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Research paper

Synthesis and characterization of nano-sized metal organic framework-5 (MOF-5) by using consecutive combination of ultrasound and microwave irradiation methods

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ABSTRACT

Nano-sized metal organic framework-5 (MOF-5) was prepared in the presence of triethylamine (TEA) via consecutive combination of ultrasound (US) and microwave irradiation (MW) methods by exploiting the benefit of obtaining MOF-5 in very short reaction times (~2 min) and high yields (~95%). The surface area of MOF-5 was found to be 1203 m^2/g. The highly crystalline structure of nano-sized MOF-5 was confirmed by XRD. Vibrational modes and thermal decomposition behavior of nano-sized MOF-5 were verified from ATR FT-IR and TGA results, respectively. Based on SEM and AFM results, MOF-5 nanoparticles are spherical in shape, and their sizes vary in the range of 20–80 nm. The high purity of nanosized MOF-5 was confirmed by XRD and EDS results. A very regular and homogenous distribution of MOF-5 nanoparticles with a size range of 20–30 nm within poly(ethylene oxide) (PEO) electrolyte was clearly observed from SEM results. The reason behind size reduction and homogenous distribution of nano-sized MOF-5 was stated as the elimination of any possible aggregation of MOF-5 nanoparticles due to favorable physical interactions between PEO and surface functional groups of MOF-5 during the solution casting process.

1. Introduction

Metal organic frameworks (MOFs) are porous inorganic materials that are composed of metal ions and organic ligands [1–5]. They have desirable properties such as elasticity, three-dimensional structure, high surface area, variability of their pore size and surface polarity by means of suitable choice of organic ligand/metal ion combinations [1–3,5]. MOFs have wide range of applications in gas storage and separation [5–9], surface adsorption [5,10], ion-exchange [2,11,12], sensors [13,14], drug delivery [15,16], catalysis [17–20], optical and magnetic materials [13,21,22], and chromatography [23,24]. In addition, the use of these materials in electrochemical capacitors [25–27] and lithium ion battery [28–31] applications has attracted great interest over the years.

MOFs containing various benzene organic linkers with single, double or three rings can be synthesized *via* room temperature (RT) [32,33,34], solvothermal (ST) [8,35], hydrothermal (HT) [23,36], US [37–41], electrochemical (EC) [42,43] and MW [44–48] methods. The MW irradiation and US methods are more advantageous in comparison with others when the criteria such as ease of method, reaction in short times, increasing the energy yield of product, and being environment friendly in obtaining products are taken into consideration [47,49–51].

MOF-5 has been the most widely studied MOF material due to its extra-high porosity and ordered structure, high thermal stability and flexible chemical functionality [1,3,4]. The structure of MOF-5 has exceptional high porosity and thermal stability due to its quite large and rigid secondary building unit and benzene links. MOF-5 is composed of a cubic lattice vacancy like in zeolites through the combination of ZnO_4 compounds with $[O_2C\text{-}C_6H_4\text{-}CO_2]$ (1,4-benzenedicarboxylate, BDC) groups [1,3,4]. Isoreticular MOFs (IRMOFs) which are size-adjustable hybrid structures consisting of Zn_4O clusters with diverse carboxylate linkers were first synthesized by Yaghi et al. MOF-5 is also known as IRMOF-1 [1,3].

Nano-sized MOFs have a high potential to display better performance in gas storage, separation and adsorption [6,7,52], drug delivery [52,53], catalysis [18,52], sensors and optical devices [13,21,54], batteries and supercapacitors [26,32,55] due to their nanometer size and high surface area. Thus, the synthesis of well-defined nano-sized

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Table 1
Studies dealing with room temperature, solvothermal, microwave radiation and sonochemical synthesis methods of MOF-5.

Metal precursor	Solvent	Coordination modulator	Synthesis method	Size of the crystals	Surface area.	Reference
$Zn(NO_3)_2{\cdot}4H_2O$	DEF		MW	2–4 μm	2869 B	64
$Zn(NO_3)_2{\cdot}6H_2O$	DEF		MW	4 ± 1 μm	No data	65
$Zn(NO_3)_2{\cdot}4H_2O$	NMP		MW	20–25 μm	1025 L	44
$Zn(NO_3)_2{\cdot}6H_2O$	NMP		MW	5–10 μm	1263 L	48
$Zn(NO_3)_2{\cdot}6H_2O$	DMF		MW	No Data	2489 B	66
$Zn(NO_3)_2{\cdot}6H_2O$	DEF	TEA	US + MW	3–10 μm	713 B	67
$Zn(NO_3)_2{\cdot}6H_2O$	DMF	CTAB + TEA	ST	200–300 nm	3005 B	6
$Zn(NO_3)_2{\cdot}6H_2O$	DMF	TEA	RT	20–30 nm	784 L	32
$Zn(NO_3)_2{\cdot}6H_2O$	DMF	TEA	RT	70–90 nm	948 B	34
$Zn(NO_3)_2{\cdot}6H_2O$	DMF	TEA + C12E4	RT	30–45 nm	666 B	34
$Zn(NO_3)_2{\cdot}6H_2O$	DMF	TEA	RT	No Data	3909 L	33
$Zn(NO_3)_2{\cdot}6H_2O$	NMP		US	4–25 μm	3208 L	37
$Zn(NO_3)_2{\cdot}6H_2O$	NMP		ST	900 μm	3200 L	37
$Zn(NO_3)_2{\cdot}6H_2O$	DEF		US + MW	4–15 μm	2473 L	68

B: BET, L: Langmuir.

MOFs with precision in size and morphology has been drawing attention in recent years. However, controlling the shape and size of MOFs is challenging, especially for nano-sized MOFs. The metal salts, reagent concentrations, aromatic co-solvents, pH, temperature and time for the synthesis of MOFs must be carefully selected as small variations in reaction conditions have significant effects on the quality of the product [40,56–60]. Same synthesis conditions for structurally related MOFs may also not give the same crystal size and morphology of MOF products [61]. While MIL-101, ~50 nm, and $Cu_3(BTC)_2$, 10–200 nm, can be produced by MW [62] and US methods [63], respectively, the synthesis of nanosized MOF-5, < 100 nm, by either MW or US have not been reported. Synthesis of nano- and microscale MOF-5 have been summarized in Table 1.

The nucleation and growth are two important processes for nanocrystal formation in a liquid medium. To describe the changes in particles size, LaMer nucleation followed by the Ostwald ripening is often used. The nucleation, the formation of seeds or nuclei, is the first stage of crystallization processes. The short nucleation period of the LaMer mechanism is critical for the synthesis of uniform nanoparticles (NPs). It is mandatory to generate large number of seeds to obtain nanosized uniform, 10–100 nm, MOFs. According to the Ostwald ripening mechanism, the particle growth is based on the changes of nanocrystal solubility as a function of their size [57,69]. During particle growth, seeds with high surface energy may redissolve and release their ligands into solution [57]. Therefore, it is important to generate large number of seeds and prevent them from dissolving to synthesize nanosized uniform MOF-5.

Literature data in Table 1 reveals that the use of TEA as a deprotonating agent is very effective in synthesizing nanosized MOF-5 [32,33,34]. The presence of TEA in precursor solutions during the secondary growth step is found to be critical to prevent the seed crystals from dissolving [70]. The concentration of TEA used in the synthesis of MOF-5 is also important. As TEA concentrations are increased from 0.75 to 1.3 mM, average sizes of MOF-5 are decreased from 2534 to 1499 nm, but the particle size distribution becomes wider [71]. Besides, higher TEA concentrations would also induce the formation of unknown crystals [72]. Mixing speed of TEA into precursor solutions is also important for quick generation of large number of seeds at the early stage of crystallization [34].

Coordination modulation is also effective in nanosized MOF synthesis by employing surfactant, blocking or capping agents [69]. The size and morphology of MOFs can be effectively controlled by addition of surfactants as capping agents [69]. The use of CTAB and C12E4 addition along with TEA leads to the synthesis of nanosized MOF-5 [6,34].

The type of zinc salt (nitrate, acetate, etc.) and its concentration in a starting solution are two important parameters in obtaining smaller particles. In the synthesis of MOF-5, the dilution of terephthalic acid from 50 mM to 0.2 mM (the metal/ligand molar ratio remained 4:3) results in particles with size of < 1 μm [56,59,61,65].

Generally, MOFs are synthesized under solvo- or hydrothermal conditions in the presence of N,N-diethylformamide (DEF) or N,N-dimethylformamide (DMF), which decomposes at elevated temperatures and slowly generates an amine base that deprotonates the linker [73]. *N*-methyl-2-pyrrolidone (NMP) was also usually used as a solvent [59]. MOF-5 materials prepared in the expensive N,N-diethylformamide (DEF) usually results in higher surface areas than that of usually obtained in inexpensive N,N-dimethylformamide (DMF). Low surface area of MOF-5 synthesized in DMF can be attributed to the interpenetrated structure [74] As DMF decompose to dimethylamine, formic acid, hydrogen cyanide, carbon dioxide and carbon monoxide [75], it is possible to obtain some impurities at elevated temperatures. NMP is also a cheap alternative to expensive DEF.

The effect of synthesis routes on nanosized MOFs is also well explored [59]. MOFs with different particle sizes and size distributions can be obtained by different synthesis routes [60,67,69,71]. RT, ST, MW, EC, US and MC synthesis routes are being used for nano/micron-sized MOF synthesis [61,60]. Although nanosized MOFs can be obtained by room temperature and solvothermal synthesis routes with the aid of coordination modulation, they are relatively slow. RT synthesis methods with TEA were used to produce well known and new MOFs such as MOF-5, MOF-74, MOF-177, MOF-199 and IRMOF-0 having the same cubic topology of MOF-5. These well-known MOFs have high storage capacities of hydrogen and methane due to ultrahigh porosity of MOF-5 and MOF-177, one dimensional pore structure of MOF-74, open metal sites of MOF-74 and MOF-199. It was also proposed that these room temperature synthesis methods can be successfully used to prepare Cu(II) and Zn(II) containing MOFs [33]. Huang et al. used the RT direct mixing method with the help of TEA to produce a highly porous nanometer-sized MOF-5, and showed that thermally stable and highly porous MOF-5 nanocrystals (30–150 nm diameter) at RT with high yield (~90%) can be synthesized in short reaction times (~0.5 h) [34]. It was possible to synthesize nanosized, 20–30 nm, MOF-5 with the aid of TEA by RT route [32].

MW and US synthesis routes have drawn attention due to the homogeneous heating, fast kinetics, high phase purity, and high yield rate of products in relatively short time [60]. MW and US techniques have substantial advantages such as fast crystallization, uniform nucleation, easy control of morphology, phase selectivity, decrease in particle size and rapid warming [38,49,50,59,76].

MW assisted synthesis is based on the interaction of electromagnetic waves with polar solvent molecules and/or ions in a solution. The direct interaction of electromagnetic waves with the solution/reactants results in high heating rates and homogeneous heating with high energy efficiency and shorter synthesis time [59]. Smaller crystals can be obtained