Self-Template-Directed Formation of Coordination-Polymer Hexagonal Tubes and Rings, and their Calcination to ZnO Rings**

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Micro- and nanoscale materials made from atomic or molecular building blocks have received great attention owing to their useful properties, which allow for applications in optics,[1,2] catalysis,[3–5] biosensing,[6,7] and medical diagnostics,[8] and because of their fundamentally interesting unique structures.[9,10] The size, morphology, and composition of these materials are important factors that dictate their characteristic properties. In this context, the shape and size of particles have been manipulated to obtain the desired properties for specific applications.[11,12] And an understanding of the particle-growth mechanism[2,13] is necessary for fine tuning of a given particle’s size and shape. In particular, particles with unusual shapes have received great attention because of their potential for extraordinary properties arising from that unusual shape.[14,15] Herein we report the formation of extraordinary hexagonal tubes and rings. These atypically shaped particles were generated through a self-template-directed growth mechanism in which the initially formed coordination-polymer particles (CPPs) acted as templates for growth of the final hexagonal tubes and rings. Furthermore, we also show that simple calcination of these unusually shaped CPPs results in the spontaneous formation of ZnO particles while the unique shape is maintained.

Recently, a novel strategy for the synthesis of micro- and nanometer-sized CPPs has been developed.[2,5,16–18] This new class of particles could extend the roles of pre-existing inorganic particles, as their chemical and physical properties could be tailored according to the types of metal and organic building block used. We have discovered that unique hexagonal-tube CPPs can be synthesized by the simple solvothermal reaction of metal ions and carboxy-functionalized building blocks (Figure 1a). In a typical synthesis, two kinds of carboxy-functionalized organic building blocks (a salen ligand (N,N’-phenylenebis(salicylideneimine))dicarboxylic acid, 1)[18,19] and 1,4-benzendicarboxylic acid (H₂bdc) in a 1:5 molar ratio), were dissolved in N,N-dimethylformamide (DMF), and the resulting solution was mixed with Zn(OAc)₂ in DMF (zinc-metalated salen complexes[18] are spontaneously generated by coordination of Zn²⁺ to the organic salen pocket during the reaction). The resulting mixture was heated at 120 °C for 15 min. During this time, formation of CPPs was observed.

The morphology of the isolated particles was characterized by field-emission scanning electron microscopy (FE-SEM; Figure 1b,c). The images revealed the formation of hexagonal-tube-type CPPs with approximate dimensions of 2.64 (outer hexagon) and 1.86 mm (inner hexagon) and a length of 2.23 mm. The formation of coordination polymers was verified by IR spectroscopy.[17–22] The IR spectrum taken after formation of CPPs showed that the carboxylate groups of the organic building blocks are coordinated to Zn²⁺ ions, as evidenced by a shift in CO stretching frequency to 1613 cm⁻¹ from 1692 and 1686 cm⁻¹ for uncoordinated building blocks 1 and H₂bdc, respectively. The chemical composition of the resulting particles was determined by energy dispersive X-ray
spectroscopy (EDX, see the Supporting Information) and \(^1\)H NMR spectroscopy. Although the as-generated hexagonal tubes are stable in several organic solvents (including DMF and DMSO, in which both organic precursors are very soluble), particles can be digested into individual building blocks by addition of organic acid. Eventually, a 1:2 ratio of \(\text{I}\) and \(\text{H}_2\text{bdc}\) incorporated within the particles was determined by the \(^1\)H NMR spectrum of particles digested in \([\text{D}_4]\text{acetic acid}\) and \([\text{D}_6]\text{DMSO}\). The particles were further characterized by optical microscopy (OM, Figure 1d) and fluorescence microscopy (FM, Figure 1e–g). The particles are fluorescent in the blue, green, and red regions of the spectrum owing to the fluorescent zinc-metalated salen building blocks.\(^{18,23}\) The featureless powder X-ray diffraction (PXRD) spectrum of hexagonal-tube CPPs reveals that the particles are not perfectly crystalline materials. Thermal stability of CPPs up to \(400^\circ\text{C}\) was verified by thermogravimetric analysis (TGA, see the Supporting Information).

To study the formation mechanism of the unusual hexagonal tubes, samples were taken from the reaction mixture at various times and monitored by SEM. Interestingly, formation of hexagonal lumps as initial products with approximate dimensions of \(1.95 \times 1.95 \times 2.14\ \mu\text{m}^3\) was observed at a very early stage before thermal treatment (Figure 2a). It was difficult to determine the differences between the initial hexagonal lumps and the final hexagonal tubes because the chemical composition, thermal stability, and optical properties of the two species were very similar, as characterized by EDX and IR spectroscopy, PXRD, TGA, emission spectroscopy, OM, and FM. However, there was a distinct difference in the ratio of incorporated building blocks between the initial and final particles. Building blocks \(\text{I}\) and \(\text{H}_2\text{bdc}\) were incorporated in a 1:6 ratio within the initial hexagonal-lump CPPs (Figure 3a) but in a 1:2 ratio in the final hexagonal tubes. Furthermore, the initial hexagonal lumps were unstable in several organic solvents (e.g. DMF and methanol), while the final hexagonal tubes were very stable in these solvents. We can conclude that both the initial and the final particles consisted of the same building blocks but in different proportions. Subsequently, \(\text{N}_2\) adsorption isotherms were measured after pre-treatment under dynamic vacuum at \(200^\circ\text{C}\). As shown in Figure 3b, \(\text{N}_2\) adsorption isotherms of initial hexagonal lumps (\(\vartriangle\)) and the final hexagonal tubes (\(\ast\)) exhibit behavior consistent with multilayer adsorption. The BET and Langmuir surface areas of the hexagonal tubes (101.72 and 122.96 \(\text{m}^2\text{g}^{-1}\)) are larger than those of the hexagonal lumps (25.116 and 29.308 \(\text{m}^2\text{g}^{-1}\)). This difference can be easily understood from the fact that hexagonal tubes have a greater exposed surface area than hexagonal lumps.

During the pathway to final formation of hexagonal tubes, the concomitant dual processes of growing new coordination polymers on the surfaces of the initial hexagonal lumps and dissolving the initial CPPs were detected by taking aliquots from the reaction mixture during the reaction and characterizing these samples by SEM (Figure 2b–e). At a very early stage of the reaction, the products consist solely of hexagonal lumps, as mentioned above (Figure 2a). After thermal treatment, new coordination polymers began to grow on the lateral facets of the initial hexagonal lumps, which act as the
template and are gradually dissolved (Figure 2b). Over time, the initial template coordination-polymer structures become thinner (Figure 2c–e) and ultimately disappear, resulting in uniform hexagonal tubes (Figure 2f). These observations indicate a novel self-template-directed CPP growth mechanism (Figure 2g) for hexagonal tubes in which the initially formed hexagonal lumps subsequently act as the template for the formation of new coordination polymers, while the initially formed coordination-polymer templates are concurrently dissolved to create the final hexagonal tubes.

A previous study reported the formation of hexagonal rings of ZnO by an etching mechanism in which the etching process begins from the center of original hexagonal disks. This etching mechanism can be viewed as another possible mechanism for the formation of hexagonal tubes from hexagonal lumps demonstrated herein. To clearly verify that hexagonal-tube CPPs were generated through the proposed self-template-directed mechanism rather than the etching mechanism, the reaction was performed in dilute solution. For the self-template mechanism, the growth rate of the final coordination polymers will be decreased and the rate of dissolution of the initial template CPPs will be increased in the presence of an excess of good solvent. Indeed, intermediates (Figure 3c), which clearly show growth of secondary coordination polymers on the lateral facets of template particles, were observed in the presence of an excess of DMF, as the growth processes was slowed. This kind of intermediate cannot be formed through an etching mechanism. Besides, incomplete hexagonal tubes and fractions of hexagonal tubes (Figure 3d) were obtained as final products because of an increase in the speed of the dissolution process of the initial template polymers in addition to the slowing of the growth process.

We also investigated the effect of varying the size of the initial template particles on the formation of the final CPPs. The initial template CPPs can be prepared as hexagonal disks rather than hexagonal lumps by reducing the amount of Zn(OAc)$_2$ used (Figure 4a,b). These initial hexagonal disks will act as templates for the formation of the hexagonal rings rather than hexagonal tubes. SEM images from the series of reaction aliquots reveal the expected result (Figure 4). Hexagonal-ring-type CPPs with approximate outer and inner hexagon dimensions of 2.34 and 1.99 μm, respectively, and a thickness of 0.756 μm were formed (Figure 4e). The size of the final hexagonal rings increased compared to that of the initial hexagonal-disk template (2.08 μm). Furthermore, the inner hexagon dimension of the hexagonal rings is similar to the size of the initial template. The intermediates generated during formation of hexagonal rings from hexagonal disks were monitored by SEM (Figure 4c,d). The hexagonal rings were further characterized by OM and FM (Figure 4f). The resulting hexagonal rings were fluorescent in the blue, green, and red regions of the spectrum.

Furthermore, we have investigated the utilization of CPPs as precursors for the formation of metal oxide particles with specific shapes. We found that metal oxides with the shape of precursor CPPs used can be generated by the decomposition of the CPPs. Typically, the hexagonal-ring-shaped CPPs were simply calcined at 550°C for 75 min using a conventional furnace to obtain ZnO products. During this time, the initial coordination polymers decomposed to metal oxides. The morphology of the resulting ZnO was characterized by SEM (Figure 5a,b). The overall size of the hexagonal-ring ZnO was reduced to approximately 1.16 μm from that of the precursor hexagonal-ring CPP (ca. 2.34 μm). The chemical composition of the hexagonal-ring ZnO was characterized by EDX spectroscopy, by which only zinc and oxygen atoms are detected (Figure 5c). Furthermore, the PXRD pattern for the resulting ZnO hexagonal rings (Figure 5d) reveals that they have a hexagonal wurtzite structure. All the observed peaks matched exactly with the reported values of the hexagonal wurtzite phase of pure bulk ZnO. We conclude that CPPs can be used as templates or precursors to generate metal oxides with a wide range of shapes.

In conclusion, we have demonstrated that fluorescent hexagonal tubes and rings made from coordination polymers can be synthesized by a simple solvothermal method. A unique particle-growth mechanism called self-template-directed growth has been proposed and verified. This...
growth mechanism is expected to significantly enhance our understanding of the nature of CPPs and their potential applications. Furthermore, metal oxide particles that maintain the morphology of the precursor CPPs used can be prepared through calcination of CPPs. Because CPPs can be prepared with a wide range of compositions and morphologies, this simple calcination method will provide a new paradigm in the manufacture of customized metal oxide nanoparticles.

Keywords: calcination · coordination polymers · crystal growth · nanostructures · template synthesis

Figure 5. a) Low-magnification SEM image, b) high-magnification SEM image, c) EDX spectrum, and d) PXRD pattern of hexagonal-ring ZnO. Red lines are the reported values of the hexagonal wurtzite phase of pure bulk ZnO (JCPDS Card No. 75-1526).

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