Electronic Supplementary Information

Tuning the Crystal Morphology and Size of Zeolitic Imidazolate Framework-8 in Aqueous Solution by Surfactants

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Experimental Section

Controllable synthesis of ZIF-8 crystals in aqueous systems: All chemicals were purchased from Sigma-Aldrich and used as received. In a typical synthesis, 0.29 g zinc nitrate hexahydrate was first dissolved in 10 mL deionized (DI) water; then 4.54 g 2-methylimidazole and specific amount of CTAB were dissolved in 70 mL DI water; after that zinc nitrate and 2-methylimidazole solutions were mixed and stirred for 5 min at room temperature, and the resulting synthesis solution was transferred into Teflon-lined autoclaves for hydrothermal synthesis at 120 ^{o}C for 6 h. After synthesis, the particles were collected by centrifuging, washed with water and methanol subsequently for 3 times, and then dried at 65 ^{o}C overnight.

Characterizations of ZIF-8 crystals: Powder X-ray diffraction (XRD) patterns were recorded at room temperature on a Bruker D8 ADVANCE diffractometer in transmission geometry using CuKα radiation (λ = 1.54059Å) at 40 kV and 40 mA. Nitrogen physisorption isotherms were measured at 77 K on an automatic volumetric adsorption apparatus (Micromertics ASAP 2420). The samples were filled into a glass ampoule and outgassed in high vacuum at 473 K for 24 h before sorption measurements. Dynamic light scattering measurements were performed on a Zetasizer Nano ZS from Malvern instrument equipped with a He-Ne laser (λ = 632.8 nm) in the backscattering detection mode. Field-emission scanning electron microscope (SEM) pictures were taken by a FEI Quanta 600 FEG, and the acceleration voltage was 30 kV. Transmission electron microscope (TEM) pictures were obtained on a Titan ST TEM operating at 300 kV. The mean particle size of the product was determined by manual measurement of about 150-200 crystals in SEM and TEM pictures. The coefficient of variation (CV) value was defined as the following equation.

$$CV = \frac{[\sum_{i=1}^{n} \frac{(d_i - d)^2}{n}]^{\frac{1}{2}}}{d}$$

Where d_i is the diameter of the ith ZIF-8 crystal, d is the average diameter and n is the total number of the crystals counted. A sample with CV value less than 5% is often considered as monodispersed.

Molecular simulation: The equilibrium and kinetically controlled crystal morphologies of ZIF-8 were predicted using the Forcite and Morphology modules implemented in Materials Studio® version 5.0. The initial ZIF-8 crystal structure was retrieved from the CCDC database (CCDC-602542) and then was optimized using the COMPASS force field. Interaction between CTAB and different surfaces were studied by molecular dynamics (MD) simulations with a canonical (NVT) ensemble using the Discover module of Material Studio version 5.0 with the COMPASS force field. Each crystal surface was modelled by a (4×4) supercell geometry with a 45 Å thick slab that contained a 100 Å vacuum region. Three different MD simulations were carried out on each surface: crystal surface with CTAB molecules, crystal surface only, and CTAB molecules only. The interaction energy (U) is calculated as $U = E_I - (E_{II} + E_{III})$, where E_I, E_{II}, and E_{III} are the potential energies of crystal surface with CTAB, crystal surface only, and CTAB only. Before running MD simulations, structures were optimized using an energy minimization method. MD simulations at 25 ^{o}C lasted for 40 ps with a time step of 1 fs. Simulation data for the last 20 ps were collected for structural and statistical analysis.

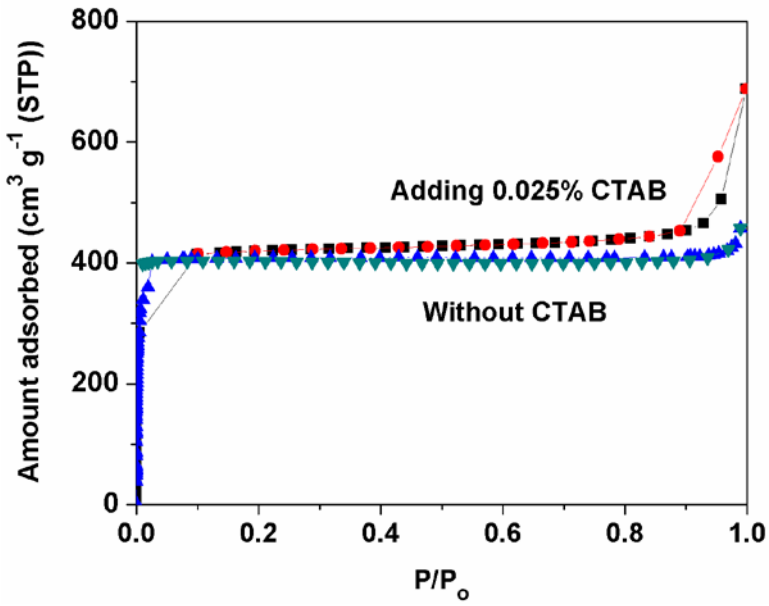

Fig. S1 N_2 adsorption isotherms of ZIF-8 crystals prepared without CTAB and with 0.025 wt% CTAB.

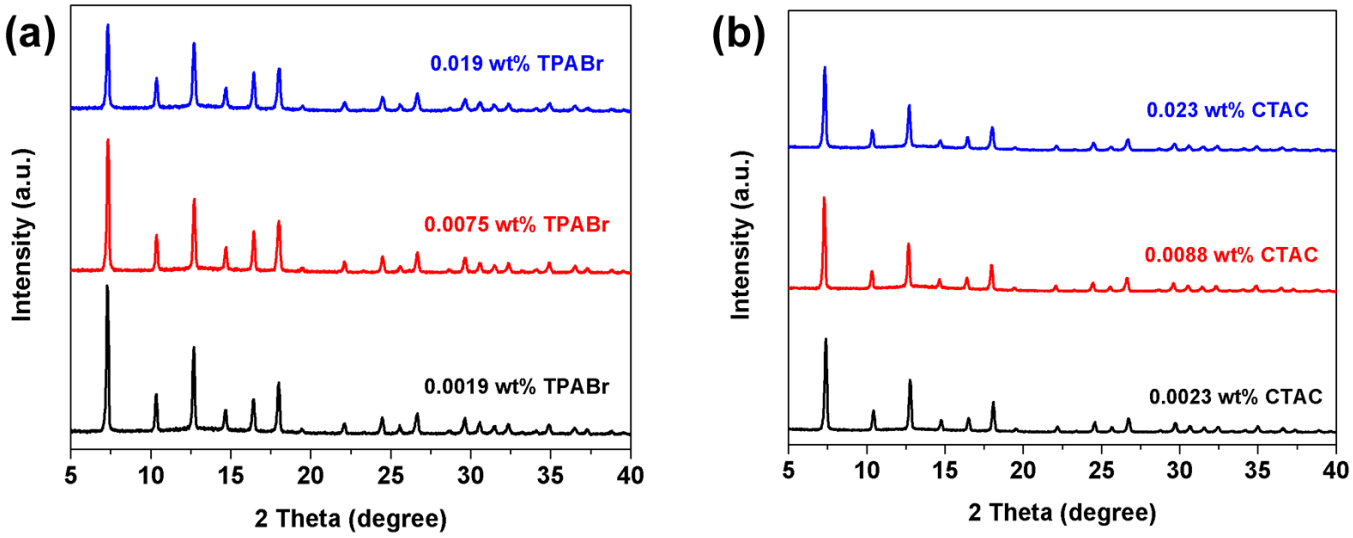

Fig. S2 XRD patterns of ZIF-8 crystals prepared with addition of various amount of (a) TPABr and (b) CTAC.

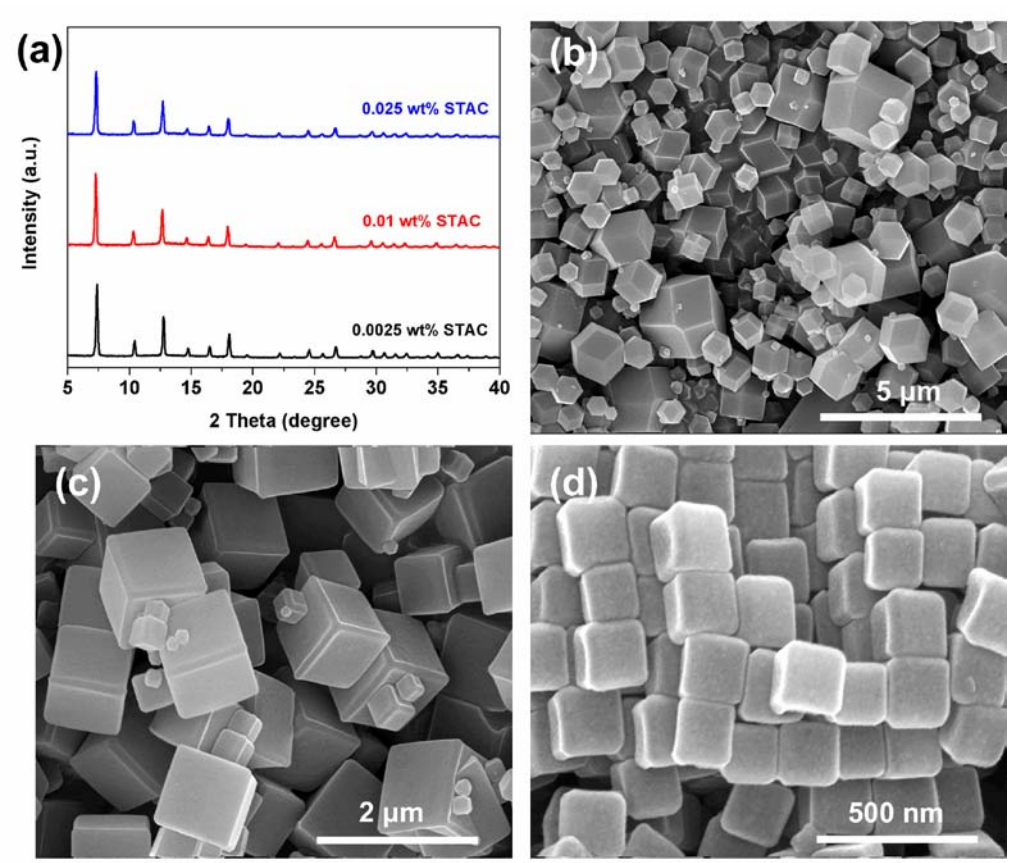

Fig. S3 (a) XRD patterns and SEM pictures of ZIF-8 crystals prepared by adding trimethylstearylammonium chloride (STAC) with various concentrations: (b) 0.0025 wt%, (c) 0.01 wt% and (d) 0.025 wt%.

Table S1 Surface Free and Attachment Energies of Various Crystal Facets Calculated Using the Morphology Module of the Material Studio

Planes	$d_{(hkl)}$ (Å)	Surface Energies (kcal/mol)	Attachment Energies (kcal/mol)
{1 0 0}	16.99	13.67	-27.36
{1 1 0}	12.01	19.84	-39.75
{1 1 1}	9.81	26.85	-53.38
{1 0 2}	7.60	32.84	-64.38
{1 1 2}	6.94	36.30	-70.54
{3 0 1}	5.37	45.66	-86.98
{1 2 2}	5.66	47.82	-72.10

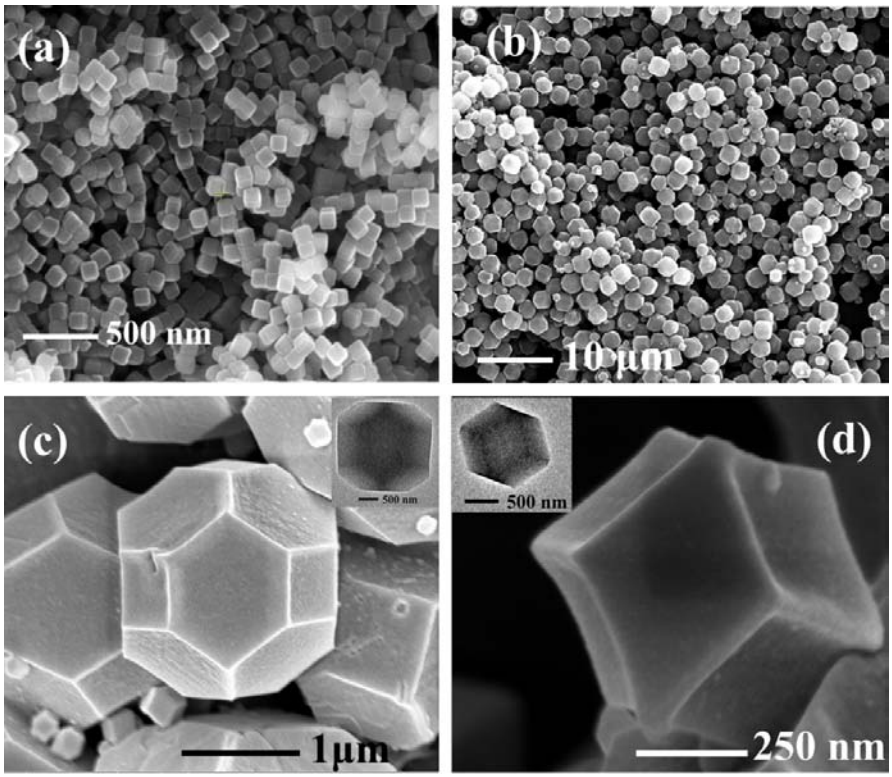

Fig. S4 SEM picture of truncated cubic ZIF-8 crystals (a) before and (b) after immersed in methanol for 1 month. (c, d) SEM pictures of ZIF-8 crystals with typical TRD and RD shape found in (b). The insets in (c) and (d) are the TEM pictures.