Short communication

Linkers and coordinated solvent molecules; the two effective factors on formation of zinc oxide nanoparticles from metal–organic frameworks

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A B S T R A C T

The host and the apohost frameworks of $Zn_2(ndc)_2(DMF)_2 \cdot (H_2O)_4$ (**1**·DMF·H_2O) and $Zn_2(bdc)_2(H_2O)_2 \cdot (DMF)_2$ (**2**·H_2O·DMF), (H_2ndc = 2,6-naphthalene dicarboxylic acid, H_2bdc = benzene-1,4-dicarboxylic acid and DMF = N,N-Dimethylformamide), were synthesized, characterized and subsequently used for preparing of ZnO nanoparticles. The morphology of initial precursors has direct influence on agglomeration tendency of resulting ZnO nanoparticles. Linkers and coordinated solvent molecules are the two effective factors on the formation of zinc oxide nanoparticles from these metal–organic frameworks.

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Metal–organic frameworks (MOFs) are a new category of advanced porous materials undergoing study by many researchers for their vast variety of both novel structures and potentially useful properties arising from them [1]. Their high porosities, tunable structures, and convenient process of introducing both customizable functional groups and unsaturated metal centers have afforded excellent gas sorption and separation ability, catalytic activity, luminescent properties, and more [2,3]. However, the robustness and reactivity of a given framework are largely dependent on its metal–ligand interactions, where the metal-containing clusters are often vulnerable to ligand substitution by water or other nucleophiles, meaning that the frameworks may collapse upon exposure even to moist air [4]. Even though, compared with zeolites, MOFs suffer a major drawback of relatively lower thermal stability, the flexible structure of MOFs contrast to rigid zeolite frameworks, yielding the unique breathing phenomena or gate-opening effect. The pore diameter of MOFs enlarges or shrinks while external stimuli are applied or removed, such as gas molecules, solvents, or pressure [5]. Generally, porous materials are synthesized by slow diffusion, hydrothermal, and solvothermal synthesis methods [6]. In many cases long reaction times, high reaction temperatures and pressures are required. To date a more efficient synthetic approach to MOFs still remains a challenge. Recently, a microwave assisted hydrothermal method is applied to prepare MOFs. This method is a highly efficient route to MOFs, although some reactions finish within several hours, but high reaction temperature and pressure are still needed [7]. Various different methods such as sol–gel [8], hydrothermal [8],

pyrolysis of appropriate precursor [9], usage of copolymer agents [10] and etc. were applied in preparation of ZnO nanomaterials. The conversion of nonporous coordination polymers into metal and metal oxide nanostructures has been used for preparing nanoscale materials [11]. The conversion of the MOF into metal oxide nanoparticles has been also used as a new strategy for preparing nanoscale functional entities [12]. Search in the case of fabrication nanomaterials from metal–organic frameworks, as new precursors, indicates that nanomaterials such as ZnO nano-structures from $[Zn_2(btec)(DMF)_2]_n$ MOF (btec = 1,2,4,5-benzenetetracarboxylate, DMF = N,N-dimethylformamide) [13], ZnO nanomaterials from $Zn_2(1,4\text{-}bdc)_2(dabco)$ MOF (1,4-bdc = 1,4-benzenedicarboxylate, dabco = 1,4-diazabicyclo[2.2.2]octane) [14], TiO_2 nanoparticles from MOFs: MIL-125 and MIL-125-NH_2 [15], CuO nanoparticles from the $[Cu_3(TMA)_2(H_2O)_3]n$ (where TMA is benzene-1,3,5-tricarboxylate) MOF [16], CuO nanostructures from $\{[Cu_2(BDC\text{-}NH_2)_2(dabco)]DMF\cdot3H_2O\}$ MOF [17], $\gamma\text{-}Fe_2O_3$ Nanoparticles from the MIL-100(Fe) MOF [18], Co_3O_4 nanoparticles from $Co_3(NDC)_3(DMF)_4$ MOF (NDC = 2,6-naphthalene-dicarboxylate; DMF = N,N-dimethyl formamide) [19] were prepared, successfully. But none of these works consider the role of guest and coordinated solvent molecules in formation of nanomaterials from MOFs. In this work, we wish to report another potential application of $Zn_2(ndc)_2(DMF)_2 \cdot (H_2O)_4$ (**1**·DMF·H_2O) and $Zn_2(bdc)_2(H_2O)_2 \cdot (DMF)_2$ (**2**·H_2O·DMF) MOFs in preparation of nano ZnO and to consider the role of guest, coordinated solvent molecules and type of the linker ligands on agglomeration of nano ZnO prepared from the host and the apohost (solvent-free) frameworks.

The reaction between 1,4-benzenedicarboxylate (bdc^{2-}) and $Zn(NO_3)_2 \cdot 6H_2O$ in DMF under reflux condition at 150 °C results in

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formation of white precipitate which was dried at room temperature. A Comparison between the XRD patterns simulated from single crystal X-ray data (Tables S1, S2 and Fig. S1a in the SI) and that of the prepared powder (Fig. S1b in the SI), approved the formation of $Zn_2(ndc)_2(DMF)_2 \cdot (H_2O)_4$ (**1** $\cdot DMF \cdot H_2O$). This nanoporous coordination polymer has similar structure to MOF-105 but with guest water molecules (Fig. 1a) [20]. The crystallizing phases possess the zinc 2,6-naphthalene dicarboxylate two-dimensional framework including chlorobenzene has been reported previously as MOF-105 which has 4^4-network topology [21]. Devi et al. have also examined the structural response of a zinc 2,6-naphthalene dicarboxylate framework solid, isostructural with MOF-105, to the inclusion during crystallization of dimethylformamide, benzene, toluene, and p-xylene [22]. The framework is made up of layers that possess cavities, partially filled from above and below by DMF molecules coordinated to zinc atoms from adjacent layers (Fig. 1b). In **1** $\cdot DMF \cdot H_2O$, ndc^{2-} acts as a four donor ligand, connected to four Zn^{II} ions (Fig. 1b). We can consider **ZnO$_6$** coordination sphere around Zn^{II} ion (Fig. 1b). The reaction between 1,4-benzenedicarboxylate (bdc^{2-}) and $Zn(NO_3)_2 \cdot 6H_2O$ in DMF under reflux condition at 150 °C results in formation of white powder which was dried at room temperature. A Comparison between the XRD patterns simulated from single crystal X-ray data (Fig. S2a in the SI) and that of the prepared powder (Fig. S2b in the SI), approved the formation of $[Zn_2(bdc)_2(H_2O)_2 \cdot (DMF)_2]_n$ (**2** $\cdot H_2O \cdot DMF$). Fig. 2a shows primary building block of **2** $\cdot H_2O \cdot DMF$. **2** $\cdot H_2O \cdot DMF$ which is also recognized as MOF-2, is one of the first MOFs exhibiting permanent porosity constructed from 1,4-benzenedicarboxylate (bdc^{2-}). For the first time, it was reported by Yaghi et al. in 1998 [23]. **2** $\cdot H_2O \cdot DMF$ similar to **1** $\cdot DMF \cdot H_2O$ is a 2D (4,4) layered framework consisting of paddle-wheel $Zn_2(COO)_4$ SBUs which are bridged by bdc^{2-} linkers [24]. The difference between **1** $\cdot DMF \cdot H_2O$ and **2** $\cdot H_2O \cdot DMF$ is that we have coordinated DMF and guest water molecules in **1** $\cdot DMF \cdot H_2O$ instead of coordinated water and guest DMF molecules in **2** $\cdot H_2O \cdot DMF$ (Figs. 1 and 2). Thermo gravimetric analyses (TGA) of compound **1** $\cdot DMF \cdot H_2O$ (Fig. 3) shows that loss of the coordinated DMF to zinc and free guest H_2O molecules are occurring between 30 and 200 °C with a mass loss of 24.5% (calcd 28.0%). After removal of coordinated solvent molecules and free guest molecules, the framework is stable up to 400 °C and then starting to decompose and completely collapse around 525 °C. Similar analyses for compound **2** $\cdot H_2O \cdot DMF$ (Fig. 3) indicates that host framework is losing its guest DMF and coordinated H_2O molecules in the temperature range of 60–195 °C. The experimental mass loss of 27.77% is consistent with
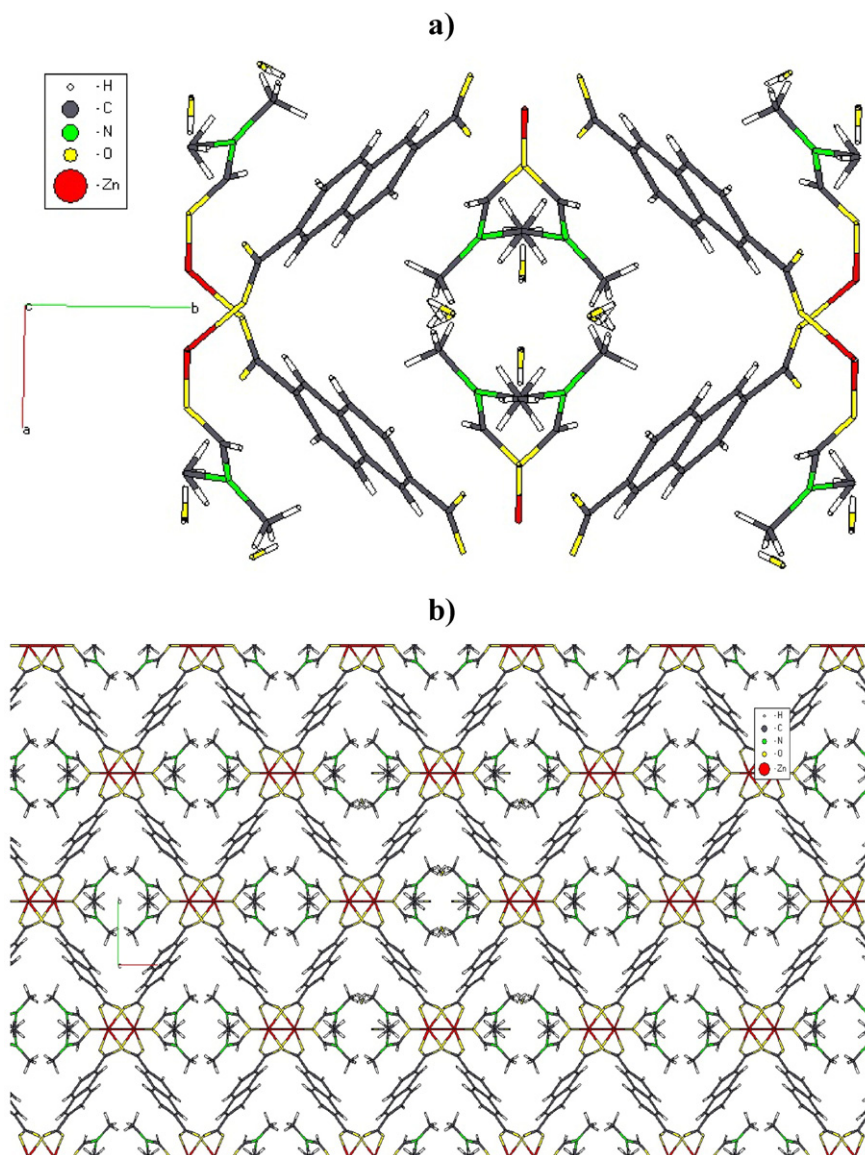
a)

b)

Fig. 1. a) Primary building block unit and b) a fragment of $Zn_2(ndc)_2(DMF)_2 \cdot (H_2O)_4$ (1·DMF·H$_2$O) two-dimensional layer which results in the formation of one-dimensional channels (guest H$_2$O molecules have been omitted for clarity).