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Zinc Oxide Nano- and Microfabrication from Coordination-Polymer Templates**

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Among the large family of metal oxides, zinc oxide is probably the most widely used inorganic oxide in advanced materials and industrial chemicals; applications include electronic materials, sunscreen cosmetics, pigments, food additives, and rubber curing agents. Furthermore, ZnO plays an outstanding role in many aspects of science and engineering owing to its unique optical, semiconducting, catalytic, magnetic, and piezoelectric properties.[1] It has practical applications as a key component for the fabrication of piezoelectric transducers, transparent conductive oxides, sensors, light-emitting diodes, and optoelectronic and spintronic devices.[1]

Over the past decade, substantial research efforts have been directed toward the synthesis of nanostructured ZnO materials with controlled sizes, morphologies, structures, and properties.[2] An extraordinary variety of ZnO nanostructures, including nanorods,[3] nanowires,[4] nanoflowers,[5] nanotubes,[6] tetrapods,[7] nanobelts,[8] nanosheets,[9] nanorings,[10] and hierarchical nanostructures[11] have been reported. These nanomaterials exhibit a plethora of phenomena and dramatically improved properties that change depending on their structures, sizes, shapes, and phases. A most notable early finding was the observation by Yang and co-workers of room-temperature ultraviolet lasing in ZnO nanowire arrays.[4a] In addition to the ordered nanowire arrays that exhibit fascinating collective optical properties, a great deal of research has been focused on individual single-crystalline ZnO nanowires and nanobelts.[12] An interesting recent development was reported by Xu and co-workers, who showed that subtle differences in individual one-dimensional ZnO nanostructures result in markedly different electrical and field emission properties.[13]

Many synthetic approaches, ranging from conventional solid-state synthesis to advanced techniques, such as physical vapor deposition, have been utilized to produce well-defined ZnO nanostructures.[2c,d] Using a catalyst-free vapor/solid growth process, Wang et al. have pioneered the synthesis of one-dimensional ZnO nanomaterials, such as nanobelts and nanosprings, with lengths of several tens to several hundreds of micrometers.[8] In contrast, large-scale arrays with vertically aligned nanowires on solid substrates are typically produced by a catalyst-assisted physical vapor-deposition method.[14] A catalyst template, which usually comprises an array of metal nanoparticles, is required to guide the nanowire growth. In their most recent work, Wang and co-workers developed a new technique, which is based on a combination of electron-beam lithography and a hydrothermal method, to achieve patterned growth of ZnO nanowires.[15] This approach provides ZnO nanowire arrays with a remarkable degree of vertical alignment without using a catalyst. Along with the relatively low-temperature growth of well-aligned nanowires, their structural uniformity and scalability over large areas make them attractive for a wide range of fundamental and technological applications.

Although conventional methods and the vapor-transport growth technique have worked well for the synthesis of nanostructured ZnO crystals, several groups have attempted a radically different approach to synthesizing micro- and nanosized ZnO crystals. The new approach employs molecular building blocks to direct the assembly of ordered metal–organic coordination-polymer templates that can be manipulated to produce ZnO crystals with controlled structures, compositions, and properties.[16] The most intriguing feature of the approach is the diversity of available molecular building blocks that are readily polymerizable by metal–ligand coordination. The large choice of these molecular building blocks makes it possible to construct coordination-polymer precursors with tailored morphologies, porous structures, and well-defined interfaces.[17] Using this emerging approach, a variety of ZnO structures, including nanoparticles, nanorods, nanofibers, nanoneedles, and microscale hollow spheres, have been synthesized.[16]

Recently, Oh and co-workers[18] have taken the established principle of the coordination-polymer template-directed approach one step further and reported the synthesis of micrometer-sized ZnO hexagonal rings. Their method (Scheme 1) utilizes two sets of organic bridging ligands, namely *N,N′*-phenylenebis(salicylideneimine)dicarboxylic acid (**A**) and 1,4-benzenedicarboxylic acid (**B**), in combina-

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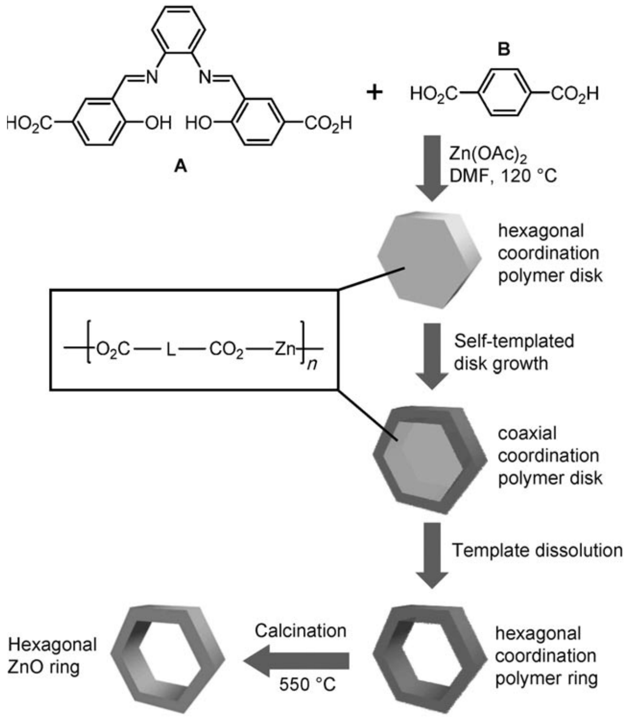

Scheme 1. Proposed mechanism for the synthesis of micrometer-sized hexagonal ZnO rings by a combination of template-directed coordination-polymer growth and thermal decomposition. $^{-}O_2C$–L–CO_2^{-} = deprotonated **A** or **B**.

tion with zinc acetate as a source of zinc, for the synthesis of coordination-polymer precursors to ZnO hexagonal rings.

The formation of unusual hexagonal rings of coordination polymers then occurs through a template-directed growth mechanism, which involves a concurrent two-step process of growing secondary coordination polymers and dissolving the initial supporting template. Upon mixing the organic bridging ligands and metal ions at a stoichiometric ratio, hexagonal disks of coordination polymers held together by strong oxygen–metal–oxygen bonds were formed in almost quantitative yield. During a heating process, the hexagonal disk plays a dual role, serving both as a template to laterally overgrow the polymer and as a reactive center for the template dissolution. Consequently, the hexagonal disk heated at 120 °C was transformed into a coaxial coordination-polymer disk and subsequently a hexagonal ring. Calcination of the amorphous hexagonal ring at 550 °C resulted in the formation of a polycrystalline ZnO ring structure.

Oh and co-workers were able to monitor the hexagonal ring growth process by taking scanning electron microscopy (SEM) snapshots of samples obtained from different growth stages. As shown in Figure 1 a, the reaction product consists exclusively of hexagonal disks during the early stage of the growth process. Upon heat treatment, lateral growth of secondary coordination polymers on the initial disk templates started to occur with no apparent change in disk thickness (Figure 1 b). The template-directed growth process during heat-up was also accompanied by gradual dissolution of the templates (Figure 1 b). Complete removal of the initial templates by polar organic solvents, such as *N*,*N*-dimethylformamide, during the final stage of the particle growth resulted in the formation of hexagonal rings of coordination polymers with an average inner diameter of 2 μm and a thickness of 1 μm (Figure 1 c). The inner diameter of the hexagonal rings is essentially the same as the lateral dimension of the initial templates, confirming the template-directed growth mechanism.

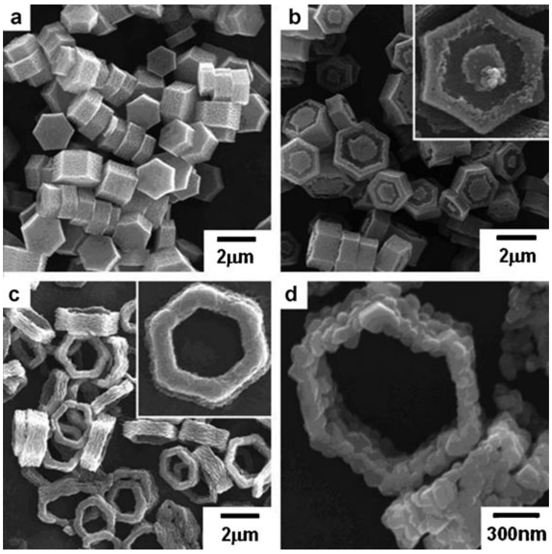

Figure 1. a) SEM image of the hexagonal coordination-polymer disks formed at the early stage of the particle growth process. b),c) SEM images of the coordination-polymer microstructures formed at the later stages of the growth process during heat-up (insets are high-magnification SEM images of the as-synthesized microstructures). d) High-magnification SEM image of the ZnO rings formed after calcination at 550 °C.

One of the most attractive features of the hexagonal coordination-polymer rings is their optical properties. Upon excitation at 400 nm, these microscale rings exhibited a strong and broad visible emission, with a maximum emission peak at about 520 nm. The resulting rings are highly fluorescent in the blue, green, and red spectral regions owing to the fluorescent metal–organic building blocks, providing exciting new applications as multicolor particle probes and tunable light-emitting displays.[19]

In addition to their optical utility, the amorphous coordination-polymer rings can also be used for the preparation of polycrystalline ZnO rings. As shown in Figure 1 d, the conversion into ZnO can be achieved by calcination at 550 °C. Importantly, the as-grown hexagonal ring-shaped crystal morphology is maintained during the solid-state transformation. The wurtzite structure and elemental composition of the ZnO rings were verified by powder X-ray diffraction (XRD) and energy-dispersive X-ray analysis (EDX) measurements, respectively.

The innovative synthetic strategy for ZnO rings used by Oh et al. can be readily extended to other materials.[20] For example, Mirkin and Oh[21] have shown that because of the open framework of zinc coordination-polymer structures (Figure 2), selective metal-ion exchange in polymer particles can be achieved owing to the labile nature of the interactions between the zinc ion and the Schiff-base ligand. Using this

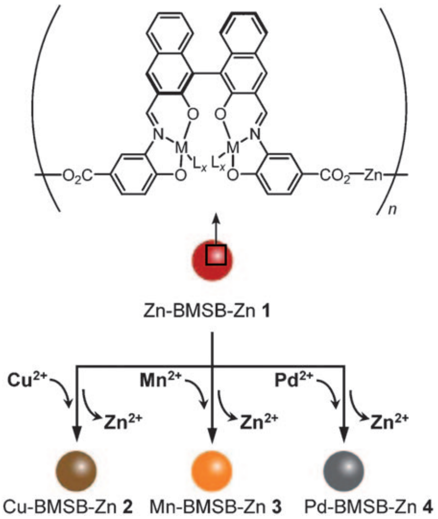

Figure 2. Representation of ion-exchange reaction in zinc coordination-polymer nano- and microparticles. The difference in relative binding strengths means Zn^{2+} ions are readily replaced from the tridentate Schiff base ligand coordination sites (M), but not from the carboxylate sites. BMSB = bimetallic tridentate Schiff base; L = pyridine, water, methanol; M = Zn^{2+} (**1**), Cu^{2+} (**2**), Mn^{2+} (**3**), Pd^{2+} (**4**).

ion-exchange approach, coordination-polymer nano- and microparticles that comprise copper(II), manganese(II), and palladium(II) ions were deliberately synthesized from one precursor set of particles in a controlled process. In contrast to their solid-state counterparts, the coordination-polymer particles exhibited significantly faster ion exchange rates. The particle transformation could even be monitored by the naked eye. Upon calcination at elevated temperatures, these composite particles could be converted into hybrid metal oxide crystals with predetermined morphologies in high yields.

The vibrant and growing field of metal–organic coordination-polymer chemistry paves the way for a valuable and versatile technique to the bottom-up design and synthesis of new functional materials that span from the molecular level to macroscopic scales. Control of the rigidity, aspect ratio, and chirality of the organic building blocks and of the coordination geometry of the metal ions allows for the self-assembly of complex and well-defined materials with novel photonic, mechanical, and optoelectronic properties. These materials are likely to find new applications in chemical sensors, catalysts, and anisotropic conductors. A challenge for materials chemists today is to understand the underlying mechanism that accounts for particle growth in metal–organic coordination-polymer composites. Understanding of the growth mechanism will require the development of reliable approaches in both experimentation and computation. Difficulties may arise both for experiments, for example in the characterization, at the nanoscopic level and for complex computations at a microscopic scale. However, such difficulties certainly offer new research opportunities for the rational design and synthesis of molecular building blocks in the quest for the next generation of functional materials.

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