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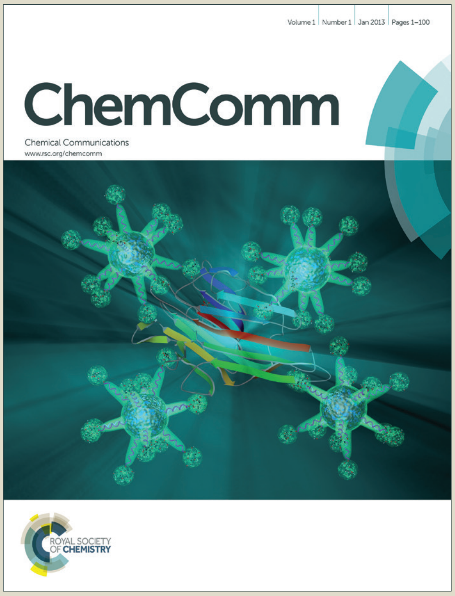

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Rapid room temperature syntheses of zeolitic-imidazolate framework (ZIF) nanocrystals

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Solvent mixture controlled rapid room temperature syntheses for facile access to uniform zeolitic-imidazolate framework nanocrystals (ZIF-7, ZIF-65-Zn and ZIF-71) are reported. ZIF thin film devices for sensing volatile organic chemicals were fabricated by dip-coating nano-ZIF (80-130 nm) suspensions.

Zeolitic imidazolate frameworks (ZIFs) are a sub-family of metal-organic frameworks (MOFs), which exhibit three-dimensional structures constructed by bridging tetrahedral metal ions (e.g., Zn, Co, Cd) with imidazolate linkers.[1] The high chemical and thermal stability of ZIFs with diverse pore size/geometry and surface functionality make them attractive candidates in various application fields including CO_2 capture,[2] separation,[3] chemical sensing,[4] biomedicine[5] and catalysis.[6] Size control of ZIF crystals in the nano-dimension is important for optimized performance and device fabrication.[7] For example, nanocrystals (NCs) can provide fast response to analytes, making them particularly useful in sensing applications.[4] A good access to nano-ZIFs is required to process them into 2D and 3D self-standing or supported structures.[8] However, only very few examples of nano-ZIFs were reported up to date (and mainly based on ZIF-8).[9] In addition, most strategies reported so far on the syntheses of nano-ZIFs (and generally nano-MOFs) need either additives (ammonia, polyvinylpyrrolidone, pyridine or triethylamine) or reaction activation (conventional heating, microwave or ultrasound irradiation).[7a] Therefore, it is quite desirable to develop and to demonstrate the feasibility of a much simplified synthesis method which is generally applicable to a broader range of different nano-ZIFs of various compositions and structures (topologies, functionalized linkers, metal ions). We selected ZIF-7 and ZIF-65-Zn, which are formed by connecting Zn ions through benzimidazole (bIm) and 2-nitroimidazole (nIm), respectively.[2,5] These materials have a sodalite topology with a crystallographic six-membered-ring (6MR) pore opening. Also ZIF-71 was studied, which has a RHO topology, and is constructed by bridging Zn and 4,5-dichloroimidazole (dcIm).[2] Reports on the syntheses of nano-ZIF-7 and nano-ZIF-71 either need long reaction time (48 h),[10] or the yield is quite low (12%),[11] and no report on ZIF-65-Zn NCs has been published up to date.

Herein, we report a general protocol for rapid room temperature syntheses of a series of nano-ZIFs. Generally, it works very well by just mixing a N,N-dimethylformamide (DMF) solution of the zinc source (either $Zn(NO_3)_2 \cdot 6H_2O$ or $Zn(CH_3COO)_2 \cdot 2H_2O$) and a methanol (MeOH) solution of imidazolate linker and subsequent stirring for 30 min. In the case of nano-ZIF-71, samples of 110 mg $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.5 mmol) and 160 mg 4,5-dichloroimidazole (dcIm, 1 mmol) were dissolved in 5 ml DMF and 5 ml methanol, respectively. After complete dissolution, the "Zn-solution" was poured into the "linker-solution". The reaction solution turned milky immediately. After 30 minutes of initial reaction time, the formed particles were separated by centrifugation (7800 rpm, 1.5 h). Work-up was done by washing with methanol (3 repetitions of sonication-centrifugation). A typical yield of ZIF-71 NCs was ~81% based on zinc. Details of syntheses of all nano-ZIF samples are given in ESI.

Figure 1 shows the powder X-ray diffraction (PXRD) patterns of the as-synthesized ZIF-7, ZIF-65-Zn and ZIF-71 in comparison with their corresponding patterns calculated from reported structure data.[2, 5] The PXRD patterns of as-synthesized ZIFs match the corresponding calculated patterns, demonstrating the efficient and phase pure synthesis of these ZIFs. The broadened reflections indicate the formation of NCs which was confirmed by bright field transmission electron microscopy (BFTEM) images (Figure 2). The as-synthesized products exhibit a very narrow size distribution. The crystal size of ZIF-7, ZIF-65-Zn and ZIF-71 are ca. 100, 130 and 90 nm, respectively. We also performed dynamic light scattering (DLS) measurements to investigate their hydrodynamic average size and uniformity. The DLS plots reveal that the average size of ZIF-7, ZIF-65-Zn and ZIF-71 is 112, 125 and 83 nm, respectively, which nicely match the observation from TEM images. The selected three ZIFs have been previously studied as materials for supported membranes and mixed matrix membranes (MMM) for gas separation.[10, 12] In the case of fabrication uniform and low defect supported ZIF membranes, the seeded growth approach requires uniform NCs as seeds.[13] In order to fabricate high quality MMM with ZIFs as fillers, again NCs are also required to avoid the polymer-particle interfacial defects and enhance the polymer-filler interfacial contact.[14] In addition, ZIF-65-Zn has been used for controlled

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light-induced release of biologically relevant molecules,[5] in which NCs could show remarkable intrinsic properties.[15]

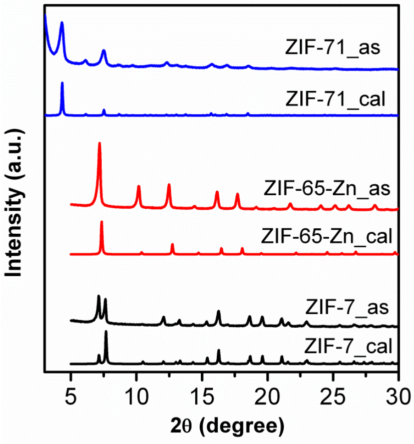

Figure 1 PXRD patterns of as-synthesized ZIF-7, ZIF-65-Zn and ZIF-71 in comparison with corresponding calculated patterns.

The synthesis medium turned out to play an important role in the coordination chemistry system and the solvent effect on the formation of ZIF NCs was investigated. As shown in Table S1, employing pure DMF as solvent, nano-ZIF-7 and ZIF-71 can be formed as well. However, then, ZIF-7 NCs are very slowly formed over a period of 48h,[10] and the yield of ZIF-71 (42%) is significantly lower as compared to the mixed DMF/MeOH system. Furthermore, the use of pure DMF leads to crystal size of ZIF-65-Zn in micrometer region. Likewise, in pure MeOH, only ZIF-65-Zn can be formed as micro sized crystals. We also investigated the formation of nano-ZIFs using other zinc sources (Table S2) based on the DMF/methanol protocol: adding DMF solution of $Zn(NO_3)_2{\cdot}6H_2O$ instead of $Zn(CH_3COO)_2{\cdot}2H_2O$ into methanol solutions of nIm and dcIm, which resulted in clear solution at room temperature. ZIF-7 with *larger* crystal size can be formed by employing $Zn(CH_3COO)_2{\cdot}2H_2O$ instead of $Zn(NO_3)_2{\cdot}6H_2O$ (Figure S7 and S8). We speculate that the mechanism of successful NCs growth depends on the solvation of the respective educts combined with modulator effects of the counter ions (e.g NO_3^-. vs. CH_3COO^-). Both should determine the coordination chemistry at the surface of the growing ZIF crystals. The growth kinetics modulated by of solvent and metal source require further detailed investigations to fully understand the mechanisms, which are currently in progress (similar to our previous work on modulated nano-MOF growth).[9a,16]

The infrared (IR) spectra of synthesized ZIFs (Figure 3a) confirm that the chemical bond structures are consistent with that reported for the corresponding ZIFs.[5, 12b, 12e] The absorption band at 740 cm^{-1} in ZIF-7 spectrum is associated with the typical out-of-plane C-H bending vibration of ortho-disubstitued benzene which is contributed from bIm ligand. The spectrum of ZIF-65-Zn possesses the typical symmetric and asymmetric stretching vibration of nitro-group at 1350 cm^{-1} and 1520 cm^{-1}, respectively. The medium band at 545 cm^{-1} in ZIF-71 spectrum can be attributed to the C-Cl stretching vibration of dcIm ligand. The thermal gravimetric analysis (TGA) curves of these ZIFs (Figure S5 and Figure 3b) both on as-synthesized and activated samples confirm the thermal stability of them. ZIF-7, ZIF-65-Zn and ZIF-71 are thermal stable as high as ca. 350, 420 and 620 °C, respectively. Moreover, the observed flat plateaus before the decomposition temperature indicate that the entire guest molecules were removed completely after activation.

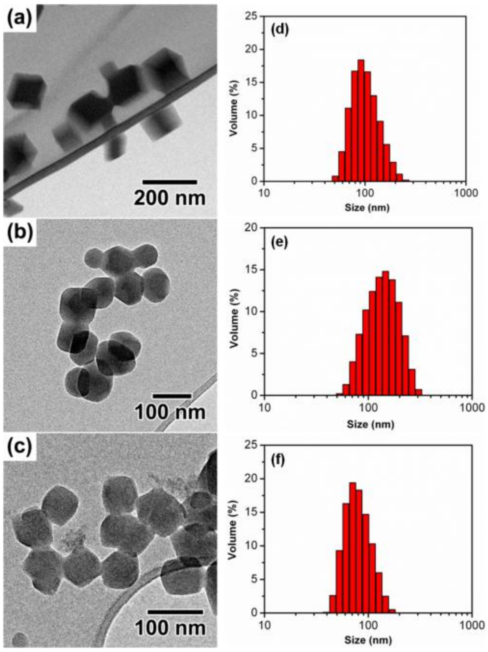

Figure 2 BFTEM images of nanosized ZIF-7 (a), ZIF-65-Zn(b), ZIF-71(c) and particle size distribution of ZIF-7 (d), ZIF-65-Zn(e), ZIF-71(f) by DLS measurements at room temperature.

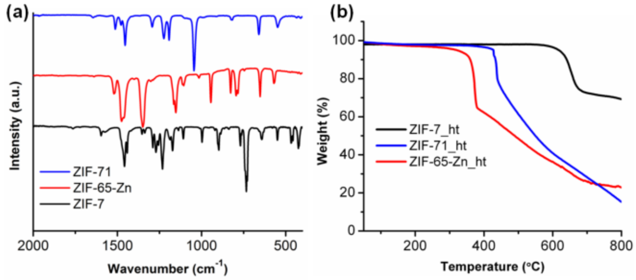

Figure 3 IR spectra (a) and TGA curves (b) of activated ZIF-7, ZIF-65-Zn and ZIF-71.

Due to the structure flexibility of ZIF-7,[17] the structure transformed from a large pore phase to a narrow pore phase after activation, resulting in no adsorption of N_2 on ZIF-7. Therefore, the porosity of ZIF-7 is confirmed by CO_2 adsorption at 195K shown in Figure 4a, which is similar to the previous report.[3] N_2 physisorption on ZIF-71 (Figure 4b) shows a typical type I isotherm with a small hysteresis at high pressure, which may arises from the large external surface area as well as the inter-particle mesopores. Brunauer-Emmett-Teller (BET) surface area (1089 m^2/g) is slightly higher than previous reported data (970 m^2/g).[11] Interestingly, ZIF-65-Zn (Figure 4b) exhibits a stepwise N_2 sorption isotherm which does not correspond to one of the six types of the current IUPAC classification of physisorption isotherms.[18] The increase of N_2 uptake at low pressure indicates the presence of micropores accessible to N_2 molecules. After a remarkable flat plateau, a second step of N_2 adsorption is observed at the pressure of ~30 kpa, which is probably because of the gate-opening process induced by the high pressure of N_2.[19] Although we cannot solve the crystal structure during the sorption process at this moment, the high flexibility of ZIF-65-Zn can be confirmed by this isotherm together with the XRD studies (Figure S2).

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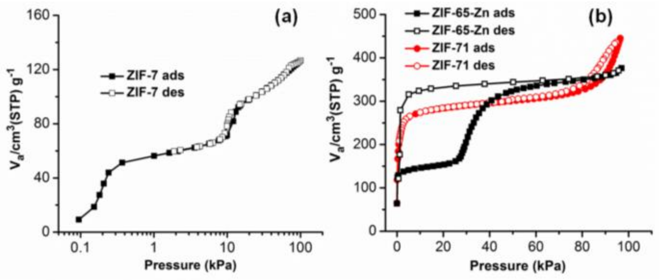

Figure 4 (a), adsorption-desorption isotherms of CO_2 on ZIF-7 at 195K; (b), adsorption-desorption isotherms of N_2 on ZIF-65-Zn (black) and ZIF-71 (red) at 77K.x

The described nano-ZIF suspensions were used for thin film fabrication on quartz crystal microbalance (QCM) substrates by the rapid dip-coating deposition technique. The obtained ZIF/QCM devices were used to detect methanol vapor on an environment controlled QCM equipment.[20] Methanol adsorption isotherms at 293K are shown in Figure 5. Due to the high hydrophobicity of ZIF-7 and ZIF-71, methanol is not adsorbed (detected) at low relative pressure. However, ZIF-65-Zn can readily adsorb methanol even at very low concentration because of the existence of polar nitro-group in the framework.

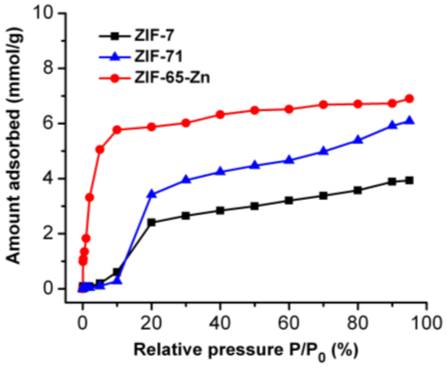

Figure 5 Vapor phase adsorption isotherms of methanol on ZIF-7, ZIF-65-Zn and ZIF-71coated QCM substrates at 293K. The saturated vapor pressure P_0 of methanol at 293K is 12.98kPa.

In summary, we reported here a uniquely facile and generally applicable synthesis protocol for the rapid syntheses of ZIF-7, ZIF-65-Zn and ZIF-71 NCs with narrow particle size distribution. Interestingly, the choice of the solvent mixture and the Zn-source allows control of particle formation and growth. Structural flexibility of ZIF-7 and ZIF-65-Zn was observed based on the XRD and sorption studies. Moreover, the developed rapid formation of NCs suspensions was applied to fabricate ZIF/QCM devices for the detection of volatile organics. Considering the various interesting properties of ZIFs together with the great advantages of NCs, we expect that this simple method can facilitate fabrication of ZIFs devices, based on thin films and membranes, for applications in separation, biomedicine, chemical sensors and heterogeneous catalysis.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [General methods, synthetic procedures and supplementary figures]. See DOI: 10.1039/c000000x/

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Rapid room temperature syntheses of zeolitic-imidazolate frameworks (ZIFs) nanocryatals

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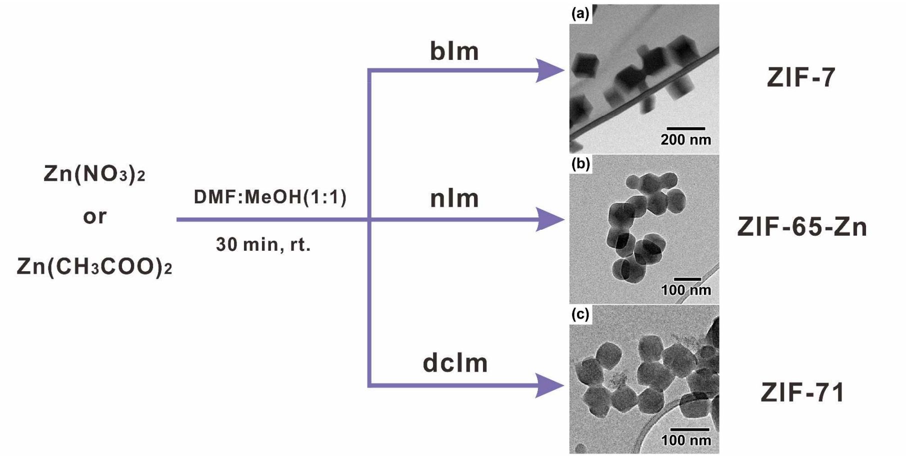
Here we report a simple solvent mixture controlled rapid room temperature syntheses for facile access to uniform zeolitic-imidazolate framework (ZIF) nanocrystals.



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