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## Nitrogen-Doped Carbon Composites with Ordered Macropores

### and Hollow Walls

**RESEARCH ARTICLE** 

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Abstract: Metal-organic frameworks provide versatile templates for the fabrication of various metal/carbon materials, but most of the derived composites possess only microspores, limiting the accessibility of embedded active sites. Herein, we report the construction of cobalt/nitrogen-doped carbon composites with a threedimensional- (3D-) ordered macroporous and hollow-wall structure (H-3DOM-Co/NC) using a single-crystal ordered macropore- (SOM-) ZIF-8@ZIF-67 as precursor. During the pyrolysis, the interconnected macroporous structure of SOM-ZIF-8@ZIF-67 is mostly preserved, while the pore wall achieves a solid-to-hollow transformation with Co nanoparticles formed in the hollow walls. The 3D-ordered macroporous carbon skeleton may effectively promote long-range mass transfer and the hollow wall can facilitate local accessibility of active sites. This unique structure can greatly boost its catalytic activity in the selective hydrogenation of biomass-derived furfural to cyclopentanol, much superior to its counterparts without this welldesigned hierarchically porous structure.

#### Introduction

Porous carbon-supported metal nanoparticles (NPs), a major category of functional materials, are critically important for a variety of applications including catalysis.<sup>[1]</sup> Among them, transition metals embedded in nitrogen-doped carbon (M/NC) materials have attracted great attention as promising heterogeneous catalysts due to their catalytically active centers.<sup>[2]</sup> For heterogeneous catalysts, their performance is determined by not only their intrinsic activity but also the number of accessible active sites.<sup>[3]</sup> Therefore, it is desirable to develop M/NC catalysts with hierarchical pore and/or hollow structures to enhance the accessibility of active sites.

Metal–organic frameworks (MOFs), with controllable pore structure and tunable composition, have provided a good platform for fabricating various functional nanomaterials.<sup>[4]</sup> In particular, Nrich zeolitic imidazolate frameworks (ZIFs) have been demonstrated to be ideal precursors to design M/NC catalysts.<sup>[5]</sup> However, most of these ZIF-derived M/NC catalysts only possess microspores, limiting the accessibility of active sites. Although some templated methods have been applied for the synthesis of ZIF-derived M/NC catalysts with mesopores and/or macropores,<sup>[6]</sup> their pore structures show a random distribution and low connectivity of mesopores and/or macropores. Recently, we reported a single-crystal ordered macroporous- (SOM-) ZIF-8,<sup>[7]</sup> which can be modified with transition metal ions (e.g., Ni, and Fe) as versatile precursors for the synthesis of various hierarchically porous M/NC materials with improved mass transfer.<sup>[8]</sup> Nevertheless, in these hierarchically porous M/NC materials, most of the active sites are buried in thick microporous walls, which still suffer from the restricted accessibility to reaction substrates. Here, we reasonably conceive that the creation of hollow walls in the hierarchically porous carbon skeleton can further decrease the diffusion resistance to enhance the accessibility of active sites and in turn greatly boost the catalytic performance.

In this work, we report the fabrication of Co/NC catalysts with three-dimensional ordered macropores and hollow walls (denoted as H-3DOM-Co/NC) by employing a SOM-ZIF-8@ZIF-67 crystal as precursor, which is synthesized through epitaxial growth of ZIF-67 nanolayers on SOM-ZIF-8. During the thermal transformation, the interconnected macroporous structure of SOM-ZIF-8@ZIF-67 crystals can be inherited to the yielded carbon composites, while the pore walls achieve a solid-to-hollow transformation accompanied by the formation of Co NPs. The 3Dordered macroporous skeleton of H-3DOM-Co/NC can promote long-range mass transfer meanwhile the hollow walls can facilitate local accessibility of active sites, allowing maximum exposure of active Co sites to reaction substrates. The H-3DOM-Co/NC catalyst exhibited significantly enhanced catalytic activity and selectivity in the hydrogenation of furfural (FFA) to cyclopentanol (CPL), as compared to conventional- (C-), hollow-(H-), and 3DOM-Co/NC catalysts derived from C-ZIF-67, C-ZIF-8@ZIF-67, and SOM-ZIF-67, respectively.

#### **Results and Discussion**

Scheme 1 illustrates the synthetic route of H-3DOM-Co/NC, consisting of four main steps. First, a mixed ammonia-methanol solution was employed to induce the formation of the ZIF-8

# **RESEARCH ARTICLE**

crystalline phase in 3D-ordered polystyrene spheres (PS) template voids filled with 2-methylimidazole and zinc nitrate hexahydrate to yield ZIF-8@PS. Thermogravimetric analysis (TGA) of the PS template showed a complete weight loss at ca. 400 °C (Figure S1). Thus, the PS template was removed by calcination at 400 °C for 5 h to obtain SOM-ZIF-8. Subsequently, the SOM-ZIF-8 served as seeds for the epitaxial growth of thin ZIF-67 nanolayers in the solution of 2-methylimidazole and cobalt nitrate hexahydrate to produce SOM-ZIF-8@ZIF-67. Finally, the SOM-ZIF-8@ZIF-67 was employed as the precursor for the synthesis of H-3DOM-Co/NC by pyrolysis in an argon atmosphere.



Scheme 1. Schematic illustration of the synthesis process of H-3DOM-Co/NC.

The SOM-ZIF-8 was synthesized using a PS template with a diameter size of 500 nm (Figure S2). Field-emission scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of SOM-ZIF-8 displayed a uniform size distribution and a cubic morphology with 3D-ordered macroporous structure (Figures 1a–c and S3). The highly ordered macropore arrangement in {100} and {111} planes of SOM-ZIF-8 was clearly evidenced from SEM images (Figure S4). The macropore diameter of SOM-ZIF-8 was measured to be ~410 nm.

SOM-ZIF-8 functioned as the crystal seeds for subsequent epitaxial growth of ZIF-67 (Co) with isoreticular structure, leading to the corresponding change in color from light yellow to light purple (Figure S5). Low-magnification SEM images of SOM-ZIF-8@ZIF-67 showed that ZIF-67 exclusively grew along with the surface of SOM-ZIF-8 without self-nucleation (Figure 1d). Highmagnification SEM and TEM images revealed a similar ordered macroporous skeleton but a smaller pore size (~340 nm) and a thicker wall of SOM-ZIF-8@ZIF-67 compared with those of SOM-ZIF-8 due to the epitaxial growth of ZIF-67 layers (with a thickness of ~35 nm) (Figures 1e-h and S4). High-angle annular dark-field scanning transmission electron microscopy images (HAADF-STEM) and the corresponding energy-dispersive X-ray spectroscopy (EDX) mapping images of SOM-ZIF-8@ZIF-67 verified the outer layers of ZIF-67 on SOM-ZIF-8 (Figure 1i). Selected-area electron diffraction (SAED) patterns taken from an entire crystal in the direction of [100] and [110] zone axes revealed the single-crystalline nature of SOM-ZIF-8@ZIF-67 (Figures 1g and h, insets).

Powder X-ray diffraction (XRD) patterns of both SOM-ZIF-8 and SOM-ZIF-8@ZIF-67 exhibited characteristic peaks ascribed to C-ZIF-8 and C-ZIF-67,<sup>[9]</sup> indicating the formation of phase-pure ZIF-8 and ZIF-8@ZIF-67, respectively (Figure S6). The peak intensity of SOM-ZIF-8@ZIF-67 was weaker than that of SOM-ZIF-8, implying the reduced crystallinity of SOM-ZIF-8@ZIF-67 after the epitaxial growth process, which is similar to previous reports.<sup>[10]</sup> Nitrogen (N<sub>2</sub>) sorption isotherms of SOM-ZIF-8 and SOM-ZIF-8@ZIF-67 showed similar type-I isotherm characteristics, implying their microporous structures (Figure S7).



Figure 1. FESEM images of (a–c) SOM-ZIF-8 and (d–f) SOM-ZIF-8@ZIF-67. (g and h) TEM images of SOM-ZIF-8@ZIF-67 in the [100] and [110] zone axis, respectively (inset shows corresponding SAED patterns). (i) HAADF-STEM image and the corresponding EDX elemental mappings of SOM-ZIF-8@ZIF-67.

After pyrolysis, the obtained H-3DOM-Co/NC preserved the cubic morphology and interconnected macroporous structure of SOM-ZIF-8@ZIF-67 but showed relatively rough surfaces due to the carbonization of the framework and formation of small Co NPs (Figures 2a-c). The pore size of H-3DOM-Co/NC (~400 nm) was larger than that of SOM-ZIF-8@ZIF-67, indicating shrinkage of the MOF during pyrolysis. Importantly, the pore walls of H-3DOM-Co/NC exhibited a solid-to-hollow transformation and were decorated with small Co NPs (Figures 2d and e). Highmagnification TEM image of H-3DOM-Co/NC clearly showed macropores surrounded by hollow walls (Figure 2f). The hollow walls of H-3DOM-Co/NC were further evidenced from elemental line scan profiles of H-3DOM-Co/NC (Figure 2h, inset). SAED patterns showed two obvious diffraction rings, assigned to the (111) plane of metallic Co and the (002) plane of graphite carbon (Figure 2e, inset). A high-resolution TEM (HRTEM) image of the embedded NPs exhibited a lattice spacing of 0.21 nm, corresponding to the (111) plane of face-centered cubic (fcc) metallic Co (Figure 2g). HAADF-STEM images and the corresponding EDX elemental mappings revealed the uniform distribution of Co NPs with an average size of ~4.9 nm on the support consisted of C and N (Figures 2h, 2i, and S8). The content of Co in the H-3DOM-Co/NC was determined to be 24.6 wt% by atomic absorption spectroscopy (AAS). The formation of the hollow wall may be governed by a surface-stabilized contraction process due to the different thermal stabilities between ZIF-67 and ZIF-8, as demonstrated by TGA (Figure S9). During the

# **RESEARCH ARTICLE**

thermal transformation, the outer ZIF-67 layers first decomposed into a rigid Co/NC shell, which then provided a driving force to pull ZIF-8 precursors outward during carbonization, resulting in the formation of hollow walls.<sup>[11]</sup>



Figure 2. (a–c) FESEM and (d–f) TEM images of H-3DOM-Co/NC. (g) HRTEM image of H-3DOM-Co/NC. (h and i) HAADF-STEM image and the corresponding EDX elemental mappings of H-3DOM-Co/NC. The insets of (e) and (h) are the corresponding SAED patterns and elemental line scan profiles, respectively.

The XRD patterns of H-3DOM-Co/NC showed two diffraction peaks at around 44.4 and 51.6°, which could be indexed to the (111) and (200) planes of fcc metallic Co, respectively, indicating the carbonization of the MOF and formation of Co<sup>0</sup> during pyrolysis (Figure 3a). Raman spectra of H-3DOM-Co/NC presented obvious D band (~1327 cm<sup>-1</sup>) and G band (~1587 cm<sup>-1</sup>), corresponding to defective carbon and graphitic carbon, respectively (Figure S10). The N<sub>2</sub> sorption isotherm of H-3DOM-Co/NC showed a steep increase at relatively low pressures (P/P<sub>0</sub> < 0.05) and a hysteresis loop at high pressures, representing the features of microporous and mesoporous structures, respectively (Figure 3b). The pore size distribution revealed that the micropore and mesopore diameters mainly centered at around 0.64 nm and 27.3 nm, respectively (Figure 3c). The Brunauer-Emmett-Teller (BET) surface area of H-3DOM-Co/NC was calculated to be 299 m<sup>2</sup>/g (Table S1). H-3DOM-Co/NC with the interconnected microporous-mesoporous-macroporous structure can effectively improve the accessibility of the active sites to reactants.

The electronic structure of H-3DOM-Co/NC was examined by X-ray photoelectron spectroscopy (XPS). The survey spectra revealed that Co, C, and N were the predominant elements in H-3DOM-Co/NC with residual Zn (Figure S11). The high-resolution Co  $2p_{3/2}$  spectrum exhibited the characteristic peaks of Co<sup>0</sup>, Co-O<sub>x</sub>, and Co-N<sub>x</sub> at 778.4, 780.1, and 781.4 eV, respectively (Figure

3d). The high-resolution N 1s spectrum of H-3DOM-Co/NC could be deconvoluted into four main peaks centered at 398.3, 398.9, 399.5, and 400.6 eV, assigned to pyridinic-N, Co-coordinated N, pyrrolic-N, and graphitic-N, respectively (Figure 3e). The strong coordination interaction between the Co and N can contribute to the electron modulation and stabilization of active Co sites, potentially benefitting for catalytic activity and stability.

FFA is a key platform molecule industrially produced from cellulosic biomass. The conversion of FFA to value-added products (e.g., CPL, cyclopentanone (CPO), furfural alcohol (FA), and tetrahydrofurfuralalcohol (THFFA)) is of great importance in both academic research and industrial application (Figure 4a).<sup>[12]</sup> Among them, CPL is widely employed in the production of pharmaceuticals, dyes, and fragrances. Many catalytic systems have been developed for the selective hydrogenation of FFA to CPL. However, it remains a big challenge to simultaneously achieve both high activity and excellent selectivity under mild conditions.



Figure 3. (a) XRD patterns, (b) N<sub>2</sub> adsorption-desorption isotherms, (c) pore size distribution calculated from the non-local density functional theory model, (d) Co 2p and (e) N 1s XPS spectra of C-Co/NC, H-Co/NC, 3DOM-Co/NC, and H-3DOM-Co/NC.

Herein, H-3DOM-Co/NC with highly dispersed ultrafine Co NPs on N-doped carbon support featuring 3D-ordered macroporous and hollow-wall structure was supposed to be an effective catalyst for this hydrogenation reaction. The reaction parameters were first screened and pointed to optimized reaction conditions of H<sub>2</sub> pressure of 2.0 MPa and temperature of 180 °C (Figures S12 and S13). The time profiles showed that CPL selectivity steadily increased when the reaction time increased from 1 to 8 h, demonstrating that FFA could be continuously converted into the final CPL product (Figure 4c). H-3DOM-Co/NC achieved a 97.2% yield of CPL within 8 h (Figure 4b). For comparison, Co-free 3DOM-NC with residual Zn derived from SOM-ZIF-8 was prepared (Figure S14), which showed no catalytic activity, suggesting the critical role of Co sites and the negligible role of Zn in the hydrogenation reaction (Table S2).

Moreover, the influence of basicity and acidity of the catalysts on the reaction was studied.  $CO_2$ -temperature-programmed desorption ( $CO_2$ -TPD) spectra of H-3DOM-Co/NC showed a strong  $CO_2$  desorption peak at ca. 166 °C, suggesting the existence of Lewis basic sites originated from abundant N dopants in the support (Figure S15). To verify the role of N in the

# **RESEARCH ARTICLE**

catalysis, Co NPs supported on N-free active carbon (Co/AC) with similar Co loading were prepared. Co/AC exhibited much larger sizes of Co NPs compared with H-3DOM-Co/NC (Figure S14), suggesting the important role of N in preventing the aggregation of Co NPs in the calcination process. Co/AC showed a lower activity (17.8% conversion) compared with that of H-3DOM-Co/NC (Table S2). But it exhibited a similar selectivity of CPL (67.4%) to that of H-3DOM-Co/NC at a similar conversion (17.8%). These results demonstrated that the effect of N doping on tuning the catalytic selectivity was negligible and the distinct activities should be attributed to the different sizes of Co NPs. We further studied the influence of acidity of catalysts on the reaction. Fourier-transform infrared spectra of pyridine adsorbed on H-3DOM-Co/NC displayed two strong peaks at 1442 and 1596 cm<sup>-1</sup>, confirming the Lewis acidic sites originated from Co species (Figure S16). In the hydrogenation of FFA, the Co acidic sites can promote the formation of carbocation intermediates for subsequent cyclization rearrangement (Figure 4d), allowing the stepwise hydrogenation of FFA to CPO/CPL.<sup>[13]</sup>

To demonstrate the advantage of the 3D-ordered macroporous and hollow-wall structures for boosting the reaction, we prepared three counterpart materials, including C-Co/NC, H-Co/NC, and 3DOM-Co/NC derived from C-ZIF-67, C-ZIF-8@ZIF-67, and SOM-ZIF-67, respectively (Figures S5, S17-S22). XRD patterns of these materials all exhibited characteristic peaks assigned to fcc metallic Co with high purity (Figure 3a). XPS measurements demonstrated the similar electronic structures of these Co-based materials (Figures 3d and 3e). The main difference between these materials is their distinct pore structures. Solid C-Co/NC possessed a micropore-dominant support embedded with Co NPs (Figure 3c and Figure S20). H-Co/NC showed a hollow structure with Co NPs dispersed in the micromesoporous shells but without interconnected macropores (Figure 3c and Figure S21). 3DOM-Co/NC showed an interconnected macroporous carbon skeleton similar to H-3DOM-Co/NC but a microporous wall (Figure 3c and Figure S22).

The catalytic activity of C-Co/NC, H-Co/NC, and 3DOM-Co/NC were examined with the same amount of Co under the same reaction conditions (Table S2). All of the materials showed similar selectivities to CPL but distinct activities (yields of CPL in 8 h) in the order of H-3DOM-Co/NC (97.2%) > 3DOM-Co/NC (62.3%) > H-Co/NC (41.7%) > C-Co/NC (21.3%). Since these Cobased catalysts possessed similar electronic structures, their different activities should be attributed to their distinct pore structures. The activity trend implies the important role of mesopores and macropores in facilitating the catalytic reaction. For a detailed analysis of the effect of the porous structure, the accessible Co sites in these materials were determined by H<sub>2</sub>-TPD measurement (Table S3). These materials showed the dispersion of Co in the order of H-3DOM-Co/NC (20.3%) > H-Co/NC (14.2%) > 3DOM-Co/NC (11.6%) > C-Co/NC (8.7%), implying the contribution of mesopores in improving the accessibility of Co sites. However, considering of the higher activity of mesopore-free 3DOM-Co/NC than macropore-free H-Co/NC, the accessbility of Co sites alone can not explain the activity improvement. Mass trasport should be another factor that could greatly affect the catalytic efficiency. The interconected macropores can greatly contribute to long-range mass transfer improvement, as demonstrated in our previous study.<sup>7</sup> Therefore, the interconnected macropores can enhance the long-range mass transfer and mesopores in hollow walls can facilitate the local accessibility of active Co sites, thus cooperatively boosting the catalytic activity.

These findings inspired us to further evaluate the effect of the sizes of macropores in the skeletons and hollow space in the walls of 3DOM-Co/NC on the accessibility of Co sites. We prepared a series of H-3DOM-Co/NC-X materials with various macropore sizes using PS templates with different diameters. PS templates with diameters of X (X = 210, 320, 410, and 600 nm) were used for the first synthesis of SOM-ZIF-8-X with macropore sizes ranging from ca. 182 to 512 nm and the subsequent SOM-ZIF-8@ZIF-67-X with reduced macropore sizes ranging from ca. 160 to 405 nm (Figures S23–S32). The thickness of the ZIF-67 layers in SOM-ZIF-8@ZIF-67-X increased from ca. 11.0 to 53.5 nm with enlarged macropore sizes (Figure S33).



**Figure 4.** (a) The possible reaction pathway for the hydrogenation of FFA to CPL. (b) The yield of CPL as a function of reaction time over C-Co/NC, H-Co/NC, 3DOM-Co/NC, and H-3DOM-Co/NC. (c) Plots of the product distribution for the conversion of FFA at different reaction times. (d) Plausible mechanism for the hydrogenation of FFA to CPL over the H-3DOM-Co/NC catalyst. (e) Reusability tests of H-3DOM-Co/NC for the FFA hydrogenation at reaction times: 8 h (pink bars), and 4 h (purple stars).

After pyrolysis, SOM-ZIF-8@ZIF-67-X was transformed to the corresponding H-3DOM-Co/NC-X with slightly increased macropore sizes (Figure S34). Interestingly, the void sizes of the walls increased along with the increase of macropore sizes (Figure S34). The hysteresis loop in the N<sub>2</sub> sorption isotherms of H-3DOM-Co/NC-X also became more and more evident with the enhancement of macropore sizes, indicating the enlarged mesopore sizes of the walls (Figures S35 and S36). This finding is similar to previous reports that a thicker rigid layer on ZIF-8 would result in a larger hollow space in the derived carbon composites.<sup>[6e]</sup> HRTEM images (Figure S34) and XRD patterns (Figure S37) of H-3DOM-Co/NC-X confirmed the successful formation of fcc metallic Co. XPS measurements revealed similar chemical environments of Co among the H-3DOM-Co/NC-X

# **RESEARCH ARTICLE**

samples (Figures S38–41). In the catalytic reactions, the activity of H-3DOM-Co/NC-X increased with the enhancement of macropore and void sizes, which may be attributed to the improved substrate diffusion and increased number of available active sites. Among the synthesized H-3DOM-Co/NC-X materials, H-3DOM-Co/NC-600 showed the highest activity, achieving a 97.8% yield of CPL in 8 h with a turnover frequency of 1.8 h<sup>-1</sup>, making it one of the most active non-noble-metal catalysts reported thus far for this hydrogenation reaction (Tables S2 and S4).

The hot filtration experiment demonstrated no further conversion of FFA after catalyst removal from the system and the Co content of the reaction mixture measured by AAS was below the detecting limit (< 5 ppb), suggesting the heterogeneous nature of the catalytic system (Figure S42). Furthermore, H-3DOM-Co/NC could be reused at least seven times without significant loss of activity (Figure 4e). The CPL yields were also similar at an incomplete reaction time (4 h) in the recycling experiments (purple stars suit in Figure 4e), revealing the high durability of this catalyst. The XRD patterns of the used H-3DOM-Co/NC matched well with those of the fresh one with almost unchanged intensity (Figure S43). The HAADF-STEM images also confirmed that the 3Dordered macropores and hollow walls of the reused catalyst were well preserved and no obvious aggregation of Co NPs was observed (Figure S44). These results demonstrate that the hierarchically porous N-doped carbon support can protect the aggregation and leaching of Co NPs during the reaction, thus allowing the active H-3DOM-Co/NC catalyst to show high stability and reusability under the investigated conditions.

#### Conclusion

In summary, we have successfully fabricated 3D-ordered macroporous H-3DOM-Co/NC with hollow walls, through epitaxial growth of ZIF-67 nanolayers on SOM-ZIF-8 followed by a simple thermal transformation process. The 3D-ordered macroporous carbon framework can effectively promote long-range mass transfer, and the hollow walls can facilitate the local accessibility of active sites, which can cooperatively maximize the exposure of embedded Co NPs to reaction substrates, thus boosting the catalytic activity in the hydrogenation of FFA. Further tuning the sizes of macropores in the skeleton and hollow space in the walls demonstrated the positive correlation between macropore/void sizes and mass transfer efficiency/accessibility of active sites. Moreover, the porous N-doped carbon support could well protect the embedded Co NPs from aggregation during the catalytic reaction to achieve good stability and reusability in the reaction. This study might provide insights into the rational design and synthesis of hierarchical and hollow structures with enhanced activity and stability for various applications.

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#### **Competing interests**

The authors declare no competing interest.

**Keywords:** hierarchical pore • hollow structure • heterogeneous catalysis • metal-organic frameworks • selective hydrogenation

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## **RESEARCH ARTICLE**

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# **RESEARCH ARTICLE**

#### Entry for the Table of Contents



Cobalt/nitrogen-doped carbon catalysts with 3D-ordered macroporous and hollow-wall structures were successfully fabricated by using ordered macroporous ZIF-8@ZIF-67 single crystals as precursors. This unique porous structure can greatly enhance mass transfer and boost catalytic activity in the selective hydrogenation of furfural.