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Bimetalic ZIFs(Zn-M) (M: Co, Ni) for photocatalytic removal of organic pollutant in aqueous solution

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Abstract. In this study, bimetallic ZIFs(Zn-M) of 2-methyl imidazole were successfully synthesized with the participation of a second metal, herein cobalt or nickel, into the ZIF network. All ZIFs samples were synthesized at room temperature, then characterized by XRD, FT-IR, SEM, DRS, nitrogen adsorption and desorption isotherms. All samples possessed a high crystallinity with a large surface area. The photocatalytic ability of all samples was examined through the degradation of indigo carmine under a solar light simulator. The presence of a second metal enhanced the photon harvesting ability of ZIF(Zn) when the materials can absorb photons in both UV and visible region. Among synthesized ZIFs, ZIF(Zn-Co) exhibited an extremely high photocatalytic ability when removed 100 % of indigo carmine from an aqueous solution. After 2 h, the ZIF(Zn-Co) adsorbed 45 % and degraded 55 % of indigo carmine under 1.5 h of solar irradiation. However, while the existence of Co^{2+} increased the surface area of ZIFs, Ni^{2+} reduced it. As a result, the photocatalytic efficiency of ZIF(Zn-Ni) was not higher than ZIF-8(Zn).

Keywords: Metal-organic frameworks, ZIF-8, bimetallic ZIFs, photocatalysis, organic pollutant removal

1 Introduction

Metal–organic frameworks (MOFs) are hybrid, crystalline, porous materials constructed from metal–ligand coordination, forming infinite networks. The inorganic nodes or vertices in the framework consist of metal ions or clusters, namely secondary building units (SBUs). These nodes are connected by coordination bonds to organic linkers, which commonly contain carboxylate, phosphonate, pyridyl, imidazolate or other azolate functional groups. The combination of ease of tunability, atomic-level structural uniformity, compositional (elemental) variety and high porosity is, in large measure, what distinguishes MOFs from other porous materials such as activated carbon, porous organic polymers and zeolites [1]. MOFs have exceptional porosity and a wide range of potential uses including gas storage, separations, and catalysis [2].

Zeolitic imidazolate frameworks (ZIFs) are a new class of porous crystals with extended three-dimensional structures constructed from tetrahedral metal ions (e.g., Zn, Co) bridged by imidazolate (Im). By combining metal salts with

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imidazole in solution, a large number of crystalline ZIFs have been made; some of these possess topologies found in zeolites, and others have yet to be made as zeolites [3].

Among ZIFs family, ZIF-8(Zn) has been explored as highly thermal and chemical stability [1], high porosity, and ease of synthesis, so become an attractive candidate for many applications such as separation and storage of gases, removal of organic pollutants in solution [4–7]. However, due to the large band gap (~5 eV), its photocatalytic ability is limited. Jing *et al.* [8] used ZIF-8 as a catalyst for photodegradation of methylene blue under UV irradiation, even though, the efficiency of dye removal is not very practically valuable.

In this research, nickel or cobalt is introduced into ZIF-8(Zn) structure with the aim of reducing the band gap and hence boosting the photocatalytic properties of the material. The radii of Ni^{2+}, Co^{2+} and Zn^{2+} are not significantly different. They can both form coordination bonds with nitrogen in imidazole [9]. Tetrahedral coordination is very popular in zinc complex compounds, and it also can appear in nickel and cobalt compounds. Therefore, nickel and cobalt ions can participate in ZIF-8 structure. This is also a novel approach to dop metal into ZIF-8 structure which has been considered to be different due to unpopular tetrahedral coordination and strong chemical bond between zinc and 2-methylimidazole.

2 Materials and Methods

2.1 Materials

Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$ (Sigma–Aldrich, 98 %), 2-methylimidazole (Hmim, $C_4H_6N_2$, Acros, 99 %), cobalt (II) nitrate hexahydrate $Co(NO_3)_2.6H_2O$ (Sigma–Aldrich, 98 %), nickel (II) nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$, Sigma–Aldrich, 98 %) and other chemicals were analytical grade. Deionized water was used where needed.

2.2 Methods

Synthesis of ZIF-8(Zn): ZIF-8 was synthesized with slight modification to a previously reported procedure [10]. Specifically, $Zn(NO_3)_2.6H_2O$ (3 mmol) was dissolved in 30 mL of methanol (MeOH) to form a clear solution, which was subsequently poured into 10 mL of MeOH containing Hmim (12 mmol). After thorough mixing, the resulting solution was incubated at room temperature for 24 h. The as-obtained precipitates were centrifuged and washed with ethanol and dry in a vacuum overnight.

Synthesis of ZIF(Zn-Ni) and ZIF(Zn-Co): ZIF(Zn-M) (M: Ni or Co) was synthesized with slight modification to a previously reported procedure [10]. Specifically, $M(NO_3)_2.6H_2O$ (1.5 mmol) and $Zn(NO_3)_2.6H_2O$ (1.5 mmol) were dissolved in 30 mL of methanol (MeOH) to form a clear solution, which was subsequently poured into 10 mL of MeOH containing 2-methylimidazole (12 mmol). After thorough mixing, the resulting solution was incubated at room temperature for 24 h. The as-obtained precipitates were centrifuged and washed with ethanol and dry in vacuum overnight.

Materials characterization: To identify the materials, X-ray diffraction (XRD) measurement was implemented by X-ray diffractometer (D8 Advance, Bruker, Germany) with Cu Kα radiation (λ =1.54 Å). A continuous scan mode run from 10-40° with scan rate of 4°/min to collect data of 2θ. To detect the presence of functional groups or the change in molecular bonds, infrared spectra of all samples were collected using an FTIR spectrophotometer (Vertex 70, Bruker Optics, Ettlingen, Germany). Morphology of samples was examined by a scanning electron microscope

(SEM, JEOL-2020). The light absorption ability was recorded by UV-Vis diffuse reflectance spectrophotometer (JASCO 570). The specific surface area of samples (S_{BET}) was determined through nitrogen isotherms collected by an ASAP 2020 automatic analyzer. Before determination, the synthesized samples were degassed at 100 °C for at least 12 h under vacuum conditions, N_2 adsorption-desorption isotherms were measured at 77K.

Photocatalytic activity tests: In a typical photodegradation experiment, 50 mg of the photocatalyst powder was dispersed in a quartz beaker containing 50 mL of an aqueous solution of indigo carmine (C_0 = 50 ppm). Before irradiation, the suspension was stirred magnetically in the dark for a couple of hours to obtain an absorption-desorption equilibrium condition. A solar simulator (150 W short arc lamp) was used as a light source. At selected time intervals, aliquots of the suspension were collected, centrifuged, and filtered by membranes to remove the catalyst particulates. The concentration of the rest (C) of the solution was evaluated using a UV-Vis spectrophotometer (Jasco-V-670).

3 Results and Discussion

The phase purity of bimetal ZIFs was confirmed by XRD patterns (Figure 1).

The existence of characteristic peaks for single-metal ZIF-8 on XRD patterns confirmed the successful synthesis of ZIF-8(Zn) [11,12]. The characteristic peaks of ZIF-8 still appeared on XRD patterns of bimetallic ZIFs, demonstrating that the zeolite structure of ZIF-8 still remained under the participation of the second metal ion (Ni^{2+}, Co^{2+}). For all ZIFs, the XRD patterns exhibited sharp peaks with no appearance of additional phases, suggesting that the obtained products are highly purity and crystallinity.

The coordination of the organic ligand with the metals was investigated by IR spectra. The spectra of Hmim showed a strong and broad band from 3400 to 2200 cm^{-1} which is assigned for the N-H•••N hydrogen bond established between two Hmim ligands and one N-H stretching vibration at 1846 cm^{-1} (Fig. 2). These two adsorption bands disappeared in as-synthesized ZIFs, indicating the deprotonation of the N-H groups of the Hmim ligands upon coordination with metal ions [11]. A shift of the C-H bending signal from 1117 cm^{-1} to 1143 cm^{-1} was observed (Fig. 2), which can be assigned for the transformation of imidazole to imidazolate [13]. All those information indicated that ligand molecules deprotonated to form coordination bonds with metal ions.

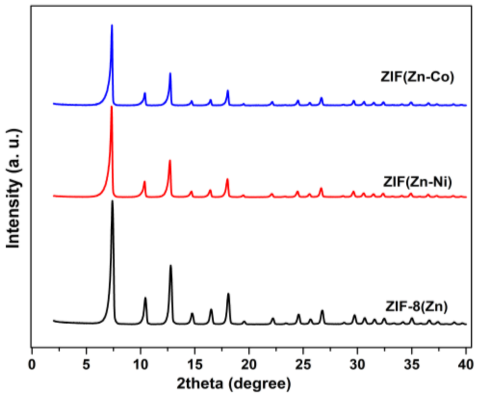

Fig. 1. XRD patterns of ZIF-8, ZIF(Zn-Ni), and ZIF(Zn-Co)

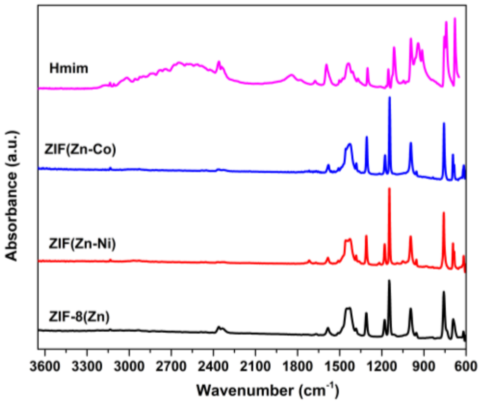

Fig. 2. IR spectra of ZIF-8, ZIF(Zn-Ni), and ZIF(Zn-Co)

The morphology and particle size of ZIFs samples were illustrated via SEM images (Fig. 3). All samples showed regular morphology and high crystallinity, particle size of the samples was about 500-1000 nm. While ZIF-8(Zn) and ZIF(Zn-Co) particles presented rhombic dodecahedral shapes, ZIF(Zn-Ni) particles had undefined shape. ZIF(Zn-Ni) particles obtained a bigger size and higher agglomeration, which might affect the specific surface area of the sample.

Figure 4 revealed the nitrogen sorption isotherms and calculated BET surface area of ZIFs samples.

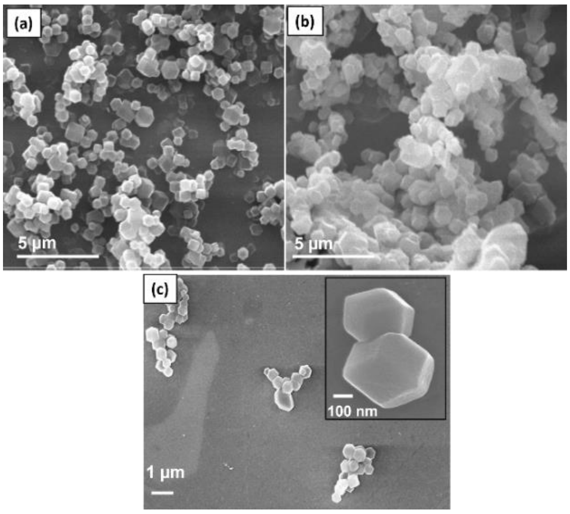

Fig. 3. SEM images of (a) ZIF-8, (b) ZIF(Zn-Ni), and (c) ZIF(Zn-Co)

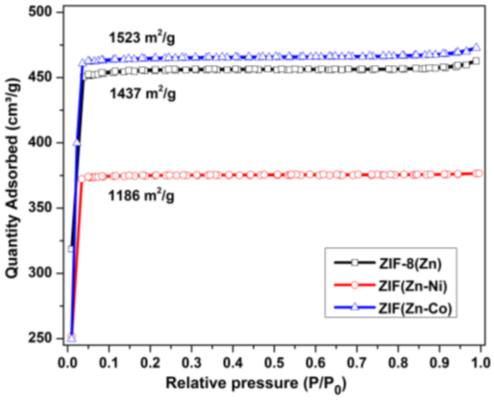

Fig. 4. Nitrogen sorption isotherms and BET surface area of ZIF-8, ZIF(Zn-Ni) and ZIF(Zn-Co)

Herein, the nitrogen sorption isotherms of all ZIFs samples were of type I, indicating the microporous structure of the ZIFs. BET surface area of ZIF-8(Zn) was 1437 m²/g that was lower than ZIF(Zn-Co) (1523 m²/g) but higher than ZIF(Zn-Ni) (1186 m²/g).

The lower surface area of ZIF(Zn-Ni) might result from the difference in coordination structure between Ni^{2+} and Zn^{2+} with imidazolate ligands. While Zn^{2+} coordinates to imidazolate ligands through four bonds to form tetrahedral structures, nickel complexes are generally in square planar or octahedral coordination that possesses lower energy than tetrahedral ones [14]. Therefore, the substitution of Zn^{2+} by Ni^{2+} in ZIF-8 network might be unfavourable, Ni^{2+} ions might coordinate to Hmim but not replace Zn^{2+} positions. As a result, nickel complex formed and partly filled the void of the sample, leading to the decrease in the surface area of ZIF(Zn-Ni). For ZIF(Zn-Co), Co^{2+} ions can coordinate with Hmim to form ZIF-67 that had a similar structure to ZIF-8, therefore the participation of Co^{2+} did not collapse the ZIF networks [15]. However, due to slight differences in ionic radius and the affinity of the metal toward nitrogen atoms of ligands, local distortion and certain stress appear in ZIF(Zn-Co) which directly determine the size of SBUs [16], thus resulting in the increase of the surface area of ZIF(Zn-Co). The better alternative of Co^{2+} than Ni^{2+} was also presented in samples morphology (Fig. 3), in which ZIF(Zn-Co) and ZIF-8(Zn) revealed a rhomic dodecahedral shape whereas the particle shape of ZIF(Zn-Ni) was undefined.

To examine the light absorption ability of bimetal-ZIFs, DRS spectra of all samples were recorded, as shown in Fig. 5.

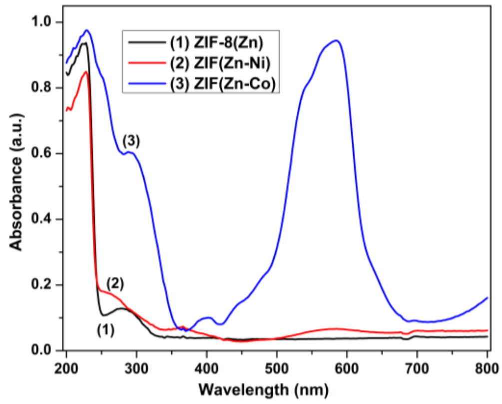

Fig. 5. UV-Vis diffuse reflectance spectra of ZIF-8, ZIF(Zn-Ni), and ZIF(Zn-Co)

Compared to ZIF-8 (Zn), the UV-Vis diffuse reflectance spectrum of ZIF(Zn-Ni) showed a small difference in absorption at UV range (250-400 nm), attributing to the process of charge transfer from imidazolate ligand to nickel in the framework. Besides, there was a low intensity peak at 550-600 nm, assignining to the d-d charge-transfer process in Ni^{2+}. It indicated that the existence of nickel improved the light absorption of ZIF(Zn-Ni) in both UV and visible regions. For ZIF(Zn-Co), UV/Vis spectra showed a strong band at 450-700 nm, corresponding to the ligand-to-metal charge transfer of tetrahedral coordinated Co^{2+}, proving the presence of tetrahedral coordination cobalt in ZIF(Zn-Co) [17].

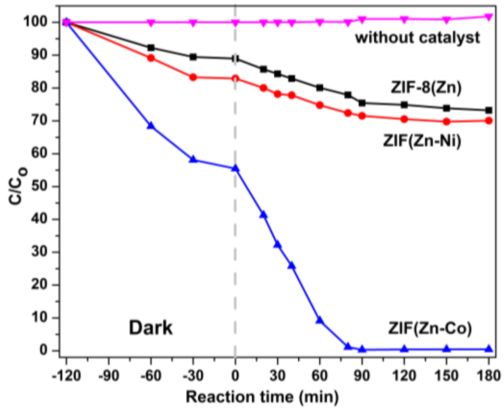

Fig. 6. Photodegradation of indigo carmine using ZIFs catalysts

The adsorption and photocatalysis ability of synthesized ZIFs has been established by the degradation of indigo carmine (IC), as shown in Fig. 6. Among ZIFs samples, ZIF(Zn-Co) exhibited the highest adsorption efficiency (45 %), whereas ZIF-8(Zn) and ZIF(Zn-Ni) only can adsorb 10 % and 17 % of IC, respectively, after 2 h in dark. The difference in adsorption ability of the ZIFs is not only from the surface area of the materials but also from the interaction of metal ions on a surface with organic matters. Indeed, ZIF-8(Zn) obtained a much higher surface area than ZIF(Zn-Ni), but the adsorption efficiency was lower. Therefore, it can be assumed that a stronger interaction formed between IC molecular and Co^{2+} and Ni^{2+} than Zn^{2+} on the surface of the ZIFs.

After 3 h of irradiation, the photocatalytic efficiency of both ZIF-8(Zn) and ZIF(Zn-Ni) was about 10 %, much lower than that of ZIF(Zn-Co). The Co-containg ZIF obtained 55 % of photodegradation efficiency after 1.5 h under solar light, so this sample removed most of IC in queous sollution (100 %). The extremely high photodegradation efficiency of IC when using ZIF(Zn-Co) as a photocatalyst is the consequence of (1) a high surface area, (2) a strong interaction of Co^{2+} and IC molecular, and (3) an effective substitution of Co^{2+} to Zn^{2+} in ZIF-8 structure. Moreover, the existance of the second metal ion (Co^{2+} to Ni^{2+}) in ZIFs networks might improve the photon-harvesting ability of the materials. Even though, ZIF(Zn-Ni) did not show a high photocatalysis efficiency as expected, because only a small amount of Ni^{2+} appeared in the sample, due to the difference in coordination structures between Ni^{2+} - imidazolate and Zn^{2+} - imidazolate.

4 Conclusion

In this study, ZIF-8(Zn) and bimetallic ZIFs of zinc with cobalt/nickel were successfully synthesized with high purity and high crystallinity. The participation of nickel and cobalt has changed the physicochemical properties of ZIF-8. In detail, ZIF(Zn-Co) obtained a larger surface area whereas the surface area of ZIF(Zn-Ni) was lower than that of single metallic ZIF-8(Zn). ZIF(Zn-Ni) particles were bigger and agglomerated more than the rest samples. Particularly, DRS spectra showed that ZIF(Zn-Co) can strongly absorb photons in a wide range of visible light, extending from yellow to red light region. Consequently, ZIF(Zn-Co) exhibited an extremely higher adsorption and photocatalysis efficiency than ZIF-8(Zn) and ZIF(Zn-Ni) when it adsorbed 45 % and degraded 55 % of indigo carmine from an aqueous solution.

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