Supporting Information

ZIF-8 Templated Fabrication of Rhombic Dodecahedron-shaped ZnO@SiO₂, ZIF-8@SiO₂ Yolk-shell and SiO₂ Hollow Nanoparticles

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EXPERIMENTAL SECTION

Materials. Cetyltrimethylammonium bromide (CTAB, \geq 99 %) and tetraethyl orthosilicate (TEOS, \geq 98 %) were purchased from Sigma (USA). 2-methylimidazole (Hmim) was purchased from Chengdu Kelong Chemical Reagent Company. Zn(NO₃)₂·6H₂O was purchased from Tianjin Fengchun Chemical Reagent Technologies Co., Ltd. Methanol and ethanol were purchased from Beijing Chemical Works. All other reagents and solvents for the synthesis were purchased from commercial sources and used as received. Deionized water (DI-water) was used in all experiments.

Characterization. Electron transmission microscopy (TEM) was performed on a JEOL-2100F transmission electron microscope under 200 kV accelerating voltage. Field-emission scanning electron microscope (FE-SEM) images and energy dispersive X-ray (EDX) spectrum were obtained by using an XL 30 ESEM-FEG field-emission scanning electron microscope (FEI Co.). Powder X-ray diffraction (PXRD) patterns were recorded on a Siemens D5005 diffractometer with Cu KR (λ =1.5418 Å) radiation in the range of 3–90°. Fourier transform infrared (FTIR) spectrum was obtained on a Magna 560 FTIR spectrometer (Nicolet, USA). Thermogravimetric analysis (TGA) experiments were performed on a Perkin-Elmer TGA 7 analyzer heated from 25 to 600 °C under air atmosphere with a heating rate of 10 °C min⁻¹. The N₂ sorption measurements were measured on an Autosorb-iQ analyzer (Quantachrome). Before gas adsorption measurements, the sample was activated by drying under a dynamic vacuum at 150 °C overnight to remove methanol.

Synthesis of ZIF-8 NPs. All solutions used methanol as solvent. Firstly, a 0.1 mL CTAB (0.2 M) solution, 4 mL solution of $Zn(NO_3)_2 \cdot 6H_2O$ (0.06 mM) were mixed together and then 4 mL solution of Hmim (0.25 mM) was added. Subsequently, the mixture was allowed to react at room temperature for 24 h without stirring, during which the solution changed the appearance from clear to milky. Finally, the product ZIF-8 NPs were collected by centrifugation at 9000 rpm for 10 min, washed three times with methanol to remove the remaining reactant and then dried under vacuum for 10 h at 50 °C in an oven to get the powder.

Synthesis of ZIF-8@SiO₂ core-shell and ZnO@SiO₂ yolk-shell NPs. The reported Stöber method was used to prepare the ZIF-8@SiO₂ core-shell NPs. Typically, 10 mL ethanol was poured into 0.2 mL of the prepared ZIF-8 ethanol solution (10 mg mL⁻¹) under vigorous magnetic stirring. Then sodium hydroxide aqueous solution (0.1 M) was added into the above solution to adjust its pH to 8. Subsequently, 0.12 mL 20 % TEOS in ethanol was dropped into the weak alkaline solution and added 40 μ L every 30 min interval. The reaction mixture was stirred for another 18 h after dropping all of the TEOS ethanol solution. Finally, the product was collected with centrifugation at 9000 rpm and washed with ethanol for several times before drying at 50 °C in an oven. ZnO@SiO₂ yolk-shell NPs were synthesized by directly calcined the ZIF-8@SiO₂ powders at 500 °C with a heating rate of 1 °C min⁻¹ in air for 2 h to complete the conversation of ZIF-8 cores into ZnO.

Synthesis of ZIF-8@SiO₂ yolk-shell and SiO₂ hollow NPs. Both of them were prepared through hydrothermal treatment process. Firstly, 2 mg of the as-prepared

ZIF-8@SiO₂ core-shell NPs powders were re-dispersed in 2 mL DI-water with 10 uL hydrochloric acid (16 mM) by ultrasound. Then the solution was placed in a HP500 microwave vessel and sealed. Finally, the reaction was heated to 100 °C and held at this temperature for 2 h. After cooling to room temperature, the resulting ZIF-8@SiO₂ yolk-shell NPs were isolated by centrifugation at 9000 rpm for 10 min and washed with ethanol and DI-water alternately. The SiO₂ hollow NPs were obtained as the same process as the ZIF-8@SiO₂ yolk-shell NPs, only with the hydrothermal treatment time extending to 24 h.



Fig. S1 (a) PXRD patterns of simulated ZIF-8 (black), as-synthesized ZIF-8 (red), ZIF-8@SiO₂ core-shell NPs (blue). (b) EDX spectrum for ZIF-8@SiO₂ core-shell NPs measured on copper substrate.



Fig. S2 TGA analysis of the ZIF-8 NPs (black) and ZIF-8@SiO₂ core-shell NPs (red) in air.



Fig. S3 (a) PXRD patterns of simulated ZnO (black), ZnO NPs (red) and ZnO@SiO₂ yolk-shell NPs (blue) obtained by direct calcination of ZIF-8 and ZIF-8@SiO₂ coreshell NPs at 500 °C, respectively. (b) FTIR spectra of ZIF-8 (black), ZIF-8@SiO₂ core-shell (blue) and ZnO@SiO₂ yolk-shell NPs (green).



Fig. S4 N₂ sorption isotherm of ZnO@SiO₂ yolk-shell NPs collected at 77.35 K.



Fig. S5 PXRD patterns of simulated ZIF-8 (black) and as-synthesized ZIF-8@SiO₂ yolk-shell NPs (red).



Fig. S6 FE-SEM image of the SiO₂ hollow NPs.