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Silica Protection-Assisted Encapsulation of Cu_2O Nanocubes into Metal-Organic Framework (ZIF-8) as Composite Catalyst

Bo Li,[a] Jian-Gong Ma*[a] and Peng Cheng*[a,b]

Abstract: The integration of metal/metal oxide nanoparticles (NPs) into metal-organic frameworks (MOFs) to form composite materials has attracted great interest due to the broad applications. However, it is still vacant to encapsulate meta-stable NPs with high catalytic activity into MOFs, due to their instability during the preparation process. For the first time, we successfully developed a template protection-sacrifice (TPS) method to encapsulate meta-stable NPs such as Cu_2O into MOFs. SiO_2 was used as both a protective shell for Cu_2O nanocubes and a sacrificial template for forming a yolk-shell structure. The obtained Cu_2O@ZIF-8 composite exhibits excellent cycle stability in catalytic hydrogenation of 4-nitrophenol with high activity. This is the first report of a Cu_2O@MOFs type composite material. The TPS method provides an efficient strategy for encapsulating unstable active metal/metal oxide NPs into MOFs or maybe other porous materials.

Metal-organic frameworks (MOFs), assembled by metal ions with organic ligands, are a class of emerging crystalline porous materials with ultrahigh porosity and surface areas.[1-4] Recently, integration of metal or metal oxide nanoparticles (NPs) into MOFs to form composite materials with collective properties and improved performance has attracted significant interest in the fields including gas storage/separation,[5-7] sensing,[8-9] drug delivery,[10] electrochemical energy conversion and storage,[11] and especially catalysis,[12-20] due to the following features: i) Uniform nano-pores/channels in MOFs provide confinement effects to prevent aggregation of NPs, and facilitate the transport and diffusion of substrates and products;[21-32] ii) the abundant MOF structures enable the selection of an appropriate MOF as the host matrix; iii) MOFs can be easily separated from reaction mixtures and be reused, extending the lifetime of the catalysts and reducing waste and contamination. Several metal/metal oxide NPs have been encapsulated into MOFs including Ru,[23,28] Au,[24,30] Pd,[25] Pt,[26,29,30] Ag,[12,27,30] Fe_3O_4,[30] TiO_2,[31] Co_3O_4,[32] which were applied in CO_2 conversion, C-C coupling, hydrolysis of ammonia borane and selective hydrogenation, and exhibited attractive activities and reusabilities. In comparison of those encapsulated noble and stable NPs, there is barely report on encapsulating meta-stable metal oxide NPs into MOFs. This is mainly due to the following two factors: i) it is very difficult to make NPs with suitable size matching the pores of MOFs; ii) these NPs lack sufficient stability to survive during the preparation and/or loading process. Therefore, there are still huge challenges to stabilize otherwise transiently stable catalysts[33-35] and encapsulate well-defined meta-stable NPs into MOFs to form highly-active composite materials.

As a rich reserves and environment-friendly catalyst, Cu_2O has gained continuous attention due to its high activity and vast applicable areas.[36-40] However, one of the major drawbacks of Cu_2O is its poor stability especially in solution. Herein, we developed a template protection-sacrifice (TPS) method to encapsulate Cu_2O nanocubes into MOF ZIF-8 to form Cu_2O@ZIF-8 composite material. This is the first report of MOF-based composite material with meta-stable NPs loading, as far as we know. We use SiO_2 both as protective shell for Cu_2O nanocubes and as sacrificial template for forming a yolk-shell structure. As a new composite material, Cu_2O@ZIF-8 shows excellent catalytic efficiency and promising recycling stability for hydrogenation of 4-nitrophenol. Our TPS method may also supply a new approach for stabilizing and/or site-isolating transiently stable catalysts.

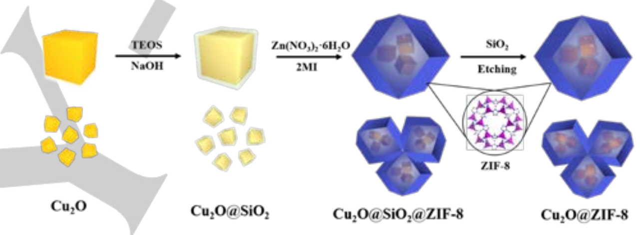

Figure 1. Schematic illustration for the synthesis of Cu_2O@ZIF-8 composite

The specific synthesis strategy is schematically illustrated in Figure 1. The general procedure consists of four steps: Firstly, uniform Cu_2O nanocubes with a size of 140 nm were obtained by an ultrasound-assisted method (See SI for details), which were characterized by scanning electronic microscopy (SEM) and powder X-ray diffraction (PXRD) (Figure S1). Secondly, a layer of silica shell was supplied to cover the surface of these Cu_2O nanocubes with TEOS as silica source. NaOH was used instead of ammonia to catalyze the hydrolysis of TEOS, because Cu_2O nanocubes could be etched by $NH_3·H_2O$ in the conventional Stöber silica encapsulation process.[41] PXRD data showed the characteristic diffraction peaks of amorphous silica (Figure S2e), indicating the successful coating of SiO_2. SEM and TEM images (Figure S2 and S3) clearly showed the uniform layer of silica with a thickness of ca 25 nm covering the surface of Cu_2O nanocubes (Figure S3f). Thirdly, the obtained core-shell material $Cu_2O@SiO_2$ was loaded into ZIF-8 through the “bottle around ship” approach (Figure S4). To reveal the spatial distribution of different elements in the $Cu_2O@SiO_2$@ZIF-8 composite, elemental mapping analysis was carried out under scanning transmission electron microscopy (STEM) mode (Figure S5). From the high-angle annular darkfield (HAADF)-STEM image, the sandwich structure of $Cu_2O@SiO_2$@ZIF-8 was clearly identified (Figure S5).

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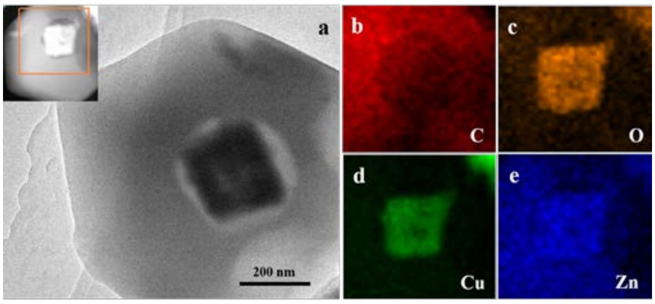

Figure 2. Elemental distributions for Cu_2O@ZIF-8. a) TEM image and the HAADF-STEM image of b) C mapping, c) O mapping, d) Cu mapping, and e) Zn mapping.

Finally, the SiO_2 layer in the sandwich structure of Cu_2O@SiO_2@ZIF-8 was selectively etched with NaOH to form a yolk-shell structure under nitrogen atmosphere, which was clearly shown by TEM images and elemental mapping with a hollow space of 40±10 nm between the Cu_2O nanocube and ZIF-8 cover (Figure 2). ZIF-8 was intact during etching process, due to its excellent chemical stability in alkaline solution. Inductively coupled plasma (ICP) analysis suggested the loading of Cu element in Cu_2O@ZIF-8 as high as 20.7% composite (Table S1), In the N_2 adsorption/desorption measurements (Figure S7), decreases in the amount of N_2 sorption and corresponding surface areas were observed for Cu_2O@ZIF-8 (1035.5 m^2/g) compared to ZIF-8 (2067.3 m^2/g), because Cu_2O nanocubes occupied a portion of the interior space of ZIF-8 crystals. In spite of this, surface area of Cu_2O@ZIF-8 is still superior in comparison of other traditional porous core-shell materials. Products of each step were subjected to phase analysis by XRD (Figure S8). The characteristic diffraction peaks of Cu_2O kept no change throughout the whole preparation process of Cu_2O@ZIF-8, indicating the Cu_2O nanocubes were successfully protected from oxidation.

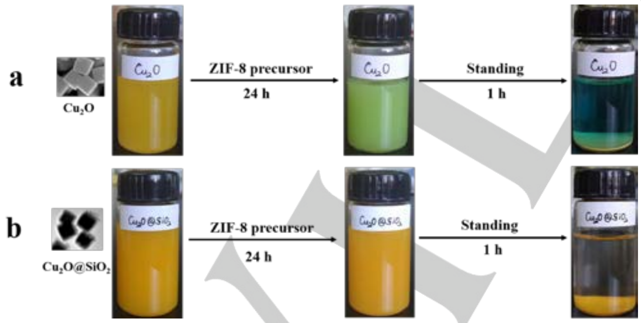

Figure 3. Comparative experiment for the stability of Cu_2O (a) and Cu_2O@SiO_2 (b) in ZIF-8 precursor methanol solution.

In our TPS strategy, SiO_2 plays a "one stone three birds" role: i) SiO_2 effectively protects Cu_2O nanocubes from oxidation in the precursor of ZIF-8. To further illustrate the protection role of SiO_2, we carried out a comparative loading experiment for the Cu_2O nanocubes without SiO_2 shell. The color change processes for Cu_2O and Cu_2O@SiO_2 loading were shown and compared in Figure 3. For Cu_2O loading, the color of the dispersion gradually changed from orange to light green during the crystal growth of ZIF-8, and finally the blue supernatant was observed. This phenomenon indicated the oxidation of Cu_2O nanocubes to Cu^{2+} (Figure 3a) which leaked into the solution from the cover of ZIF-8, and proved that Cu_2O could hardly survive in the loading process without protective means. Conversely, Cu_2O@SiO_2 loading showed no color change, and the colorless supernatant confirmed the successful protection of Cu_2O from oxidation (Figure 3b). ii) SiO_2 shell provide a sacrificial template for forming a yolk-shell structure. iii) The hollow structure formed by selective SiO_2-etching provide a favorable space and environment for catalytic reactions. As a porous shell, ZIF-8 provides transport channels for the access of reactants and delivery of products.

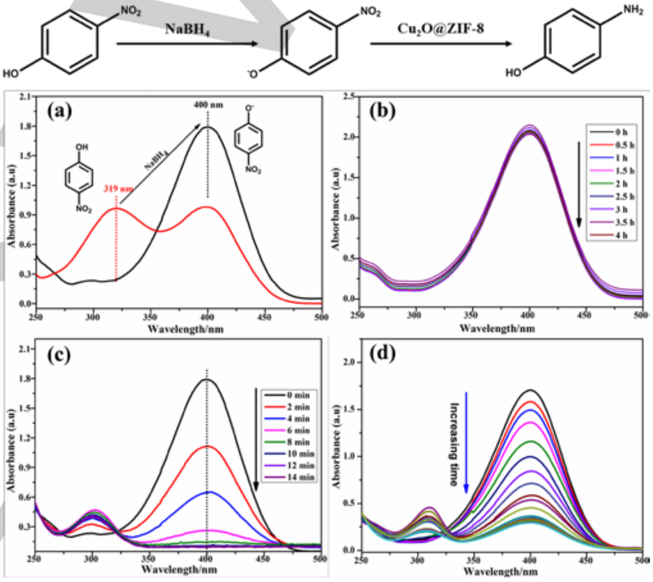

Figure 4. Catalytic reduction equation of 4-nitrophenol to 4-aminophenol with Cu_2O@ZIF-8. UV-vis spectra of 4-nitrophenol before and after the addition of $NaBH_4$ solution (a); Time-dependent UV-vis spectra of the reaction solution without Cu_2O@ZIF-8 (b), with Cu_2O@ZIF-8 (c), and with the 5th recycled Cu_2O@ZIF-8 (d).

In order to evaluate the catalytic efficiency of the new composite material, we selected the solution-phase hydrogenation of 4-nitrophenol into 4-aminophenol by $NaBH_4$as model reaction (Figure 4). The evolution process was monitored by UV-vis spectroscopy. Solution of 4-nitrophenol exhibits a strong absorption peak at 319 nm, which red-shifted to 400 nm with the addition of $NaBH_4$ due to the deprotonation of 4-nitrophenol (Figure 4a), and a color change from pale yellow to bright yellow was observed. After 4 hours, no further change was observed (Figure 4b), implying that the hydrogenation reaction could not happen in the absence of catalysts, even with a large excess of $NaBH_4$. Addition of Cu_2O@ZIF-8 into the reaction solution initiated the reduction immediately, and the intensity of absorption peak at 400 nm gradually decreased and eventually disappeared with time-passing. During the same time, an absorption peak around 300 nm appeared due to the formation of 4-aminophenol (Figure 4c). The reaction proceeded rapidly with the conversion over 99% in ca 14 min. Color of the reaction system turned from light yellow to transparent colorless, indicating the complete reduction of 4-nitrophenol.

The conversion of 4-nitrophenol is calculated from C_t/C_0 (Figure S8) by the relative intensity of UV-vis absorbance (A_t/A_0) at 400 nm (C_t is the concentration of 4-nitrophenol at the reaction time t, and C_0 is the initial concentration). The concentration of $NaBH_4$ was much higher than that of 4-nitrophenol and thus was considered as constant during the reaction. Consequently, the reductions were assumed to be pseudo first-order with respect to the concentration of 4-nitrophenol. For the freshly prepared Cu_2O@ZIF-8, the catalytic conversion of 4-nitrophenol reached 99% after 14 min. The plot of $\ln(C_t/C_0)$ versus reaction time matched the first-order reaction kinetics very well, and the rate constant (K_1) of the reaction was calculated as 0.28 min^{-1} (Figure S9a), reflecting a high catalytic reactivity of Cu_2O@ZIF-8 catalyst. Afterwards, the catalyst was conveniently separated by centrifugation. Cyclic experiments showed a promising cycle stability of Cu_2O@ZIF-8. For the fifth cycle test (Figure S9b), the conversion rate reached 98% after 20 minutes of reaction with corresponding constant (K_5) of 0.22 min^{-1}, indicating that the MOF (ZIF-8) shell effectively protected the Cu_2O core of Cu_2O@ZIF-8 against inactivation during the catalytic processes. As a comparison, we also surveyed the reduction of 4-nitrophenol by Cu_2O nanocubes. However, without MOF protection, the color of Cu_2O quickly turned black under the same conditions for Cu_2O@ZIF-8, indicating the fast decomposition of the unprotected Cu_2O nanocubes during the experiment.

In order to further explore the stability of Cu_2O@ZIF-8, H_2-Temperature-program reduction (H_2-TPR) experiments were carried out (Figure 5). Cu_2O nanocubes showed a single reduction peak with initial reduction temperature of ca 250 ºC, which should be attributed to the reduction of Cu_2O to Cu^0.[42,43] For Cu_2O@ZIF-8, reduction temperature of Cu_2O core was reduced to 200 ºC. This might be due to two reasons: i) ZIF-8 confined Cu_2O nanocubes, improved its dispersion, and prevent its aggregation; ii) ZIF-8 shell is conducive to the diffusion of gas reactant. In short, ZIF-8 shell facilitated the reduction of Cu_2O nanocubes, and improved the antioxidant capacity of Cu_2O, that further confirmed the cyclical stability of the catalyst.

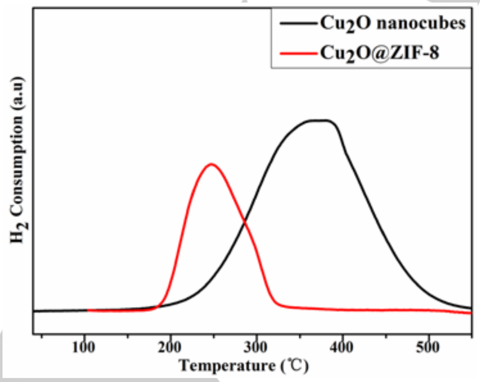

Figure 5. H_2-TPR profiles of the Cu_2O (black) and Cu_2O@ZIF-8 (red)

In summary, we have developed a TPS method for the construction of MOF-based composite materials with meta-stable metal oxide cores for the first time. Cu_2O@ZIF-8 composite material with yolk-shell nanostructure was obtained successfully based accordingly. SiO_2 serves as a protective shell, a sacrificial template and a hollow-space holder. To the best of our knowledge, this is the first report of a Cu_2O@MOFs type composite material. It is worthy to note that all the preparation process of the new materials is carried out at room temperature with low energy-consumption. The obtained Cu_2O@ZIF-8 material exhibits an excellent cycle stability in catalytic hydrogenation of 4-nitrophenol with high efficiency. This work may open a new avenue for the design, synthesis and regeneration of MOF-based composite material with unstable metal/metal oxides highly-active core and enhance their potential in various fields of application.

Acknowledgements

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Keywords: Meta-stable nano-particles • metal-organic frameworks • Cu_2O • composite material • heterogeneous catalyst

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Entry for the Table of Contents

COMMUNICATION

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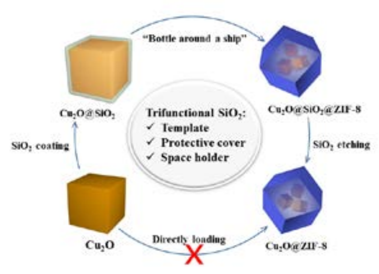

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