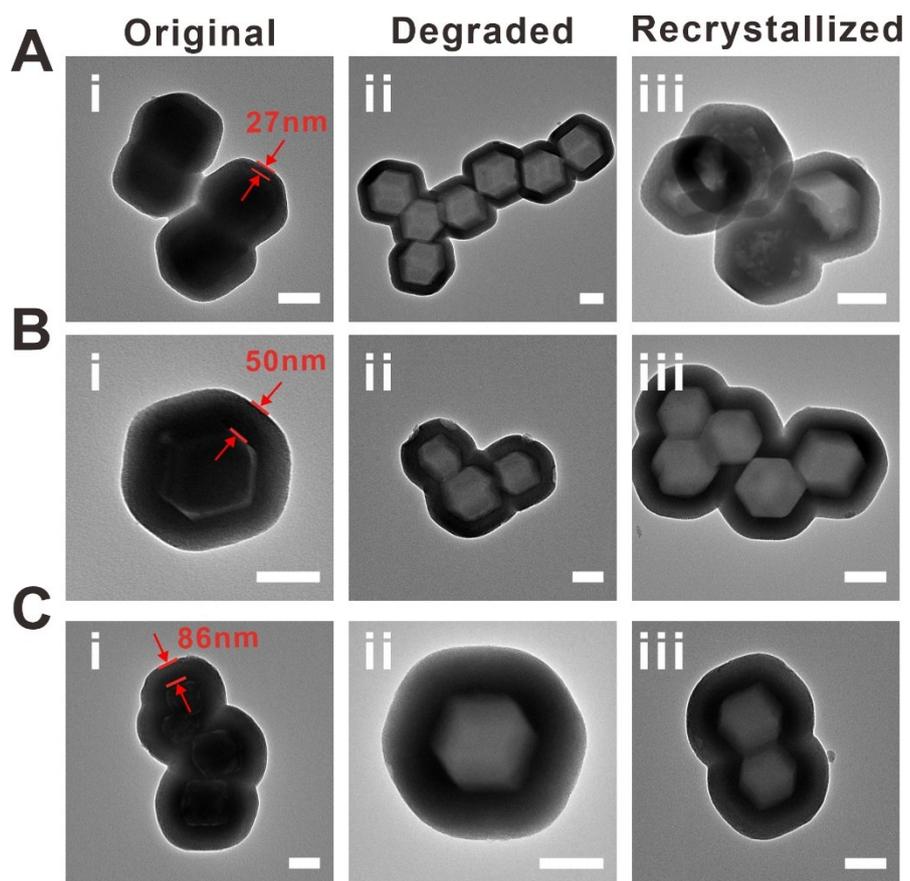


Fig. S31 TEM images of the degradation-reconstruction process of ZIF-8@MS (scale bar = 100 nm)

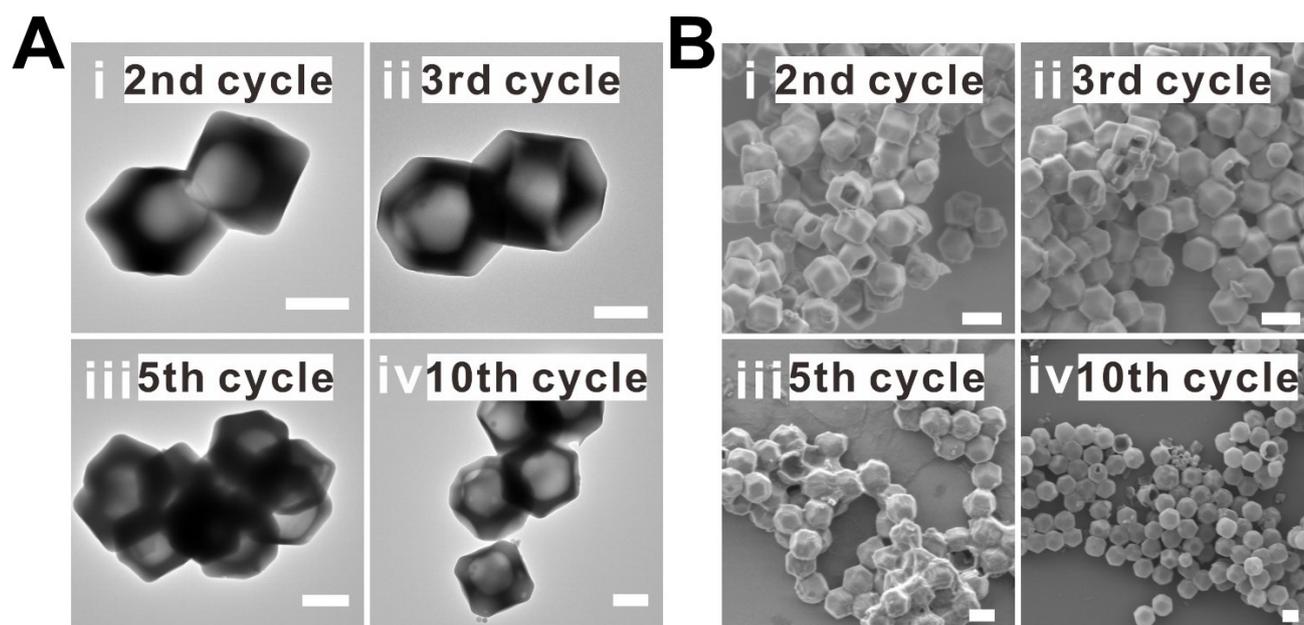


Fig. S32 (A) TEM images of ZIF-8@MS-DE_n, (B) SEM images of ZIF-8@MS-DE_n (n = 2, 3, 5, 10, scale bar = 500 nm)

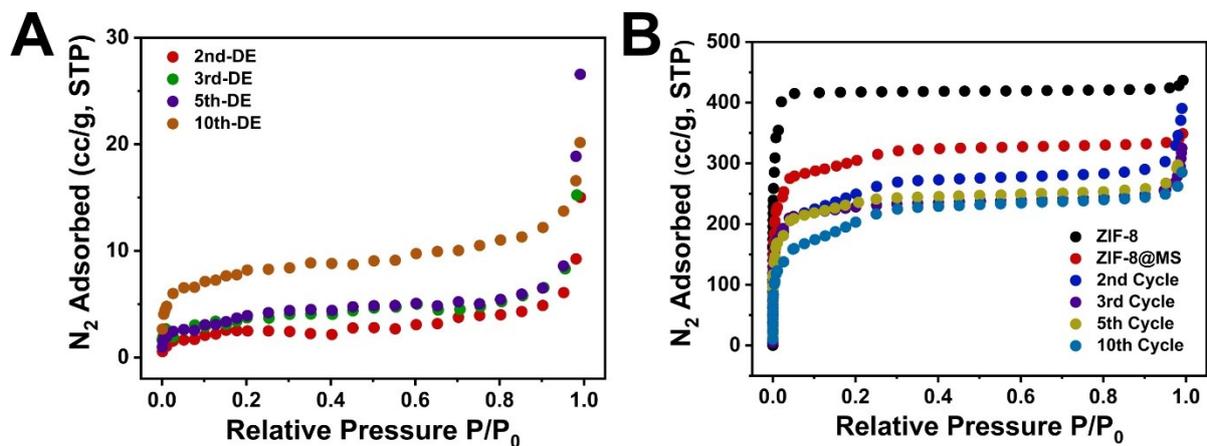


Fig. S33 N₂ adsorption isotherms of (A) ZIF-8@MS-DE_n, (B) ZIF-8@MS and ZIF-8@MS-RE_n at 77 K (n=2,3,5,10)

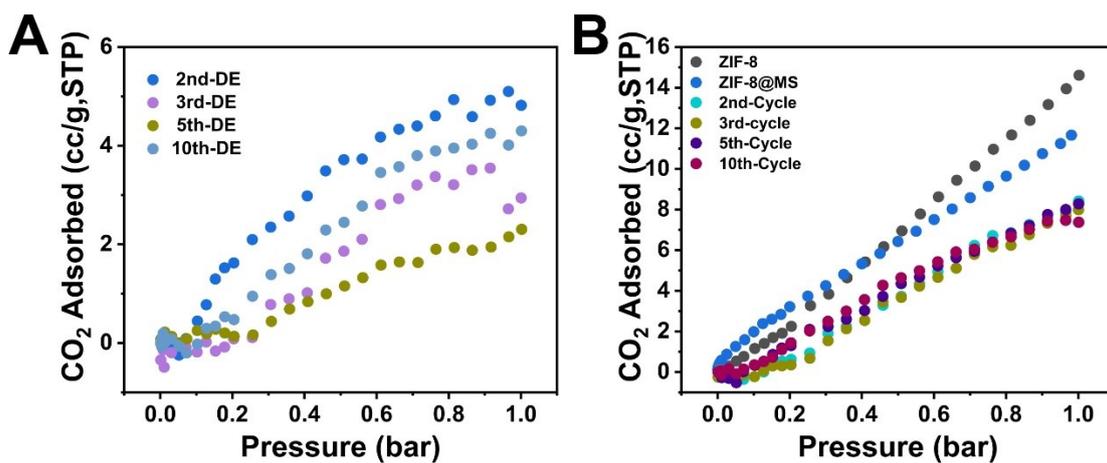


Fig. S34 CO₂ adsorption isotherms of (A) ZIF-8@MS-DE_n, (B) ZIF-8@MS and ZIF-8@MS-RE_n at 298 K (n = 2, 3, 5, 10)

Section 5. Crystal data and structure refinement for CuBTC

| | | |
|-----------------------------------|--|-----------------|
| Identification code | CuBTC | |
| Empirical formula | C ₉ H ₁₀ Cu ₂ O ₁₀ | |
| Formula weight | 405.25 | |
| Temperature | 150(2) K | |
| Wavelength | 1.54178 Å | |
| Crystal system | Monoclinic | |
| Space group | Pn | |
| Unit cell dimensions | a = 3.4664(3) Å | α = 90°. |
| | b = 9.8407(8) Å | β = 93.178(4)°. |
| | c = 17.1098(15) Å | γ = 90°. |
| Volume | 582.75(9) Å ³ | |
| Z | 2 | |
| Density (calculated) | 2.310 Mg/m ³ | |
| Absorption coefficient | 5.078 mm ⁻¹ | |
| F(000) | 404 | |
| Crystal size | 0.05 x 0.015 x 0.008 mm ³ | |
| Theta range for data collection | 4.493 to 47.231°. | |
| Index ranges | -3 ≤ h ≤ 3, -9 ≤ k ≤ 9, -15 ≤ l ≤ 16 | |
| Reflections collected | 6347 | |
| Independent reflections | 1050 [R(int) = 0.1534] | |
| Completeness to theta = 47.231° | 100.0 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 1 and 0.868 | |
| Refinement method | Full-matrix least-squares on F ² | |
| Data / restraints / parameters | 1050 / 2 / 92 | |
| Goodness-of-fit on F ² | 1.043 | |
| Final R indices [I > 2σ(I)] | R1 = 0.0695, wR2 = 0.1632 | |
| R indices (all data) | R1 = 0.0862, wR2 = 0.1735 | |
| Absolute structure parameter | 0.8(2) | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 0.917 and -0.689 e.Å ⁻³ | |

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