

Research Article

Microwave-Assisted Solvent-Free Synthesis of Zeolitic Imidazolate Framework-67

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A microporous metal-organic framework (MOF), cobalt-based zeolitic imidazolate framework-67 (ZIF-67), was synthesized by the combination of solvent-free hand-mill and microwave irradiation, without any organic solvent and within 30 minutes. The hand-milling process can mix the reactants well by the virtue of high moisture/water absorption capacity of reactants. In addition, the outstanding electromagnetic wave absorption capability of cobalt leads to efficient conversion to MOF structures before carbonization. The obtained ZIF-67 possesses high surface area and micropore volume.

1. Introduction

Metal-organic frameworks (MOFs) are a family of highly porous crystalline materials, which consist of metal ions and ligands that are coordinated into 3D structures. In light of their unique physicochemical characteristics, MOFs have great potential for applications such as gas storage [1, 2], separation [3], drug delivery [4], heterogeneous catalysts [5], luminescence [6], magnetism [7], biomedical sensors [8], and heating transformation through reversible water adsorption and desorption [9]. MOFs feature very large specific surface area and pores size controllable and adjustable by the proper selection of metal ions and organic linkers [10, 11]. In addition, the organic linkers can be functionalized independently without sacrificing the geometrical characteristics of 3D porous structures, which is another unique advantage [12, 13].

Although MOFs have garnered increasing interests of researchers, there are still several factors limiting their practical applications [14, 15]. The use of organic solvents and long

synthesis time are two of the top challenges. Organic solvents pose the risk to operators and the natural environment, leading to limited autoclave availability, whereas the long synthesis time tends to translate to high energy consumption and cost.

There are several strategies to address challenges in synthesizing MOFs, among which the solvent-free (SF) synthesis and microwave (MW) synthesis are very promising [16, 17]. For instance, Lin et al. reported that the porous metal azolate framework can be synthesized by simply heating the mixture of metal oxide/hydroxide and azole ligand only [18]. Friscic adopted “accelerated aging” to assist the synthesis of multi-gram of metal-organic framework without using solvents, high temperature, or another activation [19]. Nonetheless, with few exceptions [20], SF mixing alone without any subsequent or concurrent treatment, such as hydrothermal process, would not effectively produce MOFs. While it is essential to mix the solid reactants well in order to synthesize uniform MOF particles, this can only be partially achieved

with the aid of ball milling [21, 22]. Microwave-assisted synthesis of MOFs has proven its effectiveness in recent years [23, 24]. Microwave absorption can induce vibration of atoms and molecules and thus convert mechanical energy to thermal energy, which induces chemical reactions very efficiently [25]. The polar solvents, which have high dielectric absorptivity, function as thermal conversion agents to eliminate local superheat spots, promoting fast and homogeneous nucleation over the MOF growth process. In this study, a hypothesis to test is that the efficiency of MW treatment should also depend on the wave absorption capability of the metal ions. This factor, to the best of our knowledge, has not been considered in previous studies.

Zeolitic imidazolate frameworks (ZIFs) are a class of MOFs that are topologically isomorphic with zeolites, in which tetrahedrally coordinated transition metal ions are connected by imidazole linkers [26]. The structure of ZIFs is highly stable, and it can be heated to high temperatures without decomposing, making them suitable for use in hot environments [27]. Tanaka et al. reported a mechanochemical dry conversion of ZnO to ZIF-8 by ball milling, which avoids the use of organic solvents using excess amount of 2-methylimidazole. And the BET surface area of obtained ZIF-8 reached the maximum ($1480\text{ m}^2\text{ g}^{-1}$) after milling for 96 h [28]. Subsequently, Lanchas et al. used 1-butanol, pyridine, and 4-methylpyridine as structure directing agents to generate ZIF single crystals above $88\text{--}90^\circ\text{C}$ [29]. Lin et al. also reported that the porous metal azolate framework can be synthesized by heating the mixture of metal oxide/hydroxide and azole ligand at 100°C for 24 h [18]. Although it has been reported that ZIF-67 can be obtained within several minutes by hydrothermal methods, either excess 2-methylimidazole ($\text{Zn}^{2+} : 2\text{-methylimidazole} : \text{H}_2\text{O} = 1 : 70 : 1238$) or additives [30, 31], such as trimethylamine, are needed, which results in the waste of reactants and pollution to the environment. In addition, the samples synthesized within minutes by normal solvothermal/hydrothermal methods generally have lower surface areas and smaller pore volumes. A mechanochemical synthesis of ZIFs in which crystal formation can be completed within several minutes has not been reported. Interestingly, we also noticed that the cobalt ions in ZIFs have excellent electromagnetic wave absorption properties [32–34] and thus may facilitate the fast synthesis of ZIFs via the MW treatment method.

Here, we describe a very rapid method for the synthesis of cobalt-based zeolitic imidazolate framework-67 (ZIF-67), taking the advantages of coupling SF and MW treatments. The goal is to eliminate the use of organic solvent in the process and shorten the synthesis time to less than 30 minutes, including 20 minutes for manual grinding and 5 minutes for the crystallization.

2. Experimental Section

2.1. Materials. All the reagents, including cobalt nitrate hexahydrate (98%, Sigma-Aldrich), 2-methylimidazole (99%, Sinopharm), and cobalt nitrate hexahydrate (98%, Sigma-Aldrich) were used as received.

2.2. Preparation of ZIF-67. The preparation of ZIF-67 consisted of three steps: (1) mixing the starting materials by mechanical attrition at room temperature for 20 min; (2) production of ZIF-67 crystals with MW-irradiation; (3) washing the as-synthesized ZIF-67 with methanol for 3 times. Specifically, 895 mg 2-methylimidazole was finely powdered in an agate mortar for 5 min; then 404.8 mg $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added and the mixture was ground for another 15 min. The resulting mixture was transferred into a quartz boat and placed in a domestic microwave oven and heated for 5 min. The obtained solid, termed SF_MW ZIF-67, was washed with methanol for 3 times and then separated by centrifugation. Domestic microwave oven (G90W25M SP-WD) was used, with the power of 900 W.

We also tested whether the addition of cobalt-containing salt to the precursors of Zn-based MOFs can facilitate the formation of Zn-based MOFs. We prepared ZIF-8 with the solvent-free method by adding small amount of cobalt source ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) into the starting materials. 785 mg of 2-methylimidazole was ground for 5 minutes, followed by the addition of 642 mg of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Then 166 mg of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added and ground for another 15 minutes. The microwave treatment is the same as that of the SF_MW ZIF-67.

2.3. Characterization. The structures of the ZIF-67 crystals were investigated by scanning electron microscopy (HELIOS Nanolab 600i); X-ray diffraction (XRD, Empyrean series 2, PANalytical) and infrared spectrum (IR, Frontier Optical, PE) surface areas were measured by 3H-2000PS1 Specific & Pore Size Analysis Instrument (BeiShiDe Instrument).

3. Results and Discussion

During the solvent-free (SF) synthesis of MOF, mechanical grinding is required to promote the reactions between solid reactants through multiple mechanisms, including heating, defects formation, particle size reduction, local melting, and even phase changes to other polymorphs [32]. Ball mill is generally preferred to grind the solid reactants, since it can supply high power, being programmable, and result in smaller particles with small polydispersity [17]. In this study, however, instead of ball mill, we use hand-mill only to accelerate the moisture/water absorption of the solid reactants. Once the two reactants are mixed and ground, the solid mixture turns into blue liquid (Figures 1(a) and 1(b)) within several minutes (which is dependent on the air humidity). It is mainly caused by the high moisture absorption capability of cobalt nitrate hexahydrate. The quantity of absorbed moisture seems large enough to dissolve all reactants (cobalt nitrate hexahydrate and 2-methylimidazole) without any noticeable solid particles, making the reactants well mixed. Upon further hand-milling for several minutes, solid pink particles (Figure 1(c)) gradually precipitated until the whole liquid mixture eventually changed back into solid particles. This is because 2-methylimidazole can gradually absorb water in the liquid mixture as long as it is not saturated. Such solid-liquid-solid phase change during hand-milling

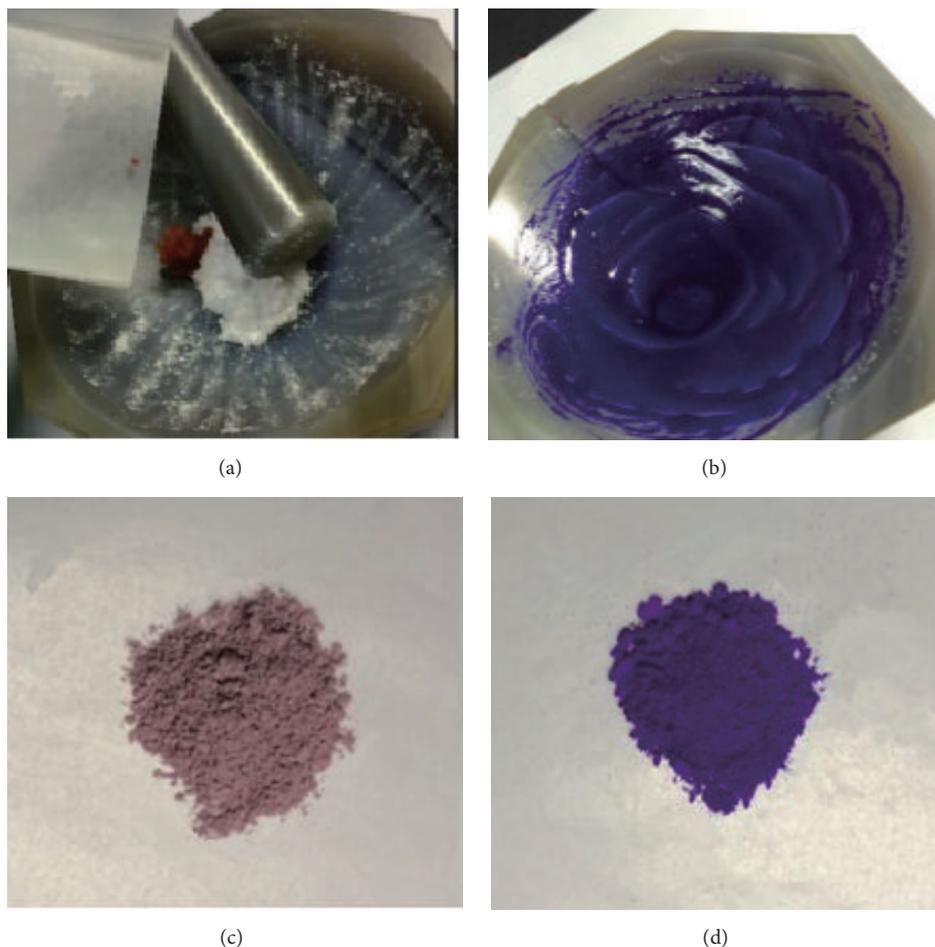


FIGURE 1: Photographs of starting materials (a), the liquid mixtures (b), and products before MW-irradiation (c) and after MW-irradiation (d).

can greatly facilitate the unprecedented uniform mixing of the solid reactants. Since the input energy to the reactants during hand-milling is negligible comparing to ball milling process, the mechanism related to the mechanochemical synthesis probably cannot be applied to the situation of hand-milling. Indeed, as will be discussed in the following, the obtained solid particles after hand-milling do not possess any structural characteristics of ZIF-67. Those pink particles are then treated by MW-irradiation, which is necessary for the synthesis of ZIF-67 in this study. Upon MW treatment, it can be observed that the color of the particles changed from pink to purple (Figures 1(c) and 1(d)). It is worth pointing out that although the MW oven we used in this study is domestic and cheap instead of programmable and expensive industry MW oven, the physical/chemical properties of the obtained ZIF-67 are quite stable for more than five times synthesis and confirm the reproducibility.

Figure 2 presents SEM images of the ZIF-67 samples synthesized by the SF method. The samples maintain the rhombic dodecahedral shape, which is consistent with ZIF-67 prepared by autoclaved method. However, the average size of the SF samples is about 500 nm, which is much

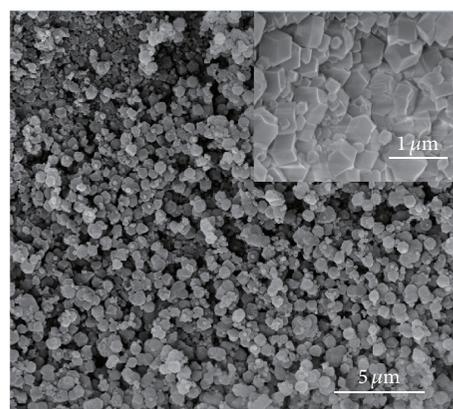


FIGURE 2: SEM images of ZIF-67 crystals.

smaller than the traditional one. This may be due to its short synthesis time resulting in a fast nucleation and short growth rate during the SF process. Figure 3 shows the structures of ZIF-67 at different MW-irradiation time. The structure

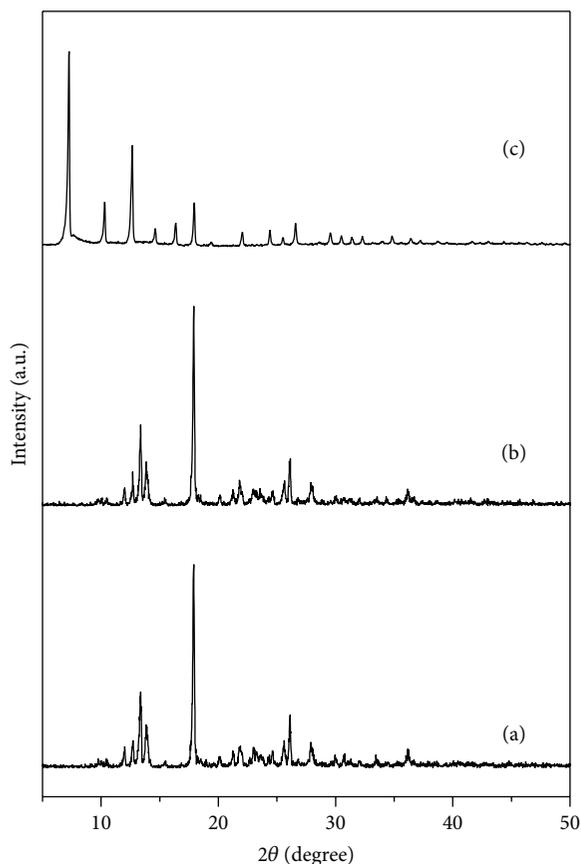


FIGURE 3: XRD patterns of as-synthesized ZIF-67 products under MW-irradiation for 0 min (a), 1 min (b), and 5 min (c).

and high crystallinity of our prepared ZIF-67 product are confirmed by the XRD patterns shown in Figure 3(c). The positions of diffraction peaks agree well with the simulated one. A favorable orientation of (110) direction was observed, from the highest peak at 2 theta value of 7.3 degrees, which represents (110) plane of ZIF-67 crystals. We can see from Figures 3(a) and 3(b) that, with no or not enough MW-irradiation, the peaks of the products do not conform to the simulated one, indicating no ZIF-67 structure was generated. This phenomenon was further certified by FTIR spectroscopy (Figure 4). From the comparison between the samples before and after MW-irradiation, we can see that, before microwave-assisted heating, the as-synthesized ZIF-67 precursors obtained by just grinding exhibit peaks in accordance with 2-methylimidazole as reported in literature [35], implying no ZIF-67 product was prepared. However, after MW treatment, a new absorption band at 477 cm^{-1} was displayed, manifesting the Co-N stretching, which proved the existence of ZIF-67 structure. On the other hand, the duration of MW-irradiation should be carefully controlled to prevent the overheating of the particles. In this study, the samples are cooled down after each 1 min in MW treatment for the prevention of the collapse of the framework and even its carbonization.

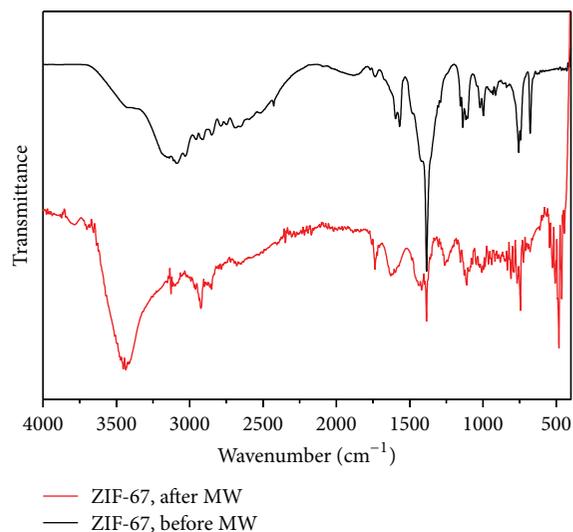


FIGURE 4: IR spectrum of SF_MW ZIF-67 crystals.

Figure 5(a) shows nitrogen adsorption isotherm of SF_MW ZIF-67, which is a Type I isotherm, representing a micropore structure. The Brunauer-Emmett-Teller (BET) specific surface area and Langmuir specific surface area of ZIF-67 are calculated to be $1120\text{ m}^2/\text{g}$ and $1562\text{ m}^2/\text{g}$, respectively. A pore size distribution ranging from 1.24 nm to 1.36 nm, based on the Horvath-Kawazoe (H-K) model, is shown as in Figure 5(b). The peak at 1.3 nm probably resulted from the distortion of the second-building unit (SBU), which is formed through the reaction of Co^{2+} and 2-MIm during the hand mixing or microwave radiation. Considerable energy will be absorbed by the reaction system during the microwave radiation treatment, and it not only accelerates the formation of MOF but also might be able to distort the already formed SBU. As can be seen from the complementary experiments, in which the microwave radiation time decreased from 1 minute to 30 seconds, the size of the pores decreases obviously and the peak at 1.3 nm disappears. Clearly, the microwave radiation treatment time has some impact on the pore size distribution.

For the solvent-free microwave heating method in this study, we prepared ZIF-67 with the reactant quantity much closer to stoichiometric Co-2MI ratio (1:7.94), in which not only does it improve the reagent utilization efficiency and avoid using of poison reagents, but also the resultant MOFs have higher surface area ($1120\text{ m}^2/\text{g}$) and micropore volume (0.52 mL/g). Actually, those values are similar to the MOFs obtained by traditional solvothermal/hydrothermal samples ($>100^\circ\text{C}$, 1 h to 1 month). We further carried out experiments by shortening the heating time during each heating and cooling process. It was found that when the heating time decreases from 1 minute to 30 seconds (Figure 6), the surface area and micropore volume can be enhanced to $1591\text{ m}^2/\text{g}$ and $0.74\text{ cm}^3/\text{g}$, respectively, which fully testified the accessibility of this approach and, by optimizing the preparation conditions, we can synthesize ZIF-67 solids with good quality within several minutes but without using any

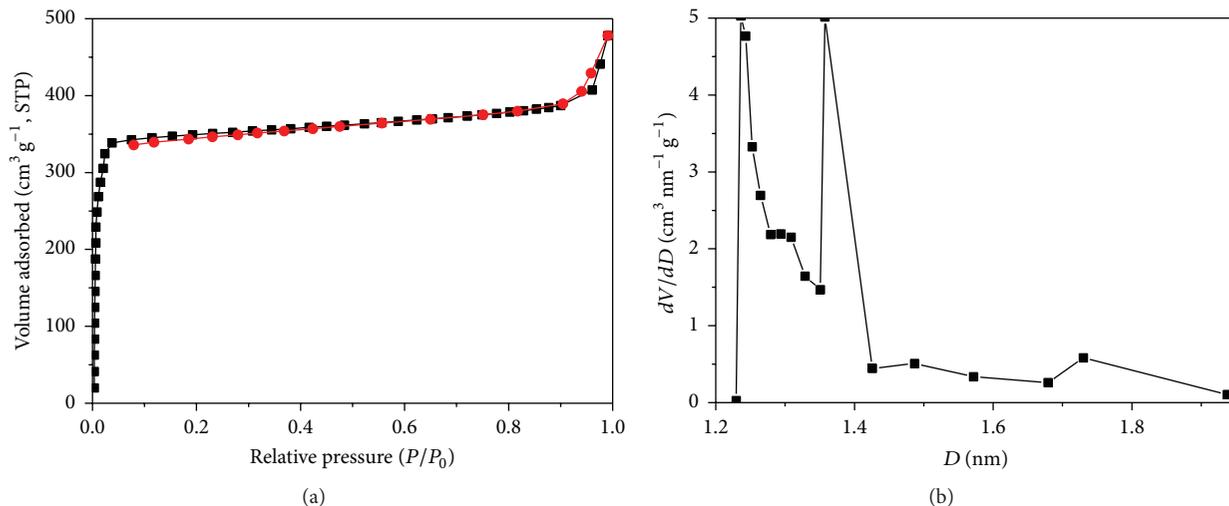


FIGURE 5: N_2 adsorption-desorption isotherms (a) and H-K micropore size distribution (b) of SF_MW ZIF-67.

TABLE 1: Physical properties of different samples.

Samples	Mean pore size (nm)	S_{BET} (m^2/g)	Micropore volume (cm^3/g)
C-ZIF-67	1.17	1725	0.82
SF_MW ZIF-67-1	1.18	1120	0.52
SF_MW ZIF-67-2	1.31	1591	0.74

C-ZIF-67, ZIF-67 samples synthesized by the conventional solvothermal method.

SF_MW ZIF-67-1, ZIF-67 samples synthesized by the SF_MW method, in which heating time is 1 minute.

SF_ZIF-67-2, ZIF-67 samples synthesized by the SF_MW method, in which heating time is 30 s.

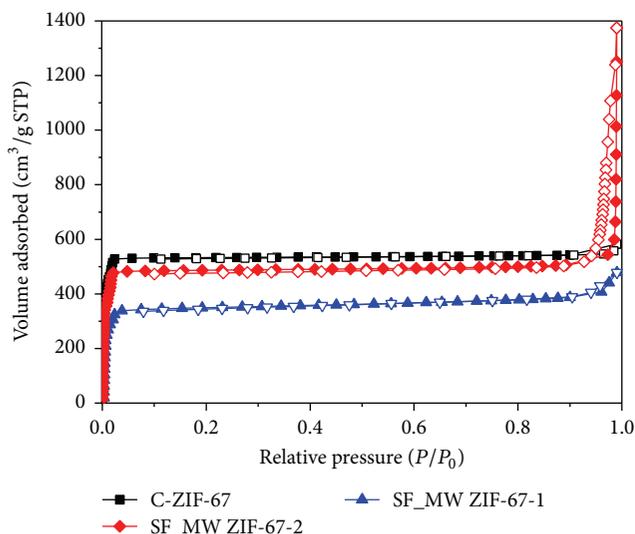


FIGURE 6: N_2 adsorption isotherms of different samples.

poisonous reagent or waste of reactants. We also compare the porous structures of ZIF-67 obtained via MW treatment with conventional solvothermal method. From Figure 7, the lattice distance of the SF_MW ZIF-67 increased, while the particle size reduced from 800 nm to 500 nm, implying that the pore size increased through MW treatment. This was confirmed by the pore size distribution by N_2 adsorption testing in Table 1,

which shows a pore size distribution ranging from 1.24 nm to 1.36 nm and a median pore diameter of 1.31 nm. This is much larger than the conventional ones with a median pore diameter of 1.17 nm and pore volume (at $P/P_0 = 0.024$) of $0.82 \text{ cm}^3/g$. In addition, the pore volume of the MW samples can be increased by tuning the heating time from 1 minute to 30 s (total MW heating time is the same, i.e., 5 min) in every MW heating interval (63%, $P/P_0 = 0.038$, $0.52 \text{ cm}^3/g$ versus 90%, $P/P_0 = 0.021$, $0.74 \text{ cm}^3/g$). Meanwhile, the mean pore size also decreases to 1.18 nm, which is similar with the traditional ones. This phenomenon illustrates that the porosity can be tuned by varying the heating intervals during the SF_MW process, which can facilitate the generation of hierarchical pores.

We also apply the same procedure to synthesize ZIF-8. However, MW-irradiation directly converts the particles into amorphous carbon instead of ZIF-8, and the addition of extra water to the precursors of ZIF-8 during hand mix still cannot prevent the carbonization (Figure 8). Further, we testified whether our method applies to those ZIF or MOF systems that can only be synthesized in solvothermal conditions, in which we tried the synthesis of MOF-5. Unfortunately, there is no MOF-5 generated according to the XRD analysis (Figure 9). Such distinct comparison clearly illustrates the importance of electromagnetic wave absorption capability of metal ions. Cobalt is one of the most effective electromagnetic wave absorbents. When irradiated by electromagnetic waves, cobalt ions act as superheat spots and trigger

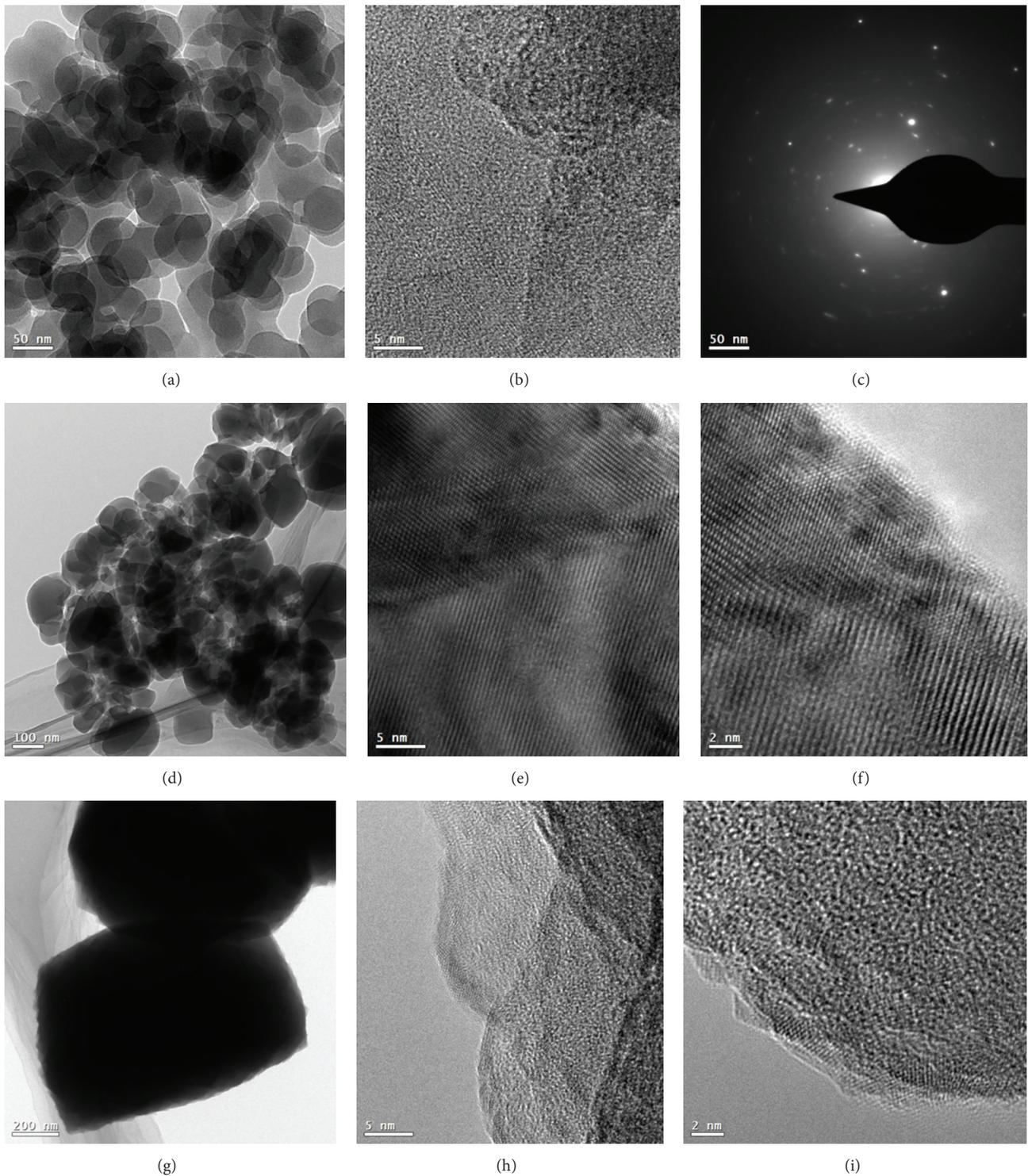


FIGURE 7: TEM images of the as-synthesized SF_MW ZIF-8 particles (a, b, c), SF_MW ZIF-67 particles (d, e, f), and C-ZIF-67 particles (g, h, i).

the complexation between the metal ions and ligands to form stable 3D microporous MOF structures. Therefore, the MOF formation mechanism during MW treatment in this study should be very different from the conventional ones where it is the organic solvent that acts as heating spot

as we discussed previously. In addition, we expected that the existence of cobalt would facilitate the production of ZIF-8 due to its microwave-absorbing properties. We added a minimum of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to the precursors for the synthesis of ZIF-8, and the results of this experiment testified

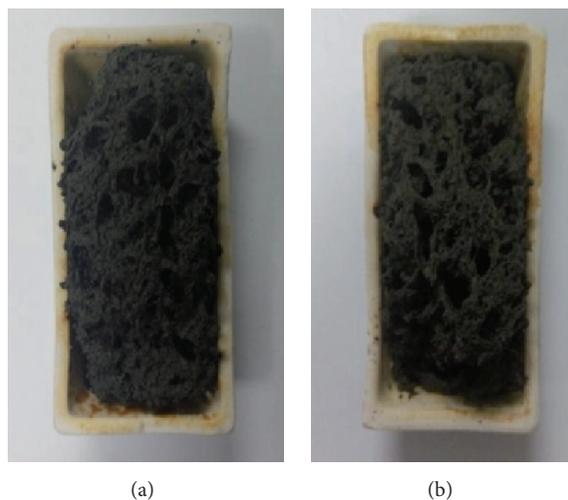


FIGURE 8: Images for the samples obtained by the microwave radiation for the precursors of ZIF-8 with extra (a) 10 mL water and (b) 100 mL water.

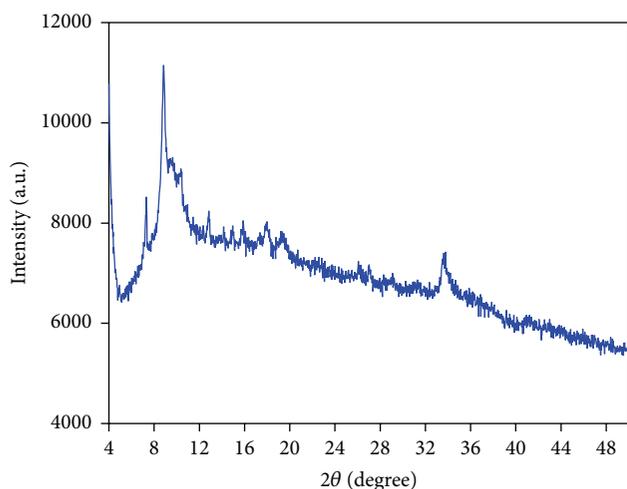


FIGURE 9: XRD for the samples obtained by hand mixing and microwave treatment for the precursors of MOF-5.

our assumption. It can be clearly seen from Figure 10 that there is a peak at 417 cm^{-1} in the IR spectrum of SF_MW ZIF-8/ZIF-67, which represented the Zn-N stretching, implying the formation of ZIF-8 structure. When compared to the IR spectrum of SF_MW ZIF-67, the difference was evident between 400 cm^{-1} and 500 cm^{-1} . In SF_MW ZIF-67, as exemplified in Figure 4, the adsorption band is at 477 cm^{-1} , which is the characteristic for Co-N stretching. Therefore, ZIF-8 was prepared successfully with the existence of cobalt nitrate. The TEM images in Figure 7(a) revealed that the particle size of ZIF-8 was about 50 nm with hexagonal shape.

4. Conclusions

In this study, we combine hand-milling with MW-irradiation methods to synthesize ZIF-67. This avoids the use of organic

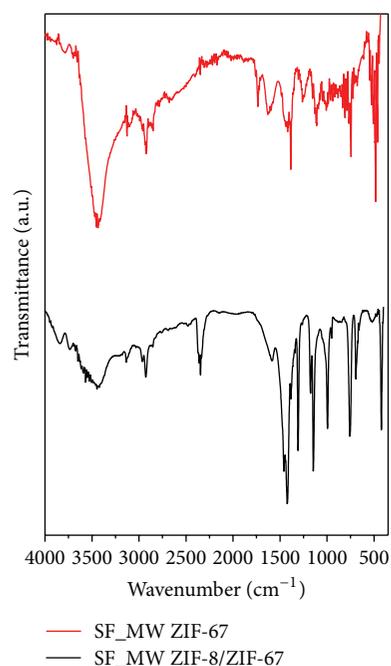


FIGURE 10: IR spectrum of SF_MW ZIF-67 (red) and SF_MW ZIF-8/ZIF-67 (black).

solvent and shortens the synthesis time to less than 30 minutes. The hand-milling process is to mix the solid reactants well, whereas the MW-irradiation successfully converts the participating reactant particles to ZIF-67. The synthesized ZIF-67 features high surface area and micropore volume. We also show that the electromagnetic wave absorption capability of metal ions plays a key role in the successful conversion of reactants to MOFs, which merits further investigation.

Competing Interests

The authors have confirmed that there are no competing interests related to this paper.

Acknowledgments

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