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# Ultrasonic synthesis of a 3D Ni(II) Metal–organic framework at ambient temperature and pressure: New precursor for synthesis of nickel(II) oxide nano-particles

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# 1. Introduction

Metal-organic frameworks (MOFs) are a relatively new class of hybrid nano-porous materials which have attracted considerable attention in recent years. This is due to the variety of characteristics they have which includes, large surface areas, low densities, regular pore sizes, and tunable structure properties that make them promising candidates in several applications. The applications consist of gas storage, heterogeneous catalysis, selective guest adsorption, and sensor technology [1-4]. Compared with well-known nano-porous materials such as carbons and inorganic zeolites, these porous MOFs composed of metal ions or metal clusters as nodes and organic ligands as linkers, have the advantage of tailoring physical and chemical characteristics during their synthesis. Usually, these porous materials are synthesized by slow diffusion techniques, hydrothermal, and solvothermal synthesis methods [5–7]. In these techniques generally long reaction time, high reaction temperatures and pressures are required.

In the past two decades, sonochemical methods have been widely used in the syntheses of MOFs [8–10] and organic materials [11]. Sonochemistry is the research area in which molecules undergo a reaction due to the application of powerful ultrasound radiation (20 kHz–10 MHz) [12]. Compared with traditional techniques, sonochemical method is more efficient and easily controlled and this has been widely used to fabricate nano-sized structures of a variety of compounds [13]. In the present work, a nickel(II) metal–

# ABSTRACT

Nano-particles of a Ni(II) metal–organic framework (MOF) with cubic building blocks and 1D open channels, i.e. { $[Na_{16}(Ni_8L_{12})(H_2O)_{20}(H_3O)_4](CH_3CN)(H_2O)_{18.5}_{\infty}(1)(H_3L = 4,5-imidazoledicarboxylic acid) were synthesized by using ultrasonic method and characterized by scanning electron microscopy (SEM), X-ray powder diffraction (XRD), IR spectroscopy and elemental analysis. The effect of concentration of starting reagents on size and morphology of nano-structured compound$ **1**has also been investigated. Calcination of the bulk powder and nano-sized compound**1**at 700 °C under air atmosphere yields NiO nano-particles. Results show that the size and morphology of the NiO nano-particles are dependent upon the particles size of compound**1**.

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organic framework (MOF) with ligand  $H_3L$ , i.e. {[Na<sub>16</sub>(Ni<sub>8</sub>L<sub>12</sub>)-(H<sub>2</sub>O)<sub>20</sub>(H<sub>3</sub>O)<sub>4</sub>](CH<sub>3</sub>CN)(H<sub>2</sub>O)<sub>18.5</sub>}<sub>∞</sub> (**1**) (H<sub>3</sub>L = 4,5-imidazoledicarboxylic acid) [14], were synthesized under ultrasonic irradiation and the effect of concentration of initial reagents on size and morphology of nano-structured compound **1** has been investigated.

Nano-structured nickel(II) oxide is a p-type semiconductor with a stable, wide band gap (3.6-4.0 eV) [15]. Important applications of nano-sized NiO include preparation of cathode materials for alkaline batteries [16], electrochemical capacitors [17], smart windows [18], active layers for gas sensors [19], and catalytic systems [20]. Different methods have been developed to synthesize of NiO nanocrystals, such as thermal decomposition [21], sputtering [22], electrodeposition [23], AAM template synthesis [24], and sol-gel techniques [25]. Also, the solid-state decomposition method has already been reported which involves thermal decomposition of MOFs in dry condition under air atmosphere [26]. In this paper nickel(II) oxide nano-particles were obtained by direct thermal decomposition of compound **1** at 700 °C. The preparation of metal oxide nanostructures through thermal decomposition of complexes opens a new view for chemists since there are many advantages in it such as: control of process conditions, particle size, particle crystal structure, and purity.

# 2. Experimental

## 2.1. Materials and physical techniques

All reagents for the synthesis and analysis were commercially available from Merck company and used as received. Doubly-





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Scheme 1. Materials produced and synthetic methods.



Fig. 1. IR spectra of (a) nano-particles of compound 1 produced by sonochemical method in concentration of initial reagents [Ni<sup>2+</sup>] = 0.025 M, [HL<sup>2-</sup>] = 0.0375 M and (b) bulk powder of compound 1.

distilled water was used to prepare aqueous solutions. Ultrasonic generators were carried out on a SONICA-2200 EP, input: 50–60 Hz/305 W. Melting points were measured on an Electrothermal 9100 apparatus. Microanalyses were carried out using a Heraeus CHN-O-Rapid analyzer. IR spectra were recorded on a SHIMADZU-IR460 spectrometer in a KBr matrix. The simulated XRD powder pattern based on single crystal data were prepared using MERCURY software [27]. X-ray powder diffraction (XRD) measurements were performed using a Philips X'pert diffractometer with monochromated Co k $\alpha$  radiation ( $\lambda$  = 1.78897 Å). The samples were characterized by a scanning electron microscope (SEM) (Philips XL 30 and S-4160) with gold coating.

# 2.2. Synthesis of {[ $Na_{16}(Ni_8L_{12})(H_2O)_{20}(H_3O)_4$ ]( $CH_3CN$ )( $H_2O$ )<sub>18.5</sub>}<sub> $\infty$ </sub> (**1**)

The compound **1** was prepared according to reported method [14]. 1.5 mmol (234 mg) 4,5-imidazoledicarboxylic acid  $(H_3L)$ 

was dissolved in 10 ml sub-stoichiometric NaOH aqueous solution then solution of 1 mmol (291 mg) Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in 10 ml acetonitrile was added to the mixture and was refluxed for 2 h. The obtained green precipitates were filtered off, washed with water and then dried at room temperature. (57.4% yield), m.p. > 300 °C (*Anal.* Calc. for C<sub>15.50</sub>H<sub>26</sub>N<sub>6.25</sub>Na<sub>4</sub>Ni<sub>2</sub>O<sub>22.625</sub>: C, 21.35; H, 2.98; N, 10.04. Found: C, 21.47; H, 2.78; N, 9.74%). IR (cm<sup>-1</sup>) selected bands: 3344(vs), 1750(m), 1555(vs), 1469(vs), 1389(m), 1249(s), 1102(m), 792(m) and 656(m).

# 2.3. Synthesis of $\{[Na_{16}(Ni_8L_{12})(H_2O)_{20}(H_3O)_4](CH_3CN)(H_2O)_{18.5}\}_{\infty}$ (1) nano-particles by using ultrasonic method

To prepare nano-scale compound **1**, 20 ml of a 0.0375 M solution of 4,5-imidazoledicarboxylic acid in a sub-stoichiometric NaOH solution was placed in a high-density ultrasonic probe, operating at 50 Hz with a maximum power output of 305 W and 20 ml



**Fig. 2.** XRD patterns; (a) simulated pattern based on single crystal data of compound **1**, (b) bulk powder of compound **1** and (c) nanoparticles of compound **1** prepared by sonochemical process in concentration of initial reagents  $[Ni^{2+}] = 0.025 \text{ M}, [HL^{2-}] = 0.0375 \text{ M}.$ 

of a 0.025 M acetonitrile solution of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was added drop wisely to that solution during 1 h and at ambient temperature. Green precipitates obtained were collected by filtration, washed with water and then dried in air. (53.9% yield), m.p. > 300 °C (Found: C, 21.22; H, 2.59; N, 10.27%). IR (cm<sup>-1</sup>) selected bands: 3340(vs) 663(m), 1745(m), 1501(vs), 1248(m), 1124(m), 790(m) and 641(m).

For studying the effect of concentration of initial reagents on size and morphology of nano-particles of compound **1**, the above processes were done under the following concentration condition of initial reagents:  $[L^{3-}] = 0.075 \text{ M}$ ,  $[Ni^{2+}] = 0.05 \text{ M}$ .

# 2.4. Preparation of NiO nano-particles

For preparation of NiO nano-particles and also to investigate the size effect of compound **1** on the size and morphology of the NiO nano-particles, calcination of bulk powder and nano-sized compound **1** were done at 700 °C in static atmosphere of air for 4 h. IR spectrum and powder XRD diffraction shows that calcination was completed and the entire organic compound was decomposed.

## 3. Results and discussion

The reaction of aqueous solution of 4,5-imidazoledicarboxylic acid and NaOH with acetonitrile solution of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O led to formation of a 3D metal–organic framework {[Na<sub>16</sub>(Ni<sub>8</sub>L<sub>12</sub>)-(H<sub>2</sub>O)<sub>20</sub>(H<sub>3</sub>O)<sub>4</sub>](CH<sub>3</sub>CN)(H<sub>2</sub>O)<sub>18.5</sub>}<sub>∞</sub> (1). Nano-particles of compound 1 were obtained under ultrasonic irradiation in a mixed solution of H<sub>2</sub>O/CH<sub>3</sub>CN (1:1, v/v), at ambient temperature and atmospheric pressure while the bulk powder of compound 1 was obtained using reflux method. Scheme 1 gives an overview of the



**Fig. 3.** SEM photograph and the corresponding particle size distribution histogram of compound **1** nanoparticles prepared by ultrasonic generator 305 W in concentration of initial reagents  $[Ni^{2+}] = 0.025 \text{ M}$ ,  $[HL^{2-}] = 0.0375 \text{ M}$ .



**Fig. 4.** SEM photograph and the corresponding particle size distribution histogram of compound **1** nanoparticles prepared by ultrasonic generator 305 W in concentration of initial reagents [Ni<sup>2+</sup>] = 0.05 M, [HL<sup>2-</sup>] = 0.075 M.

methods used for the synthesis of compound **1** using the two different routes.



Fig. 5. XRD pattern of NiO nanoparticles prepared by calcination of bulk powder of compound 1 at 700  $^\circ\text{C}.$ 



Fig. 6. SEM image and the corresponding particle size distribution histogram of NiO nanoparticles prepared by calcination of bulk powder of compound 1 at 700 °C.

The elemental analysis and IR spectra of the nano-structured compound **1** produced by the sonochemical method and of the bulk material produced by reflux method are indistinguishable (Fig. 1).

Fig. 2 shows the comparison of XRD patterns, one simulated from single crystal X-ray data (Fig. 2a) against the bulk powder of compound **1** (Fig. 2b) and that of a typical sample of compound **1** prepared by the sonochemical process, respectively (Fig. 2c). The comparison between these XRD patterns indicates acceptable matches with slight differences in  $2\theta$ . This finding proves the formation of compound **1** under reflux and sonochemical processes. The significant broadening of the peaks in the pattern of nanoparticles compound **1** (Fig. 2c) indicates that the particles are of nanometer dimensions. Compound **1** is a 3D metal–organic framework crystallized in the orthorhombic space group Pnnm and consists of  $[M_8L_{12}]^{20-}$  cubes bridged by sodium ions. Each  $[M_8L_{12}]^{20-}$  unit consists of eight Ni<sup>II</sup> ions occupying the vertices of the cube, and are linked in a bi-chelating fashion by 12 L ligands. Each Ni<sup>III</sup> ion



**Fig. 7.** SEM image of NiO nanoparticles prepared by calcination of compound **1** nanoparticles prepared by sonochemical process in concentration of initial reagents [Ni<sup>2+</sup>] = 0.025 M, [HL<sup>2-</sup>] = 0.0375 M, at 700 °C.

L ligands, producing the slightly distorted octahedral coordination geometry [14].

The reaction between of 4,5-imidazoledicarboxylic acid (H<sub>3</sub>L) and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O provided a crystalline material of the general formula  $\{[Na_{16}(Ni_8L_{12})(H_2O)_{20}(H_3O)_4](CH_3CN)(H_2O)_{18.5}\}_{\infty}$  (1). To investigate the role of the concentration of initial reagents on the nature of products, reactions were performed with two different concentrations of initial reagents under ultrasonic irradiation. The morphology and size of obtained samples were characterized by scanning electron microscopy (SEM). Fig. 3 shows the SEM images and the corresponding particle size distribution histogram of the compound 1 obtained under 0.0375 M concentration of HL<sup>2-</sup> and 0.025 M concentration of Ni<sup>2+</sup>. Also further tests were completed on different concentration of acetonitrile solution of  $Ni(NO_3)_2 \cdot 6H_2O$  and aqueous solution of ligand  $H_3$  idc and NaOH. The resultant SEM images and the particle size distribution histogram are illustrated in Fig. 4. Appropriate nano-sized particles of compound 1 were obtained under both concentrations of initial reagents (Figs. 3 and 4). Comparison of IR spectra and XRD patterns show that the reaction at both concentrations of initial reagents produces the same product. However the results indicate that the resultant nano-particles size is dependent on the concentration of initial reagents as with increasing of the concentration of initial reagents the size of the nanoparticles also increase.

The TG curve of **1** indicates the release of guest molecules up to 100 °C to give its desolvated form. At 265 °C, the ligand molecules start to be released and the decomposition process of the framework is completed at 700 °C [14].

Fig. 5 provides the XRD pattern of the residue obtained from calcination of compound **1**. The obtained pattern matches with the standard pattern of cubic NiO with the lattice parameters a = 4.1771(8) Å, S.G. = Fm3m(225) and Z = 4 which is the same as the reported values (JCPDS card number 47-1049). No characteristic peaks of impurities are detected in the XRD pattern.

Fig. 6 shows the SEM image and the corresponding particle size distribution histogram of NiO nanoparticles obtained from calcination of bulk compound **1** at 700 °C. As the calcination process was successful for the preparation of NiO nano-particles, the nano-sized compound **1** prepared by the sonochemical process was also calcinated at 700 °C. The XRD pattern of the residue shows that the resulting residue was again NiO with the same lattice parameters which are mentioned above. Fig. 7 shows the SEM image of resulting NiO nano-particles.

# 4. Conclusions

A nano-sized 3D metal-organic framework (MOF) based on Ni(II), i.e. { $[Na_{16}(Ni_8L_{12})(H_2O)_{20}(H_3O)_4](CH_3CN)(H_2O)_{18.5}$ } (1)  $(H_3L = 4,5-imidazoledicarboxylic acid)$  has been synthesized using sonochemical irradiation. Compound 1 was characterized by scanning electron microscopy (SEM), X-ray powder diffraction (XRD), IR spectroscopy and elemental analyses. To prepare the nanostructure of compound 1, two different concentrations of initial reagents were tested. Appropriate nano-sized particles of compound 1 were obtained at both concentrations. Results show a decrease in the particles size as the concentrations of initial reagents has decreased. Calcination of compound 1 at different sizes produced nano-particles of NiO. Compared with traditional thermal and solvothermal methods, as well as solvent diffusion technique, ultrasonic synthesis of porous MOFs takes place in short reaction time (ca. 30 min) and at ambient temperature and it has been demonstrated to be highly efficient and environmentally friendly, especially for the manufacture of these functional porous materials on a large scale.

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