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## COMMUNICATION

## Facile synthesis of metal-organic cobalt hydroxide nanorods exhibiting a reversible structural transition<sup>†</sup>

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Metal-organic cobalt hydroxide nanorods with controllable dimensions using salicylates as bridging ligands have been synthesized in water under mild conditions in a simple process. The nanorods exhibit a reversible structural transition on dehydration and rehydration with a concomitant color change and may find potential applications in nanodevices.

Metal–organic frameworks (MOFs, also known as coordination polymers) have attracted increasing attention due to their ability to give functional materials with promising potential applications in catalysis, sensors, optics, gas storage, and magnetism.<sup>1</sup> In particular their reversible crystal-to-crystal structural transformations under the influence of external stimuli such as heat or guest species,<sup>2</sup> which can lead to changes in physical properties—for example, color—have important implications for their use in devices. However, reported examples of this type of material are quite rare and limited to macrosize particles. For many applications in optical, electrical, magnetic and sensing devices and in medicine, however, it is necessary to limit the crystallite size of MOFs to the nanoscale.<sup>3</sup>

Over the past decade, although a variety of procedures such as microfluidics,<sup>4</sup> reverse microemulsions,<sup>5</sup> solvothermal approaches,<sup>6</sup> sonochemistry,<sup>7</sup> and microwave-assisted<sup>8</sup> and coordination modulation methods<sup>9</sup>—have been employed in attempts to prepare nanosized MOFs, however, these procedures typically involve expensive reagents (organic solvent, organometallic precursor, surfactant and modulator) or complex manipulations and equipment. And moreover, it still remains a great challenge to control the morphology, size, composition, stoichiometry, and/or crystal structure. In this communication, we report a facile, economical, and scalable synthesis of metal–organic cobalt hydroxide nanorods with uniform and tunable size in water under mild conditions,



which requires neither sophisticated techniques nor surfactants or modulators, and show that the material undergoes a novel reversible structural transition and color change on dehydration and rehydration. To the best of our knowledge, this is the first time that one-dimensional (1D) nanostructured MOFs have been shown to undergo a reversible crystal-to-crystal dehydration/ rehydration process and as a result represents a significant breakthrough in this area of chemistry.

We use a simple commercially available salicylate as the organic linking block, based on its strong coordination ability with metal ions.<sup>10</sup> The approach is very simple and involves directly mixing solutions of cobalt nitrate hexahydrate and sodium salicylate (NaHsal, where Hsal denotes o-HOC<sub>6</sub>H<sub>4</sub>COO<sup>-</sup>) in water under pH-controlled conditions (Scheme 1). Typically, an aqueous solution (100 ml) of  $Co(NO_3)_2 \cdot 6H_2O$  (0.02 mol) was added to an aqueous solution (150 ml) of NaHsal (0.04 mol) with continuous stirring. The pH of the reaction mixture was adjusted to 7 with 0.5 M NaOH solution, which ensures that the phenol proton of salicylate  $(pK_{a2} \ 13.5)^{11}$  remains non-ionized. The mixture was aged at 95 °C for 48 h. The resulting pink product was separated by centrifugation, washed repeatedly with distilled water, and dried at 40 °C in air. Elemental analysis of the nanorods was consistent with the chemical composition Co(OH)(Hsal)·H<sub>2</sub>O (Anal. Calcd: Co 25.54, C 36.36, O, 34.63, H 3.46%; found: Co 25.35, C 36.38, O, 34.71, H 3.54%).

The morphology of the synthesized nanorods was examined by SEM. As shown in Fig. 1A and B, the product exhibits a consistent rod-like morphology with an average length of about 7  $\mu$ m and diameter of 130 nm. The diameter of the nanorods is uniform throughout their length and most of the nanorods tend to form bundles of aligned nanorods. The sample uniformity and narrow diameter distribution are also confirmed by the TEM image (Fig. 1C) of a sample of nanorods cast from a colloidal suspension onto a substrate.

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Fig. 1 (A) Low-resolution SEM image, (B) high-resolution SEM image, (C) TEM image, and (D) EDX spectrum of Co(OH)(Hsal)- $H_2O$  nanorods prepared at 95 °C. SEM images of Co(OH)(Hsal)- $H_2O$  nanorods prepared at (E) 70 °C and (F) 30 °C.

The sample consists of exclusively nanorods, consistent with the SEM images. The EDX spectrum of the nanorods (Fig. 1D) shows the presence of Co, C, and O with a Co/C ratio of 1:7 and no N signal from  $NO_3^-$  detected, which agrees well with the elemental analysis results. Additional Pt signals arise from the Pt coating which was applied on the sample to avoid a charging effect.

Further experiments revealed that the dimensions of the nanorods can be easily reduced by simply decreasing the reaction temperature, with all other conditions identical to those described above. The nanorods prepared at 70 °C were found to have a length of about 1 µm and diameter of 70 nm (Fig. 1E). When the temperature was further decreased to 30 °C, nanorods 400 nm in length and 33 nm in diameter were obtained (Fig. 1F). EDX results show that the nanorods prepared at different temperatures have the same chemical composition (Fig. S1 and S2 in the ESI<sup>†</sup>). We should stress here that the dimensions of the nanorods can be tailored by simply varying the reaction temperature in the absence of any surfactant or coordination modulator, and this may provide a new way to control the size of other nanoscale MOFs. The significance of these findings can be understood in terms of the fact that the existing techniques, which are successful in controlling the size of nanostructured MOFs, rely on the surfactant or coordination modulator.5,9

PXRD studies (Fig. S3, ESI<sup>†</sup>) show that the nanorods prepared at different temperatures are crystalline and have the same structure, which closely match the bulk phase of cobalt salicylate.<sup>12</sup> They show a feature typical of layered structure with strong peaks at 6.86 (d = 12.87 Å), 13.76 (6.43 Å), and 27.82 (3.20 Å), which can be assigned to the basal reflection and its second and fourth-order harmonics of a layered structure. Based on the following detailed characterization, the structure of the nanorods may be similar to that of



Fig. 2 (A) TGA curve of Co(OH)(Hsal)·H<sub>2</sub>O nanorods. (B) PXRD patterns of Co(OH)(Hsal)·H<sub>2</sub>O nanorods heating at different temperatures in N<sub>2</sub> for 4 h and after subsequent treatment with water. (C) Photographs of (a) original Co(OH)(Hsal)·H<sub>2</sub>O nanorods, (b) after heating at 300 °C, and (c) the nanorods in (b) after treatment with water. (D) UV-visible diffuse reflectance spectra of Co(OH)(Hsal)·H<sub>2</sub>O nanorods before (a) and after heating at 300 °C (b).

layered cobalt hydroxide intercalated with terephthalate ligands, in which the Co<sup>II</sup> ions are octahedrally coordinated by  $\mu_3$ -OH and  $\mu_3$ - $\eta^1$ , $\eta^2$ -carboxylate groups.<sup>13</sup> The FT-IR spectra (Fig. S4, ESI<sup>†</sup>) confirm that the carboxylate groups are coordinated to the Co<sup>II</sup> ions, as evidenced by the multiple characteristic asymmetric and symmetric COO<sup>-</sup> bands centered at 1570/1538 and 1453/1401 cm<sup>-1</sup>, respectively,<sup>14</sup> whereas the corresponding bands of the uncoordinated NaHSal occur at 1586 and 1387 cm<sup>-1</sup>, respectively. The presence of the salicylate  $\nu$ (C–O) band at 1237 cm<sup>-1</sup> confirms that the phenol group has not been deprotonated.<sup>15</sup> A broad band centered around 3390 cm<sup>-1</sup> indicates the presence of water molecules and extensive hydrogen bonding. The intense and sharp peak at 3584 cm<sup>-1</sup> is attributed to the O-H stretching mode of the Co-OH groups, similar to that observed for layered cobalt hydroxides.14,16

Good thermal stability of MOFs is an important prerequisite for many practical applications. The thermal stability of the nanorods synthesized at 95 °C was investigated by TGA in N<sub>2</sub> (Fig. 2A). The two weight loss steps from 30 to 200 °C correspond to the removal of the water of crystallization and a second water molecule formed by protonation of the coordinated hydroxide ligand by the hydroxyl group of the salicylate moiety. The observed mass loss of *ca*. 16.1% agrees well with what is expected for the loss of two water molecules from the formula Co(OH)(Hsal)·H<sub>2</sub>O (15.6%). The weight remained constant from 200 to 400 °C and after that the framework started to decompose. The resulting product at 650 °C consists of, according to XRD (Fig. S5, ESI†), cobalt/carbon nanocomposites.<sup>17</sup>

It is especially interesting to note that dehydration followed by rehydration of the nanorods induces a reversible structure transformation. As shown in Fig. 2B, the PXRD pattern of the sample after heating in N<sub>2</sub> for 4 h at 150 °C does not indicate much change in crystallinity. A phase transition occurs at 200 °C, characterized by a decrease in the intensity of diffraction peaks at  $2\theta > 10^{\circ}$ , which becomes more marked on raising the temperature further to 350 °C. The position of the first diffraction peak corresponding to the basal reflection of the layered structure is unchanged even after 4 h of heating at 350 °C, although there is some decrease in its intensity. Accompanying this structural change is a dramatic color change from pink to dark blue (Fig. 2C). The UV-visible diffuse reflectance spectra (Fig. 2D) were measured in order to determine the absorption features responsible for the color change. The spectrum of the original nanorods is characteristic of Co<sup>II</sup> ions in an octahedral geometry with a broad major peak at 550 nm and two shoulders around 470 and 500 nm.<sup>16</sup> In contrast, the spectrum of the dehydrated nanorods displays a pair of transitions at 638 and 580 nm arising from Co<sup>II</sup> in tetrahedral coordination,<sup>18</sup> and a band at 470 nm which can be attributed to octahedral Co<sup>II</sup> with a higher ligand field splitting than in the original material.

When the dehydrated nanorods were immersed in water or exposed to air for several days at room temperature, they completely reverted to their initial color (Fig. 2C). The original structure was also recovered, as shown by comparing the PXRD pattern recorded after treating the nanorods dehydrated at 300 °C with water (Fig. 2B, top) with the original powder pattern (Fig. 2B, bottom). Accordingly, the UV-visible diffuse reflectance spectrum and TGA curve of the rehydrated nanorods, as shown in Fig. S6 and S7 (ESI<sup>+</sup>), respectively, are identical to those of the original material. It is noteworthy that the intrinsic shape of the nanorods is also retained during the dehydration/rehydration cycle (Fig. S8, ESI<sup>+</sup>).

We also investigated the structural transformation of the nanorods using FT-IR spectroscopy (Fig. S9, ESI†). The FT-IR spectrum of the dehydrated nanorods confirms the removal of the water molecule and hydroxide group by virtue of the disappearance of the absorption peaks at 3390 and 3584 cm<sup>-1</sup>. There are dramatic changes in the bands in the low-frequency region below 1000 cm<sup>-1</sup>, arising from cobalt–oxygen lattice vibrations, which can be attributed to coordination of the hydroxide group of salicylate to the cobalt center. In contrast, the absorption peaks in the range from 1300 to 1700 cm<sup>-1</sup> attributed to carboxylate groups are virtually unchanged, indicating the strong binding of these groups to Co<sup>II</sup>. The FT-IR spectrum of the rehydrated nanorods is identical to that of the starting material, which confirms that the transformation is reversible.

On the basis of our above results, we can conclude that the loss and reuptake of the bonded (coordinated) hydroxide group, and interchange of the coordination geometry of the Co<sup>II</sup> ions between octahedral and the coexistence of octahedral and tetrahedral ions is the origin of the reversible structural change. It is well known that few coordination frameworks undergo reversible structural change upon removal and reabsorption of coordinated water;<sup>2d,f</sup> however, this type of structurally dynamic process, where a solid reversibly undergoes loss and reuptake of a bonded (coordinated) hydroxide group involving significant coordination changes, is especially rare, although recently Cavka *et al.* have reported that a  $Zr_6$ -cluster can rearrange reversibly upon removal or addition of hydroxide groups.<sup>19</sup> This high stability and flexibility of the

framework is perhaps due to the presence of the phenol group in the Hsal ligands, which can interact with the Co<sup>II</sup> center, as seen by FT-IR, stabilizing the high temperature state, but allowing a return to the original structure on rehydration.<sup>20</sup> The other properties and potential applications of the material deserve further investigation. For example, the presence of unsaturated four-coordinate Co<sup>II</sup> sites in the high temperature form suggests it should have a high ability to adsorb guest molecules.<sup>1b,2b,2f</sup>

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