Core–Shell Particles

ZnO@ZIF Core–Shell Single Crystals Formed by in Situ Conversion of ZnO Particles

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Abstract: We herein report the formation of two types of ZnO@ZIF core–shell single crystals through the in situ conversion of ZnO particles. The hybrid core–shell single crystals of ZIF-8 and ZIF-71 were obtained by treating 95 nm ZnO particles with 2-methylimidazole and 4,5-dichloroimidazole, respectively, under the optimized experimental conditions. The ZnO cores are spherical, caplike and noncentrally encapsulated in the ZIF crystals. The effects of the reaction solvent, ligand concentration and ZnO particle size were investigated, and the results show that the single-site heterogeneous nucleation and growth of ZIF on the template surfaces are the key to the formation of ZnO@ZIF core–shell single crystals.

Introduction

Metal–organic frameworks (MOFs), a class of porous crystalline materials with large surface areas, uniform pore sizes and tailorable surface chemistry,[1–3] have attracted considerable attention owing to their promising applications in the fields of gas storage,[4] separations,[5] heterogeneous catalysis,[6] sensing,[7] and drug delivery.[8] Typically, MOFs are synthesized solvothermally through the reactions of metal ions with organic ligands in appropriate solvents. Nevertheless, new synthesis techniques and strategies for MOFs have been developed rapidly in the last decade to cut costs, reduce environmental pollution, enhance crystallinity, control sizes and morphologies, and introduce structural and compositional heterogeneities to make the best use of these materials.[9]

Zeolitic imidazolate frameworks (ZIFs), an important sub-group of MOF materials, are built from tetrahedral metal ions (such as Zn and Co) linked by imidazolate anions.[10–13] ZIF materials have been studied extensively for a variety of applications owing to their high thermal stability, chemical robustness and facile preparation. ZIFs can be synthesized over a wide range of temperatures in organic solutions,[11] in aqueous solutions,[14] or without any solvent.[16] In addition to metal salts, some metal oxides have also been used to prepare ZIF materials.[16,17] These diverse protocols can be applied flexibly not only to produce ZIFs as single crystals with tuneable sizes,[18] thin films,[19] and membranes[20] but also to prepare functional hybrid materials.[21,22] The first ZIF-based hybrid materials were prepared by the in situ reduction of gold nanoparticles on (or in) ZIF crystals and used as heterogeneous catalysts for CO oxidation.[23] More functionalities were imparted to ZIF materials by the controlled encapsulation of various nanoparticles, biomacromolecules and small molecules with new chemical, physical and biological properties.[21,22,24] Alternatively, some oxide/ZIF hybrid materials can be prepared directly through the partial conversion of oxides to ZIFs.[25,26] The use of metal oxides instead of soluble metal salts to prepare MOFs is attractive, because the morphologies of oxides are relatively easy to control through well-established chemical-synthesis and physical techniques and can be further transferred to MOF materials through the careful optimization of the experimental conditions.[27] This strategy has been demonstrated with Cu₂O, Al₂O₃ and ZnO to produce (patterned) thin films,[27–30] hollow spheres,[31] and hybrid MOF materials.[25,26,32,33] The reactions of ZnO templates with imidazole ligands commonly result in the formation of ZnO/ZIF core–shell structures owing to incomplete conversion, because the reactions are terminated once all of the template surfaces are enshrouded with dense ZIF shells, the small pore apertures of which prevent the diffusion of reactive species.[29] Although ZnO/ZIF core–shell structures have been prepared from nanorod- and nanoparticle-like templates,[25,26] the shells are polycrystalline and consist of intergrown crystal domains. Indeed, the synthesis of hybrid core–shell MOF single crystals is challenging but highly desirable, because the single crystals do not have the grain-boundary defects present in polycrystalline materials that can impair the diffusion of molecules and the molecular-sieving function of MOF shells.[34,35] Although hybrid MOF single crystals have been prepared by strategies based on MOF templating[23] and encapsulation,[21,22] their synthesis by the oxide conversion method has not yet been reported.
Here, we report the formation of single crystals of ZIF-8 \[\text{characterized by sodalite (SOD) topology with 11.6 Å cavities and 3.4 Å apertures}\] and ZIF-71 \[\text{featuring RHO topology characterized by sodalite (SOD) topology with 11.6 Å cavities}\] with fully encapsulated ZnO cores. These two types of ZnO@ZIF core–shell single crystals were prepared by treating ZnO particles with 2-methylimidazole and 4,5-dichloroimidazole \[\text{(Scheme 1)},\] respectively, with optimized experimental parameters including reaction solvents, ligand concentration and ZnO particle size. Our studies suggest that the single-site heterogeneous nucleation and growth of ZIF on the ZnO particle surfaces are responsible for the formation of hybrid core–shell single crystals.

**Results and Discussion**

ZnO colloidal particles with average sizes of 95, 230 and 320 nm were synthesized through the hydrolysis of zinc acetate in diethylene glycol \[\text{DEG}\] at high temperature with the control of the amount of seeds used in the second step of the reaction \[\text{see Exp. Sect.}\]. The surfaces of the ZnO colloidal particles were subsequently modified with the amphiphilic surfactant polyvinylpyrrolidone \[\text{PVP}\] to enhance their dispersibility in solvents. A transmission electron microscopy \[\text{TEM}\] image of the ZnO particles of size \[\text{95 ± 14 nm}\] is shown in Figure 1a. The ZnO particles appear to be spherical, rough and porous and are composed of aggregated tiny particulates \[\text{ca. 7 nm}\]. The crystalline nature of the ZnO particles was identified by powder X-ray diffraction \[\text{PXRD}\] measurements \[\text{Figure S1}\], though their diffraction peaks are weak and broad owing to their small grain sizes, as revealed by the TEM analysis. These 95 nm ZnO particles \[\text{containing ca. 0.004 mmol Zn, as determined by inductively coupled plasma MS (ICP-MS)}\] were treated with 2-methylimidazole \[\text{Hmim}\] \[\text{0.72 mmol}\] in vinylpyrrolidone \[\text{PVP}\] to enhance their dispersibility in solvents. A transmission electron microscopy \[\text{TEM}\] image of the ZnO particles with an average size of 95 nm and ZnO@ZIF-8 core–shell single crystals in the product obtained by the 95 nm ZnO particles with 2-methylimidazole under the optimized experimental conditions. (c) Electron diffraction pattern taken from the single hybrid ZnO@ZIF-8 particle shown in the inset. (d) Experimental PXRD pattern of ZnO@ZIF-8 core–shell single crystals and simulated XRD pattern for ZIF-8. (f) Nitrogen adsorption \[\text{filled symbols}\] and desorption \[\text{open symbols}\] isotherms for 95 nm ZnO particles and ZnO@ZIF-8 core–shell single crystals at 77 K up to 1 bar.

The formation of ZnO@ZIF-8 core–shell single crystals was investigated further by time-dependent TEM analysis \[\text{Figures 2 and S6}\]. The TEM image in Figure 2a shows a Janus particle present in the product obtained after 10 min of reaction. The hybrid particle comprises a brighter coordination-polymer sphere \[\text{ca. 100 nm}\] that enshrouds half the surface area of a darker ZnO particle \[\text{ca. 70 nm}\]. After 30 min, the ZnO particles appear to be almost encapsulated noncentrally in the rhombic-dodecahedral crystals \[\text{average size ca. 210 nm; Figures 2b and S6b}\]. The average size of the hybrid crystals increases to ca. 270 nm after 24 h \[\text{Figures 2c and S6c}\]. The ICP-MS measurements of free Zn$^{2+}$ ions in the reaction solutions at different reaction intervals suggest that the relative concentration of Zn
species that are lost to the solution and do not contribute to the formation of the ZIF-8 shell is less than 4 %.

Figure 2. TEM images of the (intermediate) products of ZnO@ZIF-8 core–shell single crystals collected after (a) 10 min, (b) 30 min and (c) 24 h.

The above TEM results reveal four facts that are important for the formation of ZnO@ZIF-8 core–shell single crystals under the experimental conditions used. First, as the dissolved Zn²⁺ ions are released gradually from ZnO particles and react with Hmim in solution, the heterogeneous nucleation of ZIF-8 on the ZnO particle surface is predominant for the crystal formation, whereas the homogeneous nucleation in solution is suppressed as core-free crystals were hardly observed. This can be attributed partially to the higher concentration of Zn²⁺ ions near the ZnO particle surface than in bulk solution and partially to the possible seed-induced nucleation effect of the ZnO particles. Second, once one coordination-polymer domain forms on the ZnO particle surface, new heterogeneous nucleation (and homogeneous nucleation in solution) is prohibited; this suggests that the energy required for the growth of the coordination polymer is much lower than that required for nucleation, and the Zn²⁺ ions released freshly from the exposed area of the ZnO surface participate predominantly in the growth of the coordination-polymer domain. Third, the complete conversion of ZnO into ZIF-8 is not achieved, because the dissolution and diffusion of Zn²⁺ ions are frustrated by the small pore apertures (3.4 Å) of ZIF-8 once it compactly enshrouds the whole surface of the ZnO particles. Fourth, the formation of noncentral and spherical caplike ZnO cores in the hybrid crystals is a result of the single-site nucleation and growth of ZIF-8 on the template surfaces along with the asymmetric dissolution of ZnO particles at their exposed areas during the encapsulation process.

The formation of ZIF-8 follows a two-step reaction, in which the Hmim molecules react initially with Zn²⁺ ions to form Zn(Hmim)₂⁺ (n = 1–4) species, which serve as building units and are further deprotonated to form ZIF-8. The formation of ZnO@ZIF-8 core–shell single crystals starts here with the dissolution of ZnO particles to release Zn²⁺ ions, which is promoted by the introduction of Hmim molecules owing to the formation of Zn(Hmim)₂⁺ and requires a balance between the dissolution of ZnO and the formation of ZIF-8, both of which are strongly dependent of the Hmim concentration used in the reaction. When a 20 mM solution of Hmim was treated with 95 nm ZnO particles, ca. 500 nm rhombic-dodecahedral hybrid crystals, containing several randomly distributed ZnO particles with sizes ranging from 20 to 70 nm, were obtained instead of the core–shell single crystals (Figure 3a). This result suggests that a low Hmim concentration does not favour the heterogeneous nucleation of ZIF-8 on the ZnO particle surfaces, presumably because the dissolution of ZnO is too slow to release sufficient Zn²⁺ ions near the particle surfaces for the nucleation of ZIF-8 before they diffuse to the bulk solution. As ZnO particles continuously release Zn²⁺ ions to the solution and decrease in size and the concentration of Zn(Hmim)₂⁺ increases to some extent in the whole reaction system, the nucleation of ZIF-8 is initiated heterogeneously on the surfaces of some ZnO particles and possibly homogeneously in bulk solution. The naked ZnO particles are adsorbed randomly on the continuously forming fresh surfaces of the growing ZIF-8 crystals and subsequently encapsulated in the hybrid crystals.[19] On the other hand, if a high Hmim concentration (e.g., 480 mM) is used in the reaction, the dissolution of ZnO particles is so fast and, thus, the concentration of the released Zn²⁺ ions near the template surfaces is so high that multipoint heterogeneous nucleation on single ZnO particle surface results in the formation of polycrystalline shells, and simultaneously the excess Zn²⁺ ions diffuse into the bulk solution, and core-free ZIF-8 crystals form through homogeneous nucleation (Figures 3b and S7).

The effect of the solvent on the formation of ZnO@ZIF-8 core–shell single crystals was further investigated. When water was used as the sole solvent, the obtained product consisted of hybrid particles, each of which contained a darker ZnO core and a bright dense thin shell ca. 13 nm thick (Figure 4a). If only DMF was used as solvent, the product was composed of ZnO particles with surfaces partially enshrouded by one or several ca. 90 nm coordination-polymer domains (Figure 4b). The above observations suggest that both DMF and H₂O as single solvents for the reaction favour the heterogenous nucleation of the coordination polymer on the ZnO particle surfaces. However, as the release of Zn²⁺ ions is much slower than the formation of the coordination polymer in water, a dense thin layer of coordination polymer forms on the whole surface of the ZnO particles, and this layer frustrates the further diffusion of reactive species (Zn²⁺ ions and 2-methylimidazole) outwards or towards the ZnO particle surfaces and, thus, terminates the reaction. In DMF, the dissolution of ZnO is too slow to produce sufficient Zn²⁺ ions in 24 h for the formation of a complete shell around the templates. Accordingly, the utilization of a mixture of DMF and H₂O as the solvent allows us to balance the formation rate of ZIF-8 and the dissolution rate of ZnO particles to yield the hybrid core–shell single crystals.
The formation of ZnO@ZIF-8 core–shell single crystals is also dependent on the size of the template. The reactions of 230 and 320 nm ZnO particles (Figure 5a and b, respectively) with Hmim under the same experimental conditions both yielded hybrid crystals with polycrystalline shells (Figure 5c and d). The shell consists of intergrown crystal domains, the number of which increases as the size of the ZnO templates increases. Although the formation of the ZnO@ZIF-8 core–shell single crystals from 95 nm ZnO particles suggests that higher energy is required for the nucleation of ZIF-8 crystals than for their growth on oxide particle surfaces, the above observation is still understandable. The larger ZnO particle size increases the distances between the first nucleation site and the freshly released Zn$^{2+}$ ions; therefore, the Zn$^{2+}$ ions preferentially form a new nucleus nearby instead of diffusing to the first nucleation site and contributing to the growth of the coordination-polymer domain. Apparently, as the template size increases, the number of nucleation sites and, thus, the number of intergrown crystal domains on the ZnO particle surfaces also increase.

The role of the PVP on the surface of ZnO particles was investigated by performing the conversion reaction with 95 nm naked ZnO particles under the same experimental conditions. As shown in Figure S8, the product consisted of both hybrid ZnO@ZIF-8 single crystals and crystals containing multiple ZnO cores; this suggests that the PVP modification prevents the ZnO particles from aggregating before and during the conversion reaction. In addition, the PVP coating on the ZnO particles might promote the retention of the released Zn species close to the template surfaces through coordination interactions[37] and, therefore, facilitate the nucleation and growth of ZIF-8 on the surfaces of the ZnO particles.

ZnO@ZIF-71 core–shell single crystals were also prepared successfully by using 4,5-dichloroimidazole as the ligand under the optimized experimental conditions (see Exp. Sect.). A TEM image of the hybrid single crystals in the product obtained with 95 nm ZnO particles as the template is shown in Figure 6a. These hybrid crystals have an average size of ca. 350 nm with a rhombic-dodecahedral morphology and contain spherical caplike cores. Similarly to the results for ZIF-8, the reactions of larger ZnO particles (230 and 320 nm) with 4,5-dichloroimidazole yielded hybrid crystals with polycrystalline shells enshrouding the ZnO particles (Figure 6b and c). PXRD analysis shows that the hybrid single crystals display diffraction patterns identical to that of ZIF-71 (Figure 6d). As indicated by the N$_2$ sorption measurements (Figure S10), the hybrid single crystals are microporous and have a BET surface area of 792 m$^2$/g, which is reasonably smaller than that of pure ZIF-71 (ca. 941 m$^2$/g).
The functionality of the ZnO in the hybrid ZIF-8 crystals was tested by the photoreduction of 4-nitrophenol in aqueous solution under irradiation with 365 nm UV light. As shown in Figure 7a, the absorbance of 4-nitrophenol solution at $\lambda = 400$ nm decreases gradually with UV irradiation time in the presence of ZnO@ZIF-8 single crystals; this suggests that the hybrid crystals are photocatalytic and can catalyze the reduction of 4-nitrophenol. In contrast to the ZnO@ZIF-8 crystals under the same experimental conditions (Figure 7b), pure ZIF-8 crystals show no clear catalytic activity towards 4-nitrophenol, which can be completely reduced in the presence of pure ZnO particles within 240 min. The above results suggest that the photocatalytic activity of ZnO@ZIF-8 crystals originates from the enshrouded ZnO cores, and the decreased catalytic efficiency is the result of the slower diffusion of 4-nitrophenol within the ZIF-8 shells.

![Figure 7](image)

**Figure 7.** (a) UV/Vis absorption spectra for 4-nitrophenol photoreduction with ZnO@ZIF-8 hybrid single crystals as the catalyst. (b) Relative concentration ($C/C_0$) versus reaction time for 4-nitrophenol photoreduction with ZnO particles, ZIF-8 crystals and ZnO@ZIF-8 hybrid single crystals as the catalysts.

**Conclusions**

We have demonstrated the synthesis of two types of ZnO@ZIF core–shell single crystals through the reactions of ZnO particles with two imidazole ligands (2-methylimidazole and 4,5-dichlorimidazole) under optimized experimental conditions. Each of these hybrid ZIF single crystals contains a spherical cap-like but noncentrally encapsulated ZnO core. The formation of ZnO@ZIF core–shell single crystals was attributed to the single-site heterogeneous nucleation and growth of ZIF on the ZnO particle surfaces; however, this growth depends strongly on the experimental parameters including the reaction solvent, ligand concentration and, most importantly, the template size.

**Experimental Section**

**Chemicals:** All reagents were available commercially and used as received unless otherwise noted.

**ZnO Particles:** The ZnO colloidal particles were synthesized according to a previous report. Typically, zinc acetate dihydrate (5 mmol) was dissolved in DEG (50 mL), and the solution was heated under reflux at 160 °C with stirring at 400 rpm for 1 h. After cooling to room temperature, the product was collected by centrifugation, washed three times with methanol and suspended in a 5 % PVP ($M_w \approx 55000$) solution, and the suspension was stirred for 24 h. The PVP-modified ZnO particles were washed three times with methanol and dispersed finally in methanol (30 mL) for further use.

**ZnO@ZIF-8 Core–Shell Single Crystals:** The PVP-modified ZnO particles in the above suspension (0.1 mL) were collected by centrifugation and dispersed in deionized water (1.5 mL), and this dispersion was mixed subsequently with a solution of 2-methylimidazole (160 mM) in DMF (4.5 mL); the reaction proceeded at room temperature without disturbance for 24 h. The product was collected by centrifugation at 7000 rpm for 5 min, washed three times with methanol and vacuum-dried overnight.

**ZnO@ZIF-71 Core–Shell Single Crystals:** The PVP-modified ZnO particles in the above suspension (0.1 mL) were collected by centrifugation and dispersed in deionized water (1 mL), and this suspension was mixed subsequently with a solution of 4,5-dichlorimidazole (24 mM) in DMF (3 mL) and water (2 mL); the reaction proceeded without disturbance at 85 °C for 24 h. The product was collected by centrifugation at 7000 rpm for 5 min, washed three times with DMF and then three times with methanol and vacuum-dried overnight.

**ZnO@ZIF-8:** A solution of zinc nitrate hexahydrate (50 mM) in methanol (30 mL) and a solution of 2-methylimidazole (100 mM) in methanol (30 mL) were mixed, and the reaction proceeded at room temperature for 24 h. The product was collected by centrifugation at 7000 rpm for 5 min, washed three times with methanol and vacuum-dried overnight.

**ZnO@ZIF-71:** A solution of zinc acetate dihydrate (22 mM) in methanol (100 mL) and a solution of 4,5-dichlorimidazole (106 mM) in methanol (100 mL) were mixed, and the reaction proceeded at room temperature for 24 h. The product was collected by centrifugation at 7000 rpm for 5 min, washed three times with methanol and vacuum-dried overnight.

**Evaluation of Photocatalytic Performance:** The photocatalytic performances were evaluated by the photoreduction of 4-nitrophenol in aqueous solution at room temperature. After activation under vacuum at 120 °C for 12 h, the catalyst (ZnO particles, ZIF-8 crystals, or ZnO@ZIF-8 hybrid crystals; 25 mg) was added to an aqueous solution (20 mL) of 4-nitrophenol (0.06 mM), and the suspension was stirred in the dark for 1 h to achieve adsorption equilibrium. Subsequently, the suspension was irradiated with a high-intensity UV lamp (365 nm, 100 W, SB-100P/FA, Spectronics Corporation Westbury), and a portion of the suspension (2.5 mL) was removed at regular intervals. After centrifugation, the supernatant was further filtered through a 200 nm syringe filter and analyzed with a UV/Vis spectrophotometer (Lambda 750, PerkinElmer). The concentration of 4-nitrophenol was evaluated through the absorbance at $\lambda = 400$ nm.

**Characterization:** The PXRD patterns were obtained with a Philips X’pert PRDMPD diffractometer with nickel-filtered Cu-$K\alpha$ radiation ($\lambda = 1.5406$ Å). The SEM images were recorded with a Zeiss supra 55 field-emission SEM with an accelerating voltage of 10 kV. The TEM micrographs were recorded with a FEI/Philips Tecnai G2 F20 (200 kV) TWIN TEM. The FTIR spectra were recorded with a Bruker Vertex 70 FTIR spectrometer. The ICP-MS was conducted with a Thermo Element 2XR ICP mass spectrometer. The TGA was performed with a Mettler Toledo TGA1 instrument in air. The nitrogen
adsorption studies were performed with a Micromeritics ASAP 2020 HD88 instrument at 77 K up to 1 bar. Before the adsorption measurements, the samples were activated under vacuum at 180 °C for 20 h.

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ZnO@ZIF-8 and ZnO@ZIF-71 core–shell single crystals can be synthesized by the in situ conversion of ZnO particles under optimized experimental conditions. The formation of these hybrid ZIF single crystals is attributed to the single-site heterogeneous nucleation and growth of ZIF on the ZnO surfaces but depends strongly on the reaction solvent, ligand concentration and ZnO particle size.

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