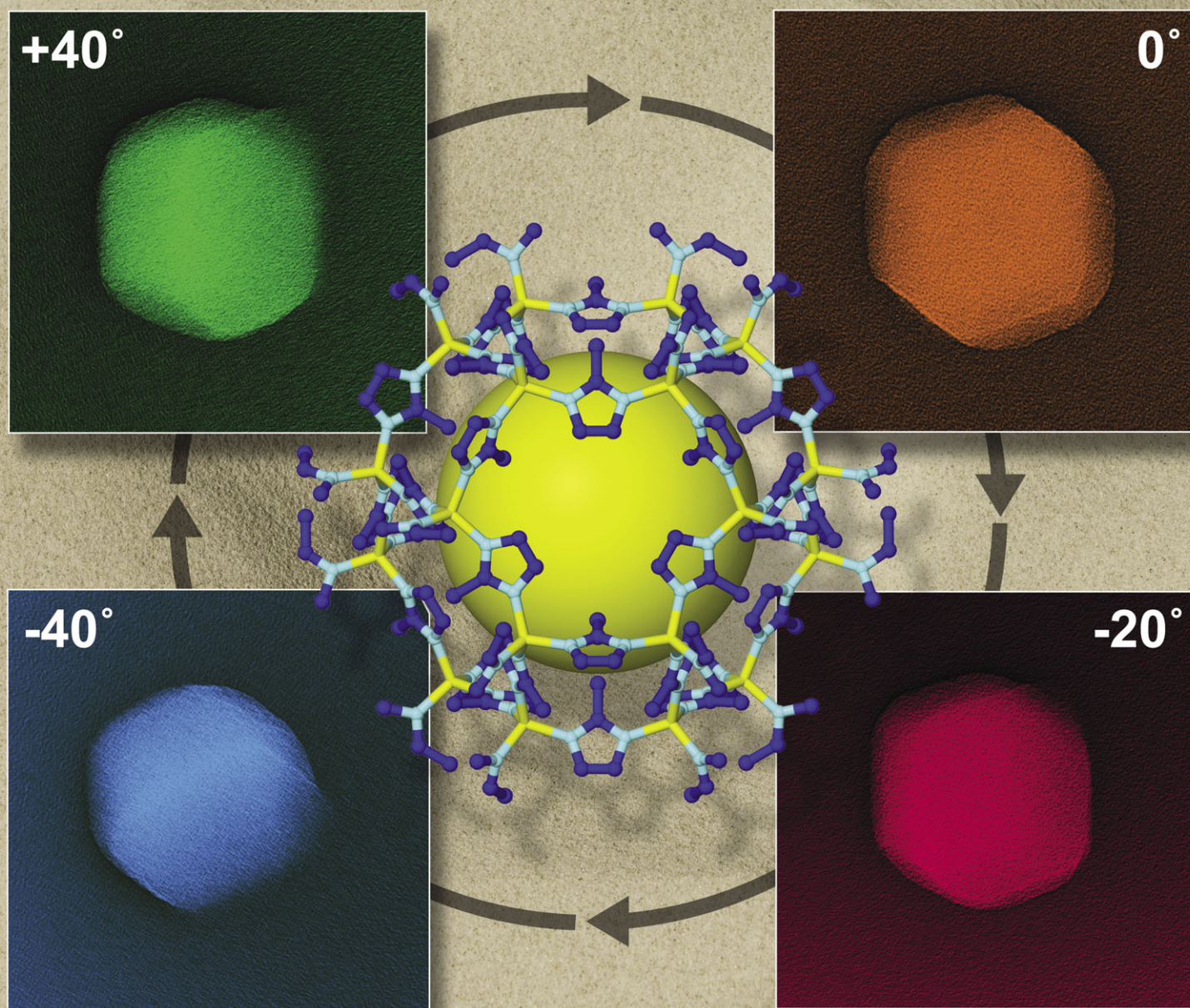


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FEATURE ARTICLE

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Synthesis and properties of nano zeolitic imidazolate frameworks†

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Nanosized zeolitic imidazolate frameworks [nZIF-8] with excellent chemical and thermal stability have been synthesized at room temperature by simple mixing of 2-methylimidazole and zinc nitrate hexahydrate in methanol/1% high molecular weight poly(diallyldimethylammonium chloride) solution for 24 h.

Porous zeolitic imidazolate frameworks [ZIFs],¹ a new class of metal organic frameworks (MOF's) that have exceptional chemical and thermal stability, have attracted considerable attention over the past few years for energy and storage applications.² Yaghi and others systematically explored the rich zeolitic chemistry of ZIFs with tetrahedral networks and have demonstrated the selective capture of carbon dioxide from several different gas mixtures at room temperature.³ Architecturally, ZIFs are obtained by replacing the Si, O atoms in zeolites with metals (M) and imidazoles. Nanoparticles exhibit unique properties that are distinct from both molecules and bulk solids.⁴ The use of engineered nanoparticles has increased exponentially in the last 5 years due to unique physical, chemical and optical properties and tunable absorption and emission properties with particle size and shape with characteristic high surface to volume ratio. Thus, reducing the ZIF's size to nanoscale might facilitate large surface area with increased uptake and selectivity.

Although, there are robust and facile synthetic methods for production of inorganic and polymeric nanoparticles with precise control over the particle size and shape, very limited attention has been devoted to the development of fine tuned nanoscale MOF's.⁵ In recent years, there have been few reports on the synthesis of nanoscale carboxylate-MOFs.⁶ Synthetic methods include simple mixing, microwave processing and application of polymer stabilizers.⁷ Herein, we report the first shape-selective synthesis of porous zeolitic imidazolate frameworks [ZIFs] protected by high molecular weight poly(diallyldimethylammonium chloride). To our knowledge this is the first shape selective synthesis of nanosized ZIF (nZIF) (see ESI†).

Hexagonally shaped nZIF-8 has been synthesized *via* the simple mixing of zinc nitrate hexahydrate (50.00 mg, 0.17 m) with 2-methyl imidazole (91.53 mg, 1.34) at room temperature in the presence of methanol (10 ML) and 1% high molecular weight poly(diallyldimethylammonium chloride) solution (average M_w 400 000–500 000) (10 ML) upon continuous stirring of the reaction mixture for 24 h. Fig. 1 illustrates the TEM and SEM images of the hexagonally shaped nZIF-8 at different magnifications. Low magnification TEM and SEM images clearly demonstrate the formation of uniform nanoparticles with narrow size distribution. To determine the thickness of the hexagonal nanoparticles (in 3D), we performed electron tomography (tilting) experiments to obtain a 3-dimensional image for determining the thickness of the hexagonal nZIF-8 (Fig. 2). Transmission electron microscopy (TEM) and tilting experiments revealed that poly(diallyldimethylammonium chloride) stabilized nZIF-8 has an average diameter of 57 ± 7 nm and a thickness of 42 nm (Fig. 2 and see ESI†). It is very important to note that thermal annealing or resident templates were not used to obtain hexagonally shaped nZIF-8. Several experiments were performed in order to understand the role of the polymer used and the reaction conditions on the formation of hexagonal

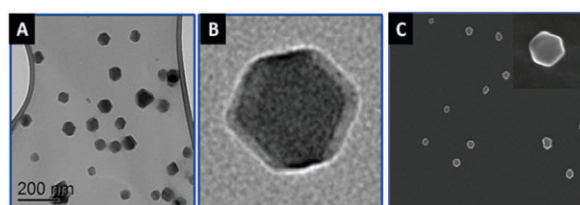


Fig. 1 (A and B) TEM and enlarged TEM image of nZIF-8, (C) SEM image of nZIF-8.

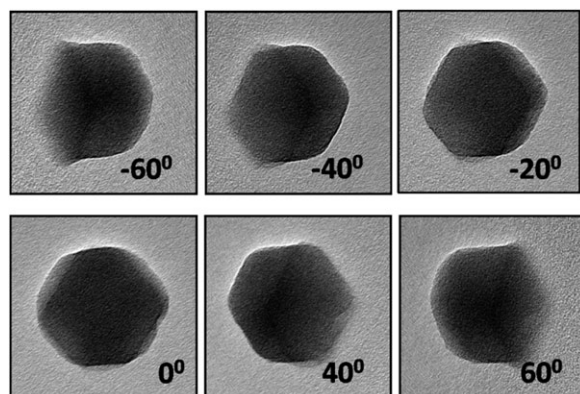


Fig. 2 Tilting experiments using transmission electron microscopy suggest the average size of the nanoparticles.

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shaped nanoparticles. In one experiment, the concentration of the polymer (poly(diallyldimethylammonium chloride)) was varied keeping the molar ratio of zinc nitrate hexahydrate and 2-methyl imidazole constant; in another experiment the concentration of the polymer was kept constant and the molar ratio of the reactants was varied. In both cases near hexagonally shaped particles were obtained. However, Wiebcke *et al.* have recently demonstrated the formation of non-uniform agglomerates in the absence of polymer.⁸ Similarly, changing the polymer to polycationic electrolyte solutions such as a mixture (1 : 1; 10 mL) of methanol and chitosan (1%), poly(ethyleneimine) PEI (1%), poly(allylamine hydrochloride) PAH and low molecular weight (poly(diallyldimethylammonium chloride) average $M_w < 100\,000$) and 2% polyvinyl pyrrolidone (PVP) did not result in the formation of hexagonally shaped nanoparticles. Therefore, the poly(diallyldimethylammonium chloride) has played a critical role in controlling the morphology of the nanoparticles during the reaction. Moreover, Zheng *et al.* demonstrated that the shape of the nanoparticles could induce texture in self-assembled superlattice arrays.⁹ Shape-controlled synthesis of nanoparticles that drives controlled self-assembly of the particles has implications to device development in the optics and magnetics industries. Therefore the method developed for obtaining hexagonally shaped nZIF-8 also finds applications requiring molecular or ionic sequestration/or in optical industry. In this regard, nZIF-8 was further characterized to understand the porosity and the gas uptake properties.

In order to confirm the porosity and crystalline nature of the nZIF-8 powder X-ray and (Fig. 3) electron diffraction experiments were performed (see ESI†). Identical PXRD patterns of experimental nZIF-8 and ZIF-8 (bulk) confirm identical structural topology (Fig. 3).^{3a} Similarly, electron diffraction experiments suggest the crystalline nature of the nZIF-8 (see ESI†). Thermal analysis of nZIF-8 shows 2% of weight loss between room temperature and 400 °C due to the loss of residual solvent molecules (see ESI†). Thus nZIF-8 exhibits considerable thermal stability as compared to the nanoscale ZIF-8 obtained by Wiebcke and co-workers (stable up to 200 °C).⁸ Microporosity of nZIF-8 was demonstrated by BET sorption isotherm measurements performed at 77 K using liquid nitrogen.¹⁰ The nZIF-8 exhibits a typical type I isotherm with 1264 m² g⁻¹ of surface area with a micropore volume of 0.51 cm³ g⁻¹ that have been estimated for the evacuated material (Fig. 4). It should be noted that the surface

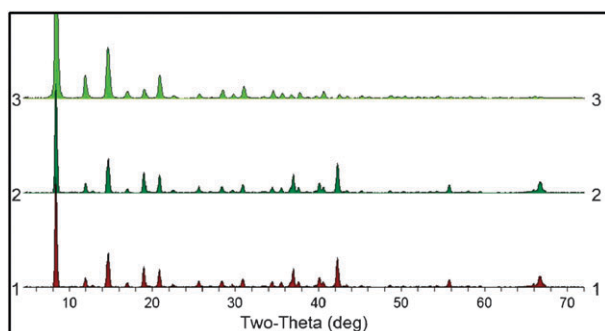


Fig. 3 Experimental PXRD patterns of ZIF-8 (1) and nZIF-8 as synthesized (2) and after activation (3).

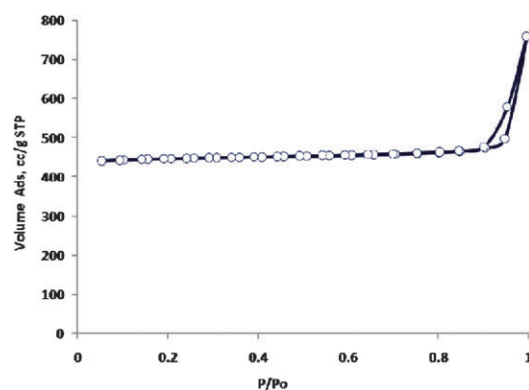


Fig. 4 BET surface area analysis of nZIF-8 using liquid nitrogen and 77 K. Type I isotherm with microporous nature.

area of micro and nanoscale ZIF-8 obtained by Huang *et al.* (BET surface area: 1030 m² g⁻¹)¹¹ and Wiebcke *et al.* (BET surface area: 962 m² g⁻¹, micropore volume: 0.36 cm³ g⁻¹)⁸ using two different synthetic protocols are in close agreement with the values we have obtained. However, the surface area of nZIF-8 is lower than the ZIF-8 obtained by Yaghi and co-workers (BET surface area: 1630 m² g⁻¹, micropore volume: 0.64 cm³ g⁻¹).^{3a} It therefore appears that some residual species is indeed present in the pores of the nZIF-8 material and the possibility of using porous nZIF-8 as a reservoir for various gases.

Therefore, gas sorption experiments were performed on nZIF-8 using HPVA-100 volumetric device at room temperature and high pressure. A known amount of nZIF-8 was placed in a sample chamber and activated at high temperature (200 °C) over night under vacuum. Fig. 5 shows the reversible uptake and release of CO₂ in nZIF-8 with 35% of weight capacity at 30 bar. At this pressure (30 bar) the calculated CO₂ weight percentage in nZIF-8 was found to be 7.9 mmol g⁻¹, which is comparable to the bulk ZIF-8, MOF's, ZIF's, zeolites and calixarene based sorbents reported by us and others.¹² The absence of hysteresis during desorption of CO₂ is not surprising and it has been found to be very common for materials with pore size ranging from 5 to 20 Å. The measurements were repeated several times by evacuating the sample and pressurizing with CO₂ again. The same weight percentage was obtained within ±5%. Similar gas sorption experiments nZIF-8 were explored further with respect to other gases including nitrogen

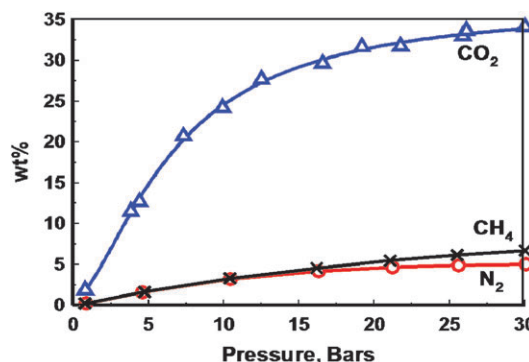


Fig. 5 CO₂, CH₄ and nitrogen adsorption isotherms of nZIF-8. Notice the selectivity of CO₂ over N₂ and methane.

and methane. At high pressure nZIF-8 appeared to sorb very small quantities of nitrogen (<5%), and methane (5 wt%, Fig. 5). These results suggest that nZIF-8 has higher uptake of CO₂ but also can differentiate among different gases. As a result potential industrial applications would seem to abound. In order to confirm the size and shape of the nanoparticles after gas sorption experiments, the resulting solid was redispersed in solution and SEM/TEM measurements were performed. Results indicate well dispersed hexagonally shaped nanoparticles (see ESI†).

In conclusion, for the first time we report the shape selective synthesis of nanosized hexagonally shaped zeolitic frameworks and their sorption properties. Further studies will be focused on the role of stabilizers on the formation of these hexagonally shaped nanoparticles as well as on the effect on particle size. Studies pertaining to the gas sorption properties of nanosized frameworks are in progress.

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