The synthesis of multi-level porous MOF composite materials with different MOF contents

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Abstract. To address the inherent limitations of current MOF synthesis, where pore size is restricted to micropores or small mesopores, we successfully synthesized MOF composite materials with well-developed porous structures using a self-template approach. These pores encompass not only the intrinsic micropores or small mesopores of MOFs but also the template-induced large pores. During the experimental process, we achieved the synthesis of composite materials with varying MOF contents by modifying experimental conditions. Through this design, we not only achieved selective adsorption of guest molecules but also significantly increased the porosity, thereby enhancing the mass transfer efficiency of guest molecules and the utilization rate of materials. This research breakthrough offers new insights and solutions for addressing critical issues in fields such as gas separation, energy storage, and catalysis.

Keywords: Metal-organic framework composites, Multi-level pores, Self-template method

1. Introduction

Metal-organic frameworks (MOFs) are a class of crystalline porous framework materials composed of organic ligands as linkers and metal ions or clusters as nodes, bonded together [1]. MOFs hold significant importance in scientific research as they ingeniously combine the fields of organic and inorganic chemistry. This material not only inherits the advantages of both organic and inorganic chemistry but also transcends their molecular units, displaying remarkable framework architectures and multifunctional properties.

In comparison to traditional porous zeolite materials, MOFs can flexibly adapt to diverse real-world applications due to their tunable building units [2] and functionalization capabilities, attracting widespread attention in academia. The introduction of charged ligands enhances the strength of chemical bonds and prevents counter ions from blocking the pores, ensuring pore accessibility. Substitution of metal ions by secondary building units (SBUs) ensures the rigidity and directionality of structural units. The combination of these aspects establishes the structural stability and permanent porosity of MOFs after pore clearance [3]. Due to their tunable pore structures, high surface areas, and ease of functionalization, MOFs have been widely applied in gas storage and separation, catalysis, and biomedical fields [4].

Although MOFs possess high porosity and surface area, their intrinsic pores are mainly micropores, severely limiting mass transfer efficiency and restricting applications involving large molecules. In recent years, scientists have employed various methods to construct mesopores or macropores on the basis of inherent micropores, forming multi-level porous MOFs. Based on the source of pores, multi-level porous MOFs are mainly divided into intrinsic multi-level pores and defect multi-level pores. Intrinsic multi-level pores refer to multi-level pore structures composed of MOFs' own structure, while defect multi-level pores are formed through defects in the MOFs structure. Preparation methods mainly include solvothermal [5-7], templating [8, 9], and etching methods [10]. Templating is a commonly used method for synthesizing well-developed porous structures.

In this study, we successfully synthesized ZIF-8/ZnO/SiO_2 composite materials with multi-level pore structures using a self-template approach [11]. In the process of this experiment, ZnO serves as a source of zinc ions (Zn^{2+}), promoting the subsequent formation of ZIF-8. Meanwhile, SiO_2 acts as a framework support, effectively preventing framework collapse and maintaining the stability of the multi-level pore structure. During the experimental process, by varying the feed amount of 2-methylimidazole, we successfully synthesized multi-level pore ZIF-8/ZnO/SiO_2 materials with different ZIF-8 contents, laying the material foundation for the application of ZIF-8 in the field of large molecules.

2. Instrument

Powder X-ray Diffraction (PXRD) instrument: Model MiniFlex 600 diffractometer, Manufacturer: Rigaku Corporation, Japan. Instrument testing conditions: Voltage 40 kV, Current 50 mA, X-ray radiation source Cu-Kα (λ = 0.154056 nm).

Surface area and pore size distribution analyzer: Model ASiQMVH002-5, Manufacturer: Quantachrome Corporation, USA. Testing conditions: N_2, 77 K. Pore size distribution calculated using Non-Localized Density Functional Theory (NLDFT). Material pre-treatment conditions before testing: Vacuum activation at 120°C for 12 hours.

Field Emission Scanning Electron Microscope (SEM): Model JEOL JSM-7500F, Manufacturer: Hitachi Corporation, Japan. High-resolution Field Emission Scanning Electron Microscope (SEM): Model Zeiss GeminiSEM 360, Manufacturer: Zeiss.

3. Experimental Section

Synthesis of 270 nm PS Sphere Template [9]: Initially, 70 mL of styrene was washed with 20 mL of 10% NaOH solution in a separatory funnel, followed by rinsing with deionized water three times to remove the stabilizer from the styrene. Subsequently, the cleaned styrene was transferred to a 1 L three-neck round-bottom flask, and 500 mL of water solution containing 2.50 g PVP was added. Nitrogen gas was bubbled through the solution for 30 min to remove oxygen. Then, a solution of 1 g $K_2S_2O_8$ in 50 mL of water was quickly injected into the flask to initiate the polymerization reaction of styrene. The reaction was carried out at 75°C with stirring at 500 rpm for 24 h, followed by cooling to room temperature to obtain white milky (with a hint of blue) monodisperse polystyrene spheres (PS spheres). Finally, centrifugation at 10000 rpm for 1 h separated the PS spheres from the mother liquor, and the PS spheres were dispersed repeatedly in deionized water (at least three times) to obtain the washed solid PS spheres, which were dried at 60°C to obtain the PS sphere template.

Synthesis of Multi-level Porous ZIF-8/ZnO/SiO_2 [11]: In the experiment, 4.36 g of $Zn(NO_3)_2 \cdot 6H_2O$ was dissolved in a mixed solvent of 10 mL of ethylene glycol (EG) and methanol, with a volume ratio of 6:4, to obtain solution one after stirring for 1 h. Subsequently, 6.24 g of tetraethyl orthosilicate (TEOS), 5.40 g of ethanol, 0.97 g of H_2O, and 0.89 g of 37 wt% hydrochloric acid were mixed to obtain solution two after stirring for 1 h. To prepare the precursor solution, 2 mL of solution one and 1.35 g of solution two were mixed, and then 2.00 g of PS sphere template was added to the above solution and soaked for 24 h. After completion, the solid was filtered and dried at 60°C. Next, the template was removed by calcination in a tube furnace to obtain the ZnO/SiO_2 framework. The specific conditions were as follows: the temperature was raised from room temperature to 300°C at a rate of 1°C/min and held at 300°C for 3 h; then raised to 500°C at a rate of 1°C/min and held for 4 h. Finally, it was cooled to room temperature to complete the calcination.

ZIF-8 was grown on the ZnO/SiO_2 framework via self-template method. Initially, 0.3 g or 0.05 g of 2-methylimidazole was dissolved in a mixed solution of 10 mL DMF/H_2O (volume ratio of 3:1), and then 20 mg of ZnO/SiO_2 framework was immersed in the solution for 24 h at 70°C. After the reaction, the mother liquor was removed, and the product was washed with methanol three times to obtain the multi-level porous ZIF-8/ZnO/SiO_2 composite material.

4. Results

SEM characterization was conducted on the synthesized PS sphere template, as shown in Figure 1a). It can be observed from the image that the template composed of PS spheres was successfully synthesized. Subsequently, to determine the size of the synthesized spheres, tests were conducted on 100 individual spheres. The results, depicted in Figure 1b), revealed an average diameter of 245 nm for the PS spheres, with both sets of data exhibiting a normal distribution, indicating minimal data error. These findings demonstrate the successful synthesis of the targeted size of sphere template, providing reliable support for the further synthesis of multi-level porous ZIF-8/ZnO/SiO_2.

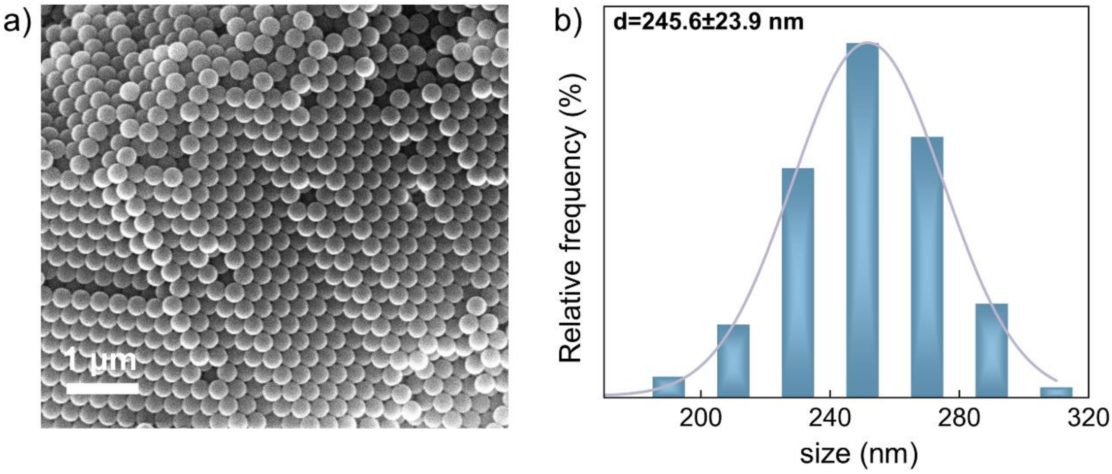

Figure 1. a) SEM image and b) size distribution of the formed PS template.

After calcination to remove the PS spheres, the formed ZnO/SiO_2 framework was characterized. SEM testing results (Figure 2) demonstrated the successful synthesis of ZnO/SiO_2 framework with uniformly sized large pores, exhibiting a well-developed pore network throughout the material. The synthesis of this material lays a solid foundation for the preparation of multi-level porous ZIF-8.

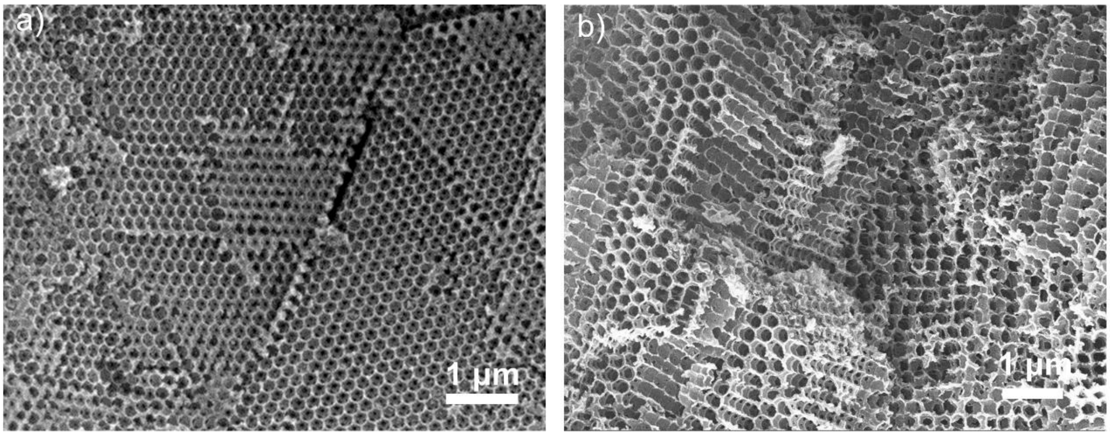

Figure 2. SEM images of ZnO/SiO_2 with a well-developed pore structure.

Subsequently, multi-level porous ZIF-8/ZnO/SiO_2 was synthesized using the ZnO/SiO_2 composite material as the framework. The PXRD testing results in Figure 3a) revealed the presence of crystalline peaks of ZIF-8 in the composite material formed after the addition of 2-methylimidazole, indicating the successful incorporation of ZIF-8 into the composite material. Additionally, by varying the dosage of 2-methylimidazole, different ZIF-8 contents of the ZIF-8/ZnO/SiO_2 composite materials (ZIF-8/ZnO/SiO_2-x: x representing the dosage of 2-methylimidazole) were successfully synthesized. According to the N_2 adsorption testing results in Figure 3b), the composite material exhibited a Type I adsorption isotherm, indicating the presence of micropores. With an increase in dosage, the adsorption of nitrogen also increased, demonstrating a proportional relationship between the amount of ZIF-8 and the dosage of 2-methylimidazole, albeit lower than pure ZIF-8. This is attributed to the presence of ZnO/SiO_2 in the composite material, which has a lower nitrogen adsorption capacity, resulting in a decrease in the proportion of nitrogen adsorbed per gram of material. Through SEM testing (Figure 4), it was observed that ZIF-8/ZnO/SiO_2-0.3 exhibited significant ZIF-8 particles compared to ZIF-8/ZnO/SiO_2-0.05, further confirming that varying the dosage of 2-methylimidazole can synthesize composite materials with different ZIF-8 contents.

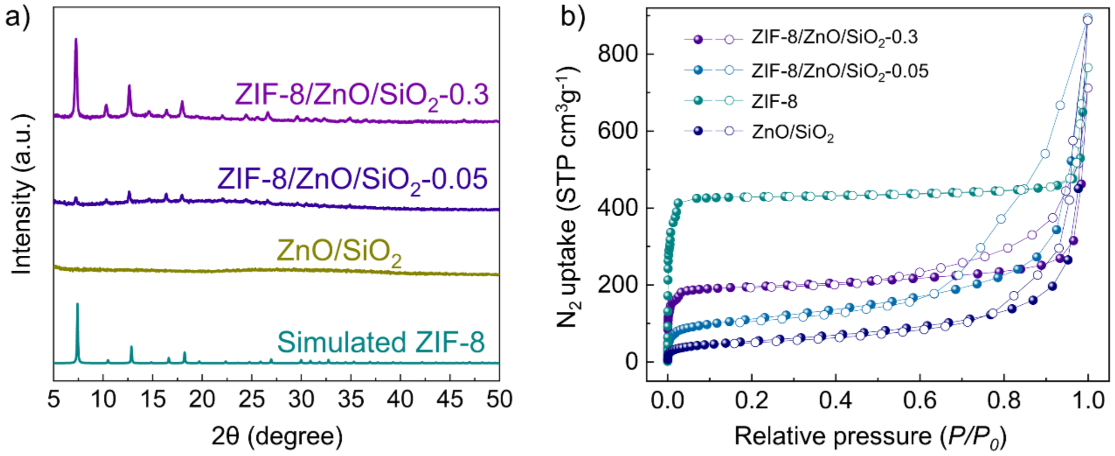

Figure 3. a) X-ray diffraction patterns of simulated ZIF-8, ZnO/SiO_2, ZIF-8/ZnO/SiO_2-0.05 and ZIF-8/ZnO/SiO_2-0.3. b) N_2 adsorption/desorption isotherms of ZIF-8, ZnO/SiO_2, ZIF-8/ZnO/SiO_2-0.05 and ZIF-8/ZnO/SiO_2-0.3.

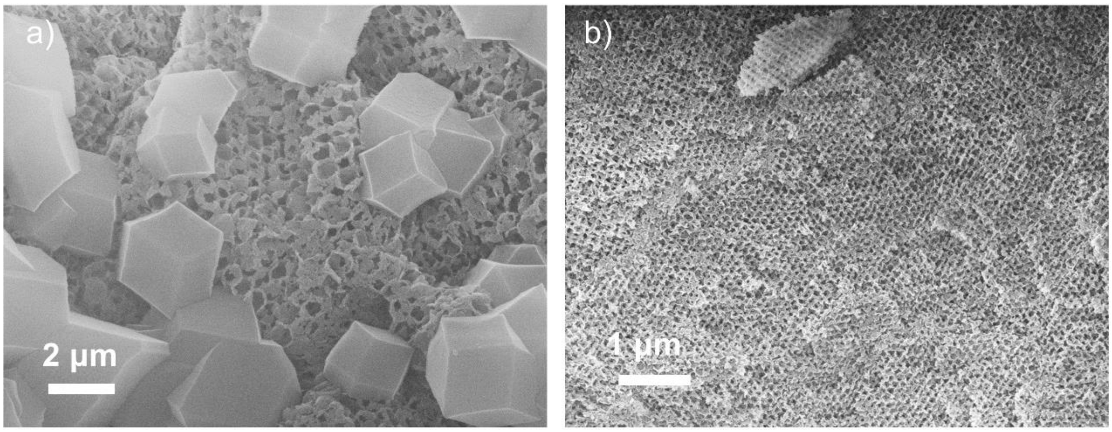

Figure 4. SEM images of a) ZIF-8/ZnO/SiO_2-0.3 and b) ZIF-8/ZnO/SiO_2-0.05.

5. Conclusion

In this study, we successfully synthesized ZIF-8/ZnO/SiO_2 materials with different ZIF-8 contents. Characterization techniques such as PXRD and SEM confirmed the successful incorporation of ZIF-8 and the well-developed pore structure. With increasing dosage of 2-methylimidazole, it was observed that the characteristic peak intensity of ZIF-8 in the composite increased, along with an increase in nitrogen adsorption and the formation of distinct ZIF-8 particles. These observations further corroborated the variation in ZIF-8 content within the composite. In summary, this study provides new insights and methods for the design and synthesis of multi-level porous materials, with significant theoretical and practical implications for applications in catalysis, adsorption, and other fields.

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