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High adsorption capacity of two Zn-based metal–organic frameworks by ultrasound assisted synthesis

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ABSTRACT

Micro- and nano-rods and plates of two 3D, porous Zn(II)-based metal–organic frameworks $[Zn(oba)(4\text{-bpdh})_{0.5}]_n\cdot(DMF)_{1.5}$ (TMU-5) and $[Zn(oba)(4\text{-bpmb})_{0.5}]_n\cdot(DMF)_{1.5}$ (TMU-6) were prepared by sonochemical process and characterized by scanning electron microscopy, X-ray powder diffraction and IR spectroscopy. These MOFs were synthesized using a non-linear dicarboxylate (H_2oba = 4, 4-oxybisbenzoic acid) and two linear N-donor (4-bpdh = 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene and 4-bpmb = N^1,N^4-bis((pyridin-4-yl)methylene)benzene-1,4-diamine) ligands by ultrasonic irradiation. Sonication time and concentration of initial reagents influencing size and morphology of nano-structured MOFs, were also studied. Calcination of TMU-5 and TMU-6 at 550 °C under air atmosphere yields ZnO nanoparticles. TMU-5 and TMU-6 exhibited maximum percent adsorption of 96.2% and 92.8% of 100 ppm rhodamine B dye, respectively, which obeys first order reaction kinetics.

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1. Introduction

The global warning effect is believed to be associated with increasing concentrations of hazardous materials in water and atmosphere. Among pollutants, industry dyes can lead to serious and devastating environmental and health problems. Several advanced technologies for the removal of various pollutants have been studied, among which adsorption over nano structure materials appears to be very attractive [1–4]. In the future, it is hoped to extend nano scale adsorbent application to removal of pollutants from water.

Porous coordination polymers (PCPs) or three-dimensional (3D) metal–organic frameworks (MOFs) are a new class of porous materials which are highly attractive because of their applications such as gas storage and separation, ion exchange, sensing, catalysis, and drug delivery [5–13]. Desired MOFs can be synthesized by choosing appropriate organic ligands and inorganic secondary building units (SBUs) [14].

Over the past decade, high intensity ultrasound for nanomaterials synthesis has been widely used because ultrasound offers a rapid, mild, cost-effective, reproducible, and environmentally friendly way for preparation of nano/microscale coordination complex compounds with novel morphologies and unique properties [15–19].

In the research area of sonochemistry the process of acoustic cavitation created by powerful ultrasound radiation (20 kHz–10 MHz) causes molecules to undergo chemical reactions [20]. Cavitation involves formation, growth, and instantaneously implosive collapse of bubbles in a liquid, which generates local hot spots having temperatures up to 5000 °C, 500 atm pressures within very short lifetimes of a few microseconds [21–23]. As a result, these extreme conditions can enhance the formation of nano-sized structures, mostly via an increase of crystallization nuclei [24].

ZnO is a well-known n-type semiconductor material with a wide band gap energy of 3.37 eV [25], and is an excellent material for potential applications including solar cells, luminescent materials, transparent conductors and gas sensors [26–30]. Up until now, various synthetic methods have been developed to produce zinc oxide nanostructures [31,32]. Thermal decomposition of MOFs under various conditions has been widely studied for the preparation of ZnO nanostructures with different sizes and morphologies [12].

In this work, two Zn(II) metal–organic frameworks have been synthesized by sonochemical method and the effects of ultrasonic irradiation time and concentration of initial reagents on shape and size of particles were investigated. Adsorption capacity of these MOFs has been shown in presence of rhodamine B dye. Also, ZnO nanoparticles have been obtained via calcination of these two MOFs at 550 °C.

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Table 1
Experimental details for synthesis of nano TMU-5 and TMU-6.

Samples name	Molar ratio (oba:N-donor:Zn(OAc)$_2$) mmol in 20 ml DMF	Concentration [oba]/[N-donor]/[Zn(OAc)$_2$] (M)	Time (min)	Elemental analysis, found (%)*	Yield (%)	Morphology
TMU-5						
TMU-5A	0.5:0.25:0.5	[0.025]/[0.0125]/[0.025]	30	C: 55.8, H: 4.6, N: 9.3	72	Micro-sphere contain nanorod
TMU-5B	0.5:0.25:0.5	[0.025]/[0.0125]/[0.025]	60	C: 55.7, H: 4.7, N: 9.2	78	Micro-sphere contain nanorod
TMU-5C	0.5:0.25:0.5	[0.025]/[0.0125]/[0.025]	90	C: 55.4, H: 4.5, N: 9.2	80	Nanorod
TMU-5D	1:0.5:1	[0.05]/[0.025]/[0.05]	90	C: 55.5, H: 4.9, N: 9.6	82	Non-uniform Nanorod
TMU-5E	0.25:0.125:0.25	[0.0125]/[0.0063]/[0.0125]	90	C: 55.3, H: 4.5, N: 9.3	79	Nanorod
TMU-5F	0.5:0.25:0.5	[0.025]/[0.0125]/[0.025], TEA = 3 ml, pH = 7	90	C: 55.9, H: 4.7, N: 9.4	54	Nanorod
TMU-6						
TMU-6A	0.5:0.25:0.5	[0.025]/[0.0125]/[0.025]	30	C: 57.9, H: 4.3, N: 8.1	87	Microrod
TMU-6B	0.5:0.25:0.5	[0.025]/[0.0125]/[0.025]	60	C: 57.6, H: 4.4, N: 8.3	75	Nanoplate
TMU-6C	0.5:0.25:0.5	[0.025]/[0.0125]/[0.025]	90	C: 57.8, H: 4.2, N: 8.4	80	Microplate
TMU-6D	1:0.5:1	[0.05]/[0.025]/[0.05]	60	C: 57.7, H: 4.4, N: 8.2	84	Non-uniform nanoplate
TMU-6E	0.25:0.125:0.25	[0.0125]/[0.0063]/[0.0125]	60	C: 57.5, H: 4.5, N: 8.3	84	Nanoplate
TMU-6F	0.5:0.25:0.5	[0.025]/[0.0125]/[0.025], TEA = 3 ml, pH = 7	30	C: 57.8, H: 4.5, N: 8.5	54	Nanorod

* Calculated for TMU-5, $[Zn(C_{14}O_5H_8)(C_{14}H_{14}N_4)_{0.5}]\cdot(C_3NOH_7)_{1.5}$: C: 55.6, H: 4.7, N: 8.9 and for TMU-6, $[Zn(C_{14}O_5H_8)(C_{18}H_{14}N_4)_{0.5}]\cdot(C_3NOH_7)_{1.5}$: C: 57.6, H: 4.6, N: 8.5.

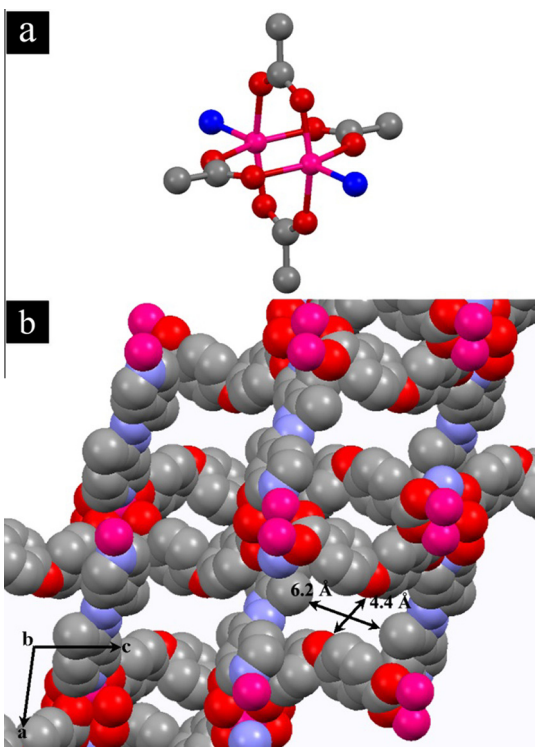

Fig. 1. (a) Representation of the Zn_2 paddlewheel unit within TMU-5. (b) Spacefill representation shows aperture size of pores. Hydrogen atoms and DMF molecules are omitted for clarity. (O: red; N: blue; C: grey; and Zn: pink). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

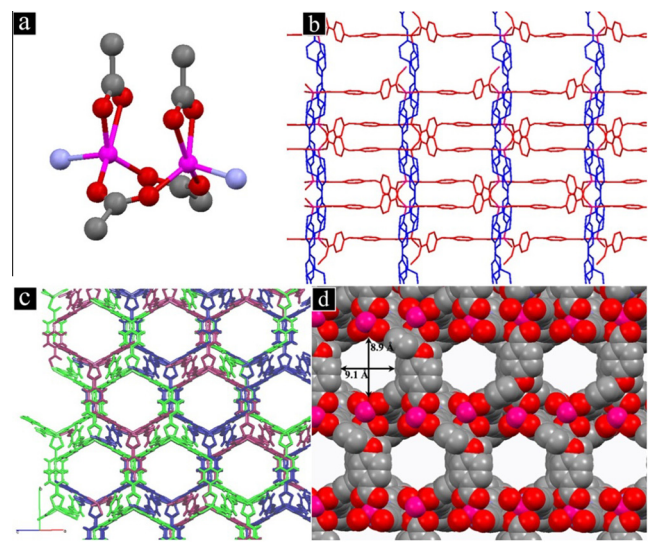

Fig. 2. Views of TMU-6. (a) Binuclear Zn_2 cluster (O: red; N: blue; C: grey; and Zn: pink). (b) Layers of Zn(II)-oba (in red) pillared by 4-bpmb (in blue), (c) Representation showing the pore channels and that the network is threefold interpenetrated (in purple, green and blue). (d) Spacefill representation shows aperture size of pores. Hydrogen atoms and DMF molecules are omitted for clarity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2. Experimental

2.1. Materials and physical techniques

All reagents for the synthesis and analysis were commercially available from Aldrich and Merck Company and used as received. The ligands 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene (4-bpdh) and N^1,N^4-bis((pyridin-4-yl)methylene)benzene-1,4-diamine (4-bpmb) were synthesized according to previously reported methods [33]. Melting points were measured on an Electrothermal 9100 apparatus. IR spectra were recorded using Thermo Nicolet IR 100 FT-IR.

Ultrasonic generation was carried out in an ultrasonic bath SONICA-2200 EP (frequency of 40 kHz). The samples were characterized with a field emission scanning electron microscope (FE-SEM) Philips XL30, TESCAN MIRA (Czech) and ZEISS SIGMA VP (Germany) with gold coating. X-ray powder diffraction (XRD) measurements were performed using a Philips X'pert diffractometer with mono chromated Cu-K_α radiation. Elemental analyses were collected on a CHNS Thermo Scientific Flash 2000 elemental analyzer.

2.1.1. Synthesis of TMU-5 and TMU-6 nanostructure

Ultrasonic syntheses of TMU-5 and TMU-6 were carried out in an ultrasonic bath at ambient temperature and atmospheric

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