Supporting Information

Growth Pattern Control and Nanoarchitecture Engineering of Metal–Organic Framework Single Crystals by Confined Space Synthesis

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Materials and Methods

Materials

Tetraethyl orthosilicate (TEOS, 98%, Aladdin Industrial Corporation), NH$_3$·H$_2$O (28%, Aladdin Industrial Corporation), zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O, 99%, Shanghai Chemical Reagents), cobalt (II) nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O, AR, Aladdin Industrial Corporation), copper nitrate trihydrate (Cu(NO$_3$)$_2$·3H$_2$O, AR, Aladdin Industrial Corporation), 2-methylimidazole (2-MeIM, 98%, Aladdin Industrial Corporation), sodium formate dihydrate (HCOONa·2H$_2$O, AR, Aladdin Industrial Corporation), benzene-1,3,5-tricarboxylic acid (BTC, 98%, Aladdin Industrial Corporation), cetyltrimethylammonium bromide (CTAB, 99%, Aladdin Industrial Corporation), benzaldehyde (99%, Tianjin Kemiu Chemical Co., Ltd.), malononitrile (99%, Aladdin Industrial Corporation), dimethyl formamide (DMF, 99.5%, Guangdong Guanghua Sci-Tech Co., Ltd.), methanol (CH$_3$OH, 99%, Guangdong Guanghua Sci-Tech Co., Ltd), hydrofluoric acid (HF, 40%, Aladdin Industrial Corporation), 2,2 azobisisobutyronitrile (AIBN, >98%, Aladdin Industrial Corporation), dichloromethane (CH$_2$Cl$_2$, 99.5%, Aladdin Industrial Corporation), styrene (99%, Lingfeng Chemical Co., Ltd.).

All chemicals were used as received without further purification.

Methods

Fabrication of silica opals (denoted as 3DO-SiO$_2$).

Monodisperse silica spheres (SiO$_2$) with an average diameter of 235 nm were synthesized by the hydrolysis of TEOS in an alcohol medium in the presence of water and ammonia by a modified procedure originally described by a classical Stöber method. Three-dimensionally (3D) ordered SiO$_2$ templates were assembled from the above monodisperse SiO$_2$ spheres via a centrifugation method. About 40 mL of SiO$_2$ colloidal dispersion was ultrasonicated to form an uniform emulsion, which was then centrifuged at a rate of 2 krpm for 12 h. The obtained precipitation was then dried at 70 °C overnight, followed by a high-temperature treatment at 650 °C under pure Argon flow (30 mL·min$^{-1}$) for 6 h to produce robust 3DO-SiO$_2$. In addition, monodisperse silica spheres with other diameters of 370, 460, 530 and 635 nm were also synthesized by this modified Stöber method, which were then assembled to produce their corresponding silica opals (denoted as 3DO-SiO$_2$(x), in which x represents the average diameter of silica spheres). The hydrolysis parameters for the preparation of silica spheres with five different sizes are listed in Table S1.
Preparation of three-dimensionally ordered macroporous polystyrene (3DOM-PS) template.

Pieces of 3DO-SiO$_2$ were immersed into a 10 mL of styrene monomer solution with 0.05 wt% AIBN as an initiator in a 25 mL Schlenk tube. Then, the tube was immersed into liquid nitrogen to freeze the mixture. After the mixture was completely frozen, it was then maintained at this state and treated with vacuum degassing for 30 min. Subsequently, the frozen mixture was thawed by flowing water (30 °C). The above mixture was subjected to three above freeze-to-thaw cycles. After being separated from the solution, the obtained 3DO-SiO$_2$ based composite was heated to 60 °C for 12 h in a closed vial to allow the polymerization of monomer. Excess PS on the 3DO-SiO$_2$ was removed by wiping the exposed 3DO-SiO$_2$ surface with CH$_2$Cl$_2$. Subsequently, the silica spheres were removed by corrosion using a 15 wt% HF solution (Caution should be taken when using HF during the etching of SiO$_2$, because HF is extremely toxicity and corrosively.) for one day to obtain a freestanding 3DOM-PS inverse opal template. In addition, 3DOM-PS templates with macropore sizes of 330, 425, 500 and 610 nm were also prepared by using 3DO-SiO$_2$ with diameters of 370, 460, 530 and 635 nm as the corresponding nanocasting materials, respectively, which were named as 3DOM-PS(y) (y represents the average diameter of the macropores).

Fabrication of three-dimensionally ordered sphere-assembled ZIF-8 single crystals (denoted as 3DOSA-ZIF-8) and three-dimensionally ordered single-crystalline ZIF-8 sphere arrays (denoted as 3DOSC-ZIF-8).

Both of 3DOSA-ZIF-8 and 3DOSC-ZIF-8 were obtained by the controllable growth of ZIF-8 crystals in above 3DOM-PS template.$^2$ For the synthesis of 3DOSA-ZIF-8 and 3DOSC-ZIF-8, a methanol solution with low precursor concentration (containing 0.163 g/mL of Zn(NO$_3$)$_2$·6H$_2$O and 0.135 g/mL of 2-MeIM), and a methanol solution with high precursor concentration (containing 0.815 g/mL of Zn(NO$_3$)$_2$·6H$_2$O and 0.675 g/mL of 2-MeIM), were prepared as precursor solutions, respectively. In a typical procedure, pieces of 3DOM-PS with an average macropore size of about 200 nm were immersed into the above low or high concentration precursor solution for 1 h and further treated with vacuum degassing until no bubble came out from the PS template. The impregnated composite samples were carefully separated from the precursor solutions and dried at 60 °C for several hours to obtain the corresponding precursor@PS(0.135) (produced by using the low concentration precursor solution as a feedstock) and precursor@PS(0.675) (produced by using the high concentration
precursor solution as a feedstock). The above two dried composite samples were severally putted into a 40 mL CH$_3$OH/NH$_3$·H$_2$O (1:1 v/v) mixed solution and further treated with vacuum degassing for an hour. After crystallizing at room temperature and atmospheric pressure for 24 h, the obtained products were filtrated and dried at 50 °C overnight. Then the PS templates were dissolved by DMF completely. The precipitates were collected by centrifuging at 4000 rpm for 5 min, and then washed with DMF for several times to make sure that all PS templates were removed completely. Finally, the obtained 3DOSA-ZIF-8 and 3DOSC-ZIF-8 were washed and soaked with CH$_2$Cl$_2$ fully to wash off the DMF and vacuum-drying at 150 °C overnight.

In addition, 3DOM-PS(y) templates with other macropore sizes were also used to control the diameters of ZIF-8 spheres in 3DOSA-ZIF-8 and 3DOSC-ZIF-8 (denoted as 3DOSA-ZIF-8(z) and 3DOSC-ZIF-8(z), in which z represents the average diameter of ZIF-8 spheres) by using the above procedure. To explore the role of precursor concentration, we monitored the structural evolution of the products harvested at different stages by using three representative concentrations of precursor, namely 0.075, 0.135 and 0.675 g/mL on a 2-MeIM basis (holding the molar ratio of 2-MeIM/Zn(NO$_3$)$_2$ to be 3). Other steps were identical to those for the preparation of 3DOSA-ZIF-8 and 3DOSC-ZIF-8.

**Fabrication of single-crystalline ZIF-8 (SC-ZIF-8) spheres.**

In a typical synthesis, isolated SC-ZIF-8 spheres with an average diameter of about 200 nm were obtained by the disassembly of 3DOSC-ZIF-8 by using a simple sonication method. First, 0.1 g of 3DOSC-ZIF-8 was added to 20 mL of methanol in a conical tube. The 3DOSC-ZIF-8 suspension was then sonicated for 180 min, during which ice was added to the water bath of sonicator to lower the temperature to below 25 °C. After the sonication, the produced SC-ZIF-8 spheres were separated from the methanol solution by centrifugation at 6000 rpm for 5 min, and then dried at 70 °C for 6 h. Besides, 3DOSC-ZIF-8(z) with other diameters of 330, 425, 500 and 610 nm were also applied to fabricate the corresponding SC-ZIF-8(z) by using the same disassembly procedure. The resulting products were named as SC-ZIF-8(330), SC-ZIF-8(425), SC-ZIF-8(500) and SC-ZIF-8(610).

**Fabrication of three-dimensionally ordered sphere-assembled ZIF-67 single crystals (denoted as 3DOSA-ZIF-67) and three-dimensionally ordered single-crystalline ZIF-67 sphere arrays (denoted as 3DOSC-ZIF-67).**
3DOSA-ZIF-67 and 3DOSC-ZIF-67 were synthesized by using the same concentration-assisted confined growth procedures as 3DOSA-ZIF-8 and 3DOSC-ZIF-8, respectively, except using Co(NO$_3$)$_2$·6H$_2$O instead of Zn(NO$_3$)$_2$·6H$_2$O as a metal source. For the synthesis of 3DOSA-ZIF-67 and 3DOSC-ZIF-67, a methanol solution with low precursor concentration (0.4 g/mL of Co(NO$_3$)$_2$·6H$_2$O and 1 g/mL of 2-MeIM), and a methanol solution with high precursor concentration (1 g/mL of Co(NO$_3$)$_2$·6H$_2$O and 2.5 g/mL of 2-MeIM) were used as the precursor solutions, respectively.

Fabrication of three-dimensionally ordered sphere-assembled HKUST-1 single crystals (denoted as 3DOSA-HKUST-1) and three-dimensionally ordered single-crystalline HKUST-1 sphere arrays (denoted as 3DOSC-HKUST-1).

To fabricate 3DOSA-HKUST-1, 1.825 g of Cu(NO$_3$)$_2$·3H$_2$O was dissolved in 50 mL of deionized water, and 0.5292 g of benzene-1,3,5-tricarboxylic acid (BTC) was dissolved in 50 mL of ethanol. Then the above two solutions were mixed to form a low-concentration precursor solution for further use. To fabricate 3DOSC-HKUST-1, 1.825 g of Cu(NO$_3$)$_2$·3H$_2$O was dissolved in 15 mL of deionized water, and 0.5292 g of benzene-1,3,5-tricarboxylic acid (BTC) was dissolved in 15 mL of ethanol. Then two solutions were mixed to form a high-concentration precursor solution for further use. It is worth noting that, to avoid the slow spontaneous crystallization of HKUST-1 precursor, the above two types of precursor solutions should be freshly prepared for further synthesis steps.

Subsequently, 1.04 g of HCOONa·2H$_2$O (10 mmol) was added into 80 mL of mixed solution of deionized water and methanol (the volume ratio is 1:1) under magnetic stirring to form an induction solution. Then the 3DOM-PS(200) template was filled with the above induction solution by vacuum degassing for 1 h, and the obtained composite template was dried at 60 °C overnight for next step.

The above dried composite template containing sodium formate was quickly immersed into the aforementioned low- or high-concentration precursor solutions, which were further treated with vacuum degassing for 60 min. After crystallizing at room temperature and atmospheric pressure for 12 h, 3DOSA-HKUST-1 or 3DOSC-HKUST-1 were obtained by removing the PS template, followed by washing thoroughly with ethanol and drying at 70 °C overnight.

Preparation of conventional ZIF-8 (denoted as C-ZIF-8).
For comparison, C-ZIF-8 was synthesized using a previously reported method. In a typical synthesis, 0.29 g of zinc nitrate hexahydrate was first dissolved in 10 mL of deionized water; then 4.54 g of 2-methylimidazole and 1 mg of CTAB were dissolved in 70 mL of deionized water. After that, the zinc nitrate and 2-methylimidazole solutions were mixed and stirred for 10 min at room temperature to form a mixed solution, which was then transferred into a Teflon reactor inside a stainless-steel autoclave for hydrothermal synthesis at 120 °C for 6 h with a heating rate of 2 °C min\(^{-1}\) from room temperature. After cooling the autoclave to room temperature, the obtained C-ZIF-8 was collected by centrifuging at 4000 rpm for 5 min, continuously washed with anhydrous methanol via several centrifugation–redispersion cycles, and then dried at 65 °C overnight.

**Preparation of conventional ZIF-67 (denoted as C-ZIF-67).**

C-ZIF-67 was prepared by using a previously reported procedure. In a typical synthesis, 1.746 g of Co(NO\(_3\))\(_2\)·6H\(_2\)O and 1.968 g of 2-methylimidazole were severally added into 150 mL of methanol under stirring to obtain two methanolic solutions. After complete dissolution, the methanolic solution of Co(NO\(_3\))\(_2\) was carefully poured into the methanolic solution of 2-MeIM at room temperature. After continuous stirring of 15 s, the final solution was maintained undisturbed at room temperature for 24 h. The purple precipitate was collected by centrifugation at a rate of 6000 rpm for 2 min, which were further washed in methanol three times and dried at 60 °C overnight.

**Preparation of conventional HKUST-1 (denoted as C-HKUST-1).**

The C-HKUST-1 was prepared by following a previously reported solvothermal method. In a typical synthesis, 3.5 g of Cu(NO\(_3\))\(_2\)·3H\(_2\)O and 1.68 g of BTC were dissolved in 48 mL of deionized water and 48 mL of ethanol, respectively. The two solutions were then mixed together under ultrasonication for 15 minutes. Subsequently, the mixed solution was transferred into a Teflon autoclave, which was kept at 120 °C for 14 h. The resulting blue powder was separated by centrifugation at a rate of 4000 rpm for 1 min and washed with the ethanol for three times.

**The control experiment.**

A control experiment was conducted to prove that different concentrations of precursor can lead to the different aggregation states of dry precursor gel in 3DOM-PS, which finally determine the growth pattern and nanoarchitecture of the resultant ZIF-8 single crystals in
confined spaces. In this control experiment, a freeze-drying method was employed to control the distribution of dry precursor gel in the drying step (the used concentration of precursor is 0.135 g/mL). We design this experiment by holding the idea that the removal of solvents (mainly water) by cryogenic sublimation can minimize the movement of precursor solution in 3DOM-PS, and thus keep the precursor where it is during the freeze-drying process.

First, a methanolic solution (A) and an aqueous solution (B) with the same concentration of precursor (0.135 g/mL) were prepared as follows: the solution A was prepared by dissolving 4.89 g of Zn(NO$_3$)$_2$·6H$_2$O and 4.05 g of 2-MeIM into 30 mL of methanol under magnetic stirring, while the solution B was prepared by dissolving 4.89 g of Zn(NO$_3$)$_2$·6H$_2$O and 4.05 g of 2-MeIM into 30 mL of mixed solution of deionized water and concentrated hydrochloric acid (the volume ratio is 9:1) under magnetic stirring.

Subsequently, the 3DOM-PS(200) template was immersed into the solution A for 1 h and further treated with vacuum degassing for 60 min to make all the spherical macropores of 3DOM-PS(200) filled with precursor solution. After being separated, the impregnated composite was further immersed into the solution B and let it sit at room temperature and atmospheric pressure for 24 h to replace the methanol in 3DOM-PS(200) with water. Then, the obtained composite was dried by freeze-drying. The other steps were identical to those for the fabrication of 3DOSA-ZIF-8 and 3DOSC-ZIF-8. The resultant product was named as F-3DO-ZIF-8.

**Characterization**

Powder X-ray diffraction patterns of the samples were obtained on a Rigaku diffractometer (D/MAX-IIIA, 3 kW) using Cu Kα radiation (40 kV, 30 mA, λ = 0.1543 nm). BET surface area and pore size measurements were performed with N$_2$ adsorption/desorption isotherms at 77 K on a Micromeritics ASAP 2460 instrument. Before measurements, the samples were degassed at 150 °C for 12 h. The size and morphology of materials were investigated using a high resolution scanning electron microscope (SEM, Hitachi SU8220) equipped with an energy dispersive X-ray spectrometer (EDS). Thermo Scientific Talos L120C, transmission electron microscopy (TEM, JEM-1400F) and high-resolution transmission electron microscope (TEM, JEOL, JEM-2100F) were employed to determine the structures and morphologies of the catalysts. High-angle annular dark-field scanning TEM (HAADF-STEM) measurements were obtained in an FEI Titan Cubed Themis G2 300 transmission electron microscope operated at an acceleration voltage of 300 kV and equipped with double spherical aberration (Cs) correctors. The samples for TEM test were prepared by
dispersing the samples in ethanol under ultrasound. After that, a very small amount of suspensions was taken out using microsyringe and then dropped on a copper online. Digital CMOS Camera (MC2000C) was used to evaluate optical properties of as-prepared crystals. The length scale of the microscope was calibrated prior to measurements. Freeze-drying of materials were performed on Biosafe-10A lyophilizer.

**Catalytic Activity Testing**

Typically, 11.5 mg of 3DOSA-ZIF-8 in THF (6 mL) was first placed in a 25 mL Schlenk tube. Then, 0.265 g of benzaldehyde (2.5 mmol) and 0.33 g of malononitrile (5 mmol) were added to the above mixture. The resulting solution was stirred at room temperature for a preset time. After completion, the 3DOSA-ZIF-8 in the reaction solution was filtered off by centrifugation, and the solution was diluted by ethyl acetate for further quantitative analysis. Conversions and yields were obtained by GC/MS (Agilent Technologies 7890B-5977A GC/MS). To compare the catalytic properties, 3DOSC-ZIF-8(200), C-ZIF-8, SC-ZIF-8(200), SC-ZIF-8(330), SC-ZIF-8(425), SC-ZIF-8(500) and SC-ZIF-8(610) were also used as heterogeneous catalysts for this reaction under the same condition.

To investigate the stability and recyclability, the catalysts were removed from the reaction mixtures by centrifugation at the end of catalytic reaction. The remained catalysts were washed with THF, dried under vacuum to remove the residual solvent, and then reused as catalysts in the next cycle (27.6 mg of catalyst, 0.636 g of benzaldehyde and 0.792 g of malononitrile in 14.4 mL THF, magnetically stirring, room temperature, 0.5 h of reaction time).
Figures S1. to S57.

Figure S1. Photographs of the 3DOM-PS(200) template immersed in (a) 0.075, (b) 0.135 and (c) 0.675 g/mL of precursor solutions. (d) Photograph of a bag of 3DOM-PS(200) template immersed in a 0.675 g/mL of precursor solution.

It is obvious that when using 0.075 and 0.135 g/mL of precursor solutions as feedstocks, the 3DOM-PS(200) template can completely sink into the bottom of the precursor solutions and its color also changes from light blue into green, suggesting that the spherical macropores of the inverse opal are filled with precursor solutions. In sharp contrast, when further increasing the concentration of precursor to 0.675 g/mL, the 3DOM-PS(200) template would float on the surface of the precursor solution, which is unfavorable for the accessibility of ZIF-8 precursor into its macropores. Therefore, when using 0.675 g/mL of precursor solution as a feedstock, we should use a permeable bag to pack the 3DOM-PS(200) template with a stirring magneton for achieving a good impregnation. As expected, the bag can easily sink into the solution and the color of the template also turns to green, suggesting that this strategy is very effective.
Figure S2. Representative low-magnification SEM images of (a) 3DO-SiO$_2$ and (b) 3DOM-PS. (c) The corresponding particle size distribution of 3DO-SiO$_2$ on the basis of (a). (d) The corresponding macropore size distribution of 3DOM-PS on the basis of (b).
Figure S3. (a, b) Representative SEM images of 3DOSA-ZIF-8 at different magnifications. (c) The corresponding crystal size distribution of 3DOSA-ZIF-8 on the basis of (a). (d) The XRD patterns of 3DOSA-ZIF-8 and simulated ZIF-8.
Figure S4. (a, b) Low-magnification SEM images of 3DOSA-ZIF-8. (c-e) High-magnification SEM images of three representative 3DOSA-ZIF-8 crystals.
Figure S5. Representative SEM images and corresponding schematic models of (a) 3DOSA-ZIF-8 and (b) C-ZIF-8. Clearly, the well arrangement of 3D ordered ZIF-8 spheres can be identified by the individual crystals taken from three different directions.
Figure S6. (a, b) Representative SEM images of C-ZIF-8 at different magnifications.
Figure S7. (a-c) High-magnification TEM images of three representative 3DOSA-ZIF-8 crystals with the (110) or (111) plane of FCC arrangement of the ZIF-8 spheres.
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Figure S9. (a, b) Representative SEM images of the edge of 3DOSC-ZIF-8 at different magnifications, showing the high ordered arrangement of ZIF-8 spheres in the edge of 3DOSC-ZIF-8.
Figure S10. (a) Arrangement of spheres on different planes of FCC arrangement. The SEM images of the FCC \{111\} planes for different samples at different magnifications: (b, c) 3DO-SiO$_2$, (f, g) 3DOM-PS, (j, k) 3DOSC-ZIF-8. The SEM images for the FCC \{100\} planes for different samples at different magnifications: (d, e) 3DO-SiO$_2$, (h, i) 3DOM-PS, (l, m) 3DOSC-ZIF-8.
Figure S11. (a, b) STEM and (c, d) TEM images of 3DOSC-ZIF-8 at low magnifications (a, c) and high magnifications (b, d), clearly indicating the ZIF-8 spheres in 3DOSC-ZIF-8 are neatly arrayed.
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Figure S13. (a, b) Representative SEM images of 3DOSC-ZIF-8 at different magnifications. (c) The corresponding particle size distribution of 3DOSC-ZIF-8 on the basis of (a). (d) The XRD patterns of 3DOSC-ZIF-8 and simulated ZIF-8.
Figure S14. (a) TEM image of an individual ZIF-8 sphere in 3DOSC-ZIF-8. (b) High-resolution TEM image of the white square region in the edge of the sphere shown in (a). (c) Intensity profile plot of the image in (b) after applying a bandpass filter. The periodicity of the intensity profile is constant and continuous with a period of ~ 11 Å.
Figure S15. (a) HRTEM image of 3DOSC-ZIF-8, and (b, c) lattice-resolution TEM images taken from the different regions in (a) (the insets of a, b and c are their corresponding FFT patterns).
Figure S16. (a) The XRD patterns of SC-ZIF-8 and simulated ZIF-8. (b) TEM image of SC-ZIF-8 particles.
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Figure S18. XRD patterns of high-c-precursor@PS, 3DOSC-ZIF-8@PS and simulated ZIF-8, indicating the generation of ZIF-8 phase after soaking high-c-precursor@PS with a CH$_3$OH/NH$_3$·H$_2$O mixing solution for 24 h (high-c-precursor@PS and 3DOSC-ZIF-8@PS were obtained by using 0.675 g/mL of precursor solution as a feedstock).
Figure S19. Photographs of C-ZIF-8, 3DOSA-ZIF-8 and 3DOSC-ZIF-8.
Figure S20. Photographs of (a, b) 3DOSC-ZIF-8 and (c, d) C-ZIF-8, illuminated from the same side as the camera (reflectance mode) (a, c) or from the rear side of the camera (transmittance mode) (b, d). All samples were saturated with methanol.
Figure S21. (a, b) Representative SEM images of 3DOSA-ZIF-8(330) at different magnifications. (c) The corresponding crystal size distribution of 3DOSA-ZIF-8(330) on the basis of (a). (d) The XRD patterns of 3DOSA-ZIF-8(330) and simulated ZIF-8.
Figure S22. (a, b) Representative SEM images of 3DOSA-ZIF-8(425) at different magnifications. (c) The corresponding crystal size distribution of 3DOSA-ZIF-8(425) on the basis of (a). (d) The XRD patterns of 3DOSA-ZIF-8(425) and simulated ZIF-8.
Figure S23. (a, b) Representative SEM images of 3DOSA-ZIF-8(500) at different magnifications. (c) The corresponding crystal size distribution of 3DOSA-ZIF-8(500) on the basis of (a). (d) The XRD patterns of 3DOSA-ZIF-8(500) and simulated ZIF-8.
Figure S24. (a, b) Representative SEM images of 3DOSA-ZIF-8(610) at different magnifications. (c) The corresponding crystal size distribution of 3DOSA-ZIF-8(610) on the basis of (a). (d) The XRD patterns of 3DOSA-ZIF-8(610) and simulated ZIF-8.
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Figure S26. (a) HAADF-STEM image and (b) the corresponding EDX element mappings of 3DOSC-ZIF-8(330), reflecting that the elements of Zn, N and C were homogeneously distributed in the entire crystal.
Figure S27. (a, b) Representative SEM images of 3DOSC-ZIF-8(425) at different magnifications. (c) The corresponding particle size distribution of 3DOSC-ZIF-8(425) on the basis of (a). (d) The XRD patterns of 3DOSC-ZIF-8(425) and simulated ZIF-8.
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Figure S29. (a, b) Representative SEM images of 3DOSC-ZIF-8(500) at different magnifications. (c) The corresponding particle size distribution of 3DOSC-ZIF-8(500) on the basis of (a). (d) The XRD patterns of 3DOSC-ZIF-8(500) and simulated ZIF-8.
Figure S30. (a) HAADF-STEM image and (b) the corresponding EDX element mappings of 3DOSC-ZIF-8(500), reflecting that the elements of Zn, N and C were homogeneously distributed in the entire crystal.
Figure S31. (a, b) Representative SEM images of 3DOSC-ZIF-8(610) at different magnifications. (c) The corresponding particle size distribution of 3DOSC-ZIF-8(610) on the basis of (a). (d) The XRD patterns of 3DOSC-ZIF-8(610) and simulated ZIF-8.
Figure S32. (a) HAADF-STEM image and (b) the corresponding EDX element mappings of 3DOSC-ZIF-8(610), reflecting that the elements of Zn, N and C were homogeneously distributed in the entire crystal.
Figure S33. Controlled growth of 3DOSA-ZIF-8 and 3DOSC-ZIF-8 with spherical element diameters ranging from 330 to 610 nm by carefully controlling the macropore sizes of the 3DOM-PS templates molded from the corresponding silica opals. SEM images of the silica opals with diameters ranging from 370 to 635 nm: (a) 370 nm, (e) 460 nm, (i) 530 nm and (m) 635 nm. SEM images of the 3DOM-PS templates and the resulting 3DOSA-ZIF-8 and 3DOSC-ZIF-8: (b-d) 330 nm, (f-h) 425 nm, (j-l) 500 nm and (n-p) 610 nm. The average diameters of silica opals were larger than the macropore sizes of the corresponding 3DOM-PS, which indicated that the pores contracted when the silica spheres were removed. In sharp contrast, the diameters of the ZIF-8 spheres well matches with the macropore sizes of 3DOM-PS, indicating that the ZIF-8 spheres did not contract during the removal of 3DOM-PS templates.
Figure S34. Representative low-magnification SEM images of (a) 3DO-SiO$_2$(370) and (b) 3DOM-PS(330). (c) The corresponding particle size distribution of 3DO-SiO$_2$(370) on the basis of (a). (d) The corresponding macropore size distribution of 3DOM-PS(330) on the basis of (b).
Figure S35. Representative low-magnification SEM images of (a) 3DO-SiO$_2$(460) and (b) 3DOM-PS(425). (c) The corresponding particle size distribution of 3DO-SiO$_2$(460) on the basis of (a). (d) The corresponding macropore size distribution of 3DOM-PS(425) on the basis of (b).
Figure S36. Representative low-magnification SEM images of (a) 3DO-SiO$_2$(530) and (b) 3DOM-PS(500). (c) The corresponding particle size distribution of 3DO-SiO$_2$(530) on the basis of (a). (d) The corresponding macropore size distribution of 3DOM-PS(500) on the basis of (b).
Figure S37. Representative low-magnification SEM images of (a) 3DO-SiO$_2$(635) and (b) 3DOM-PS(610). (c) The corresponding particle size distribution of 3DO-SiO$_2$(635) on the basis of (a). (d) The corresponding macropore size distribution of 3DOM-PS(610) on the basis of (b).
Figure S38. The correlation of the diameters of 3DOSA-ZIF-8/3DOSC-ZIF-8 with those of the employed SiO$_2$ sphere templates, laying guidances for the synthesis of desired 3DOSA-ZIF-8/3DOSC-ZIF-8 with a specific size.
Figure S39. Photographs of 3DOM-PS(200) template immersed in (a) an aqueous solution of ZIF-8 precursor (0.135 g/mL) and (b) a methanol solution of ZIF-8 precursor (0.135 g/mL). It is obvious that when using water as a solvent, the 3DOM-PS(200) template would float on the surface of the solution, which is unfavorable for the infusion of ZIF-8 precursor into its macropores. In sharp contrast, when using methanol as a solvent, the 3DOM-PS(200) template can completely sink into the bottom of the solution and its color also changes from light blue into green, suggesting that the spherical macropores of the inverse opal are filled with the precursor solution.
Figure S40. XRD patterns of 3DOSA-ZIF-67, C-ZIF-67 and simulated ZIF-67, indicating the high crystallinity and good phase purity of the 3DOSA-ZIF-67.
Figure S41. (a, b) Low-magnification SEM images of 3DOSA-ZIF-67. (c-e) High-magnification SEM images of three individual 3DOSA-ZIF-67 particles.
Figure S42. SEM images of C-ZIF-67 at different magnifications.
Figure S43. Representative SEM images and corresponding schematic models of (a) individual 3DOSA-ZIF-67 and (b) C-ZIF-67 particles from different orientations. The three-dimensionally well-ordered arrangement of highly uniform ZIF-67 spheres can be clearly identified by these SEM images.
Figure S44. XRD patterns of 3DOSA-HKUST-1, C-HKUST-1 and simulated HKUST-1, indicating the high crystallinity and good phase purity of 3DOSA-HKUST-1.
Figure S45. (a, b) Low-magnification SEM images of 3DOSA-HKUST-1. (c-e) High-magnification SEM images of three individual 3DOSA-HKUST-1 particles.
Figure S46. SEM images of C-HKUST-1 at different magnifications.
Figure S47. Representative SEM images and corresponding schematic models of (a) individual 3DOSA-HKUST-1 and (b) C-HKUST-1 particles from different orientations. The three-dimensionally well-ordered arrangement of highly uniform small HKUST-1 spheres can be clearly identified by these SEM images.
Figure S48. (a, b) Representative SEM images of 3DOSC-ZIF-67 at different magnifications. (c) The corresponding particle size distribution of 3DOSC-ZIF-67 on the basis of (a). (d) The XRD patterns of 3DOSC-ZIF-67 and simulated ZIF-67.
Figure S49. (a) STEM and (b) TEM images of 3DOSC-ZIF-67 at low magnifications, clearly indicating the ZIF-67 spheres of 3DOSC-ZIF-67 were neatly arrayed.
Figure S50. (a) Arrangement of spheres on different planes of FCC arrangement. SEM images for the {111} plane of FCC arrangement at different magnifications: (b, c) 3DO-SiO$_2$, (f, g) 3DOM-PS, (j, k) 3DOSC-ZIF-67. SEM images for the {100} plane of FCC arrangement at different magnifications: (d, e) 3DO-SiO$_2$, (h, i) 3DOM-PS, (l, m) 3DOSC-ZIF-67.
Figure S51. XRD patterns of 3DOSC-HKUST-1, C-HKUST-1 and simulated HKUST-1, indicating the high crystallinity and good phase purity of 3DOSC-HKUST-1.
Figure S52. (a, b) Representative SEM images of 3DOSC-HKUST-1 at different magnifications. (c) The corresponding particle size distribution of 3DOSC-HKUST-1 on the basis of (a). (d) The XRD patterns of 3DOSC-HKUST-1 and simulated HKUST-1.
Figure S53. (a) STEM and (b) TEM images of 3DOSC-HKUST-1 at low magnifications, clearly indicating the HKUST-1 spheres of 3DOSC-HKUST-1 are neatly arrayed.
Figure S54. (a) Arrangement of spheres on different planes of FCC arrangement. SEM images for the \{111\} plane of FCC arrangement at different magnifications: (b, c) 3DO-SiO$_2$, (f, g) 3DOM-PS, (j, k) 3DOSC-HKUST-1. SEM images for the \{100\} plane of FCC arrangement at different magnifications: (d, e) 3DO-SiO$_2$, (h, i) 3DOM-PS, (l, m) 3DOSC-HKUST-1.
Figure S55. Above calculation equations indicate that the total external surface area per gram of SC-ZIF-8 is inversely proportional to its diameter.
Figure S56. The SEM image of the used SC-ZIF-8(200) after eight cycles of reaction, indicating the recycling operation could slightly break its spherical structure, and some broken spheres and small fragments can be observed.
**Figure S57.** The SEM image of the used 3DOSA-ZIF-8 after eight cycles of reaction, indicating its 3DO sphere-assembled structure can be maintained after the recyclability tests.
Tables S1 and S2

**Table S1.** Variation in hydrolysis parameters for the preparation of silica spheres with five different sizes.

| Name            | TEOS/g | V(NH₃·H₂O)/mL | V(C₂H₅OH)/mL | m(H₂O)/g |
|-----------------|--------|----------------|---------------|----------|
| 3DO-SiO₂(235)   | 2.31   | 7.80           | 90            | 2.25     |
| 3DO-SiO₂(370)   | 4.62   | 7.80           | 90            | 2.25     |
| 3DO-SiO₂(460)   | 5.10   | 7.80           | 90            | 2.25     |
| 3DO-SiO₂(530)   | 4.09   | 10.0           | 90            | 1.45     |
| 3DO-SiO₂(635)   | 4.54   | 10.0           | 90            | 1.45     |
**Table S2.** The average diameters of 3DO-SiO$_2$, 3DOM-PS, 3DOSC-ZIF-8 and the pore diameter contractions.

| Average diameter (nm) | 3DO-SiO$_2$ (x) | 3DOM-PS (y) | 3DOSC-ZIF-8(z) | Contraction (x-y)/x |
|-----------------------|-----------------|-------------|----------------|---------------------|
| 235                   | 200             | 201         |                | 14.9%               |
| 370                   | 330             | 332         |                | 10.8%               |
| 460                   | 425             | 425         |                | 7.6%                |
| 530                   | 500             | 502         |                | 5.7%                |
| 635                   | 610             | 611         |                | 3.9%                |
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