Coordination Polymer Nanoparticles

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Monitoring Shape Transformation from Nanowires to Nanocubes and Size-Controlled Formation of Coordination Polymer Particles**

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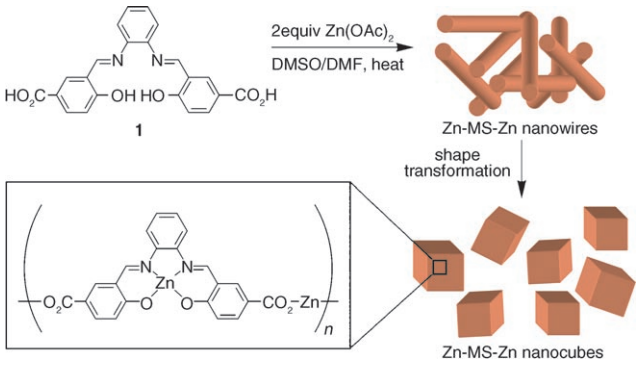
Infinite coordination polymers in which metal ions or metal clusters are connected by molecular building blocks consisting of organic molecules or organometallic complexes have received a great deal of attention due to their useful applications in gas storage,[1] catalysis,[2] optics,[3] recognition, and separation.[4] Rationalization of their chemical and physical properties from structural studies is of fundamental interest in the field of coordination polymer materials. Similarly, micro- and nanostructured materials are essential in many different areas, such as catalysis,[5] optics,[6] biosensing,[7] medical diagnostics,[8] and data storage,[9] and their size, shape, and composition are the key parameters that dictate chemical and physical properties.[10] Recently, a synthetic strategy for the preparation of micro- and nanoparticles made from infinite coordination polymers has been demonstrated by several groups.[11] This new class of materials promises to advance nanoparticle science into the realm of infinite coordination polymers, and thereby circumvent the nominal composition limitations generally ascribed to nanoparticles.

Control of the composition of nanoparticles generated from functionally defined precursors is a promising research area due to the fundamental interest in materials that have practical applications in chemistry, biology, physics, and related interdisciplinary fields. Coordination polymer particles (CPPs) made from functional metalloligand building blocks have been shown to have a high degree of tailorability.[11a,b] The development and application of CPP materials requires an understanding of how the particles are formed, and the ability to control their size and shape. Herein we describe a solvothermal approach for the synthesis of CPPs made from transition-metal ions and metallosalen (salen = *N*,*N*′-bis(salicylidene)ethylenediamine) building blocks. We also describe an interesting nanoparticle wire-to-cube morphological transformation, and the utilization of this transformation process to control CPP formation.

In a typical synthesis, fluorescent cubic nanoparticles were prepared by the following simple procedure (Scheme 1):



Scheme 1. Preparation of Zn-MS-Zn coordination polymers as nanowires and their subsequent transformation into nanocubes.

carboxy-functionalized salen ligand *N*,*N*′-phenylenebis(salicylideneimine)dicarboxylic acid[12a] (**1**, 3 mg) was dissolved in DMSO (1 mL), and the solution was added to DMF (2 mL) containing two equivalents $Zn(OAc)_2$. One equivalent of Zn^{2+} coordinates to the salen pocket to give Zn-metalated salen (Zn-MS)[12] complex. The other Zn^{2+} ion acts as a node that connects to the Zn-MS metalloligands through the carboxylate groups to form coordination polymer (Zn-MS-Zn); when one equivalent Zn^{2+} is used, the coordination polymer does not form. The resulting solution was heated at 120 °C for 60 min. During this time, formation of particles was observed. The reaction mixture was cooled to room temperature, and the precipitate was collected by centrifugation and washed several times with DMSO and methanol. The resulting particles were found to be stable in organic solvents (methanol, acetone, DMF, DMSO, and nonpolar solvents), water, and in the dried state.

The morphology was characterized by field-emission scanning electron microscopy (SEM; Figure 1). The images show cubic particles with an average size of (308 ± 36) nm. Dynamic light scattering (DLS) measurements on a colloidal

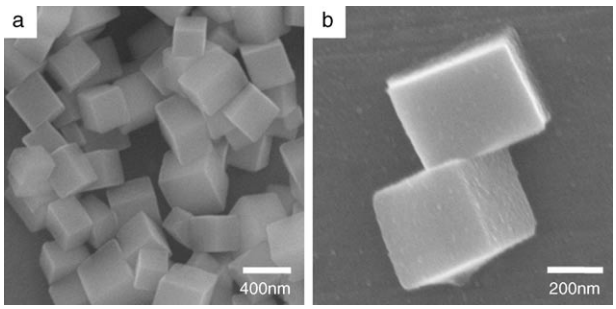


Figure 1. a) Low-magnification SEM image and b) high-magnification SEM image of the nanoscale Zn-MS-Zn cubes with an average diameter of (308 ± 36) nm (s.d., $n = 100$).

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suspension revealed a mean particle size of 356 nm, which is in reasonable agreement with the values determined by SEM. The chemical composition of the Zn-MS-Zn particles was determined by energy-dispersive X-ray (EDX) spectroscopy (see the Supporting Information). The formation of coordination polymers from metal ions and carboxylate-functionalized building blocks is well known in transition-metal coordination chemistry, and they can be conveniently characterized by IR spectroscopy.[1–4,11] The infrared spectrum taken after formation of the CPP particles shows that the carboxylate groups are coordinated to Zn^{2+} ions, as evidenced by a shift in CO stretching frequency to 1613 cm^{-1}. This value can be compared to the CO stretching frequency of 1692 cm^{-1} for organic precursor **1**. The Zn-MS-Zn particles were further characterized by optical microscopy (OM) and fluorescence microscopy (FM, Figure 2a). The particles are fluorescent in the green region of the spectrum due to the fluorescent Zn-MS metalloligand building blocks.[12b]

The SEM images of the Zn-MS-Zn particles taken at an early stage show that nanowires and not nanocubes are the initial products (Figure 3a and b). The formation of coordination polymer nanowires seems to be similar to that of the fiber structure in organogels.[13] The chemical composition of the Zn-MS-Zn nanowires was verified by EDX spectroscopy (see the Supporting Information), and formation of coordination polymers was confirmed by a shift in CO stretching frequency to 1613 cm^{-1}. The Zn-MS-Zn nanowires have the same optical properties as the Zn-MS-Zn nanocubes (Figure 2). Aggregation of the nanowires at intermediate stages on the path to the final nanocube product was observed by taking aliquots from the reaction mixture at various times and recording SEM images (Figure 3). At very early stages of the reaction, the products consist solely of nanowires with an average diameter and length of 40 and 600 nm,[14] respectively

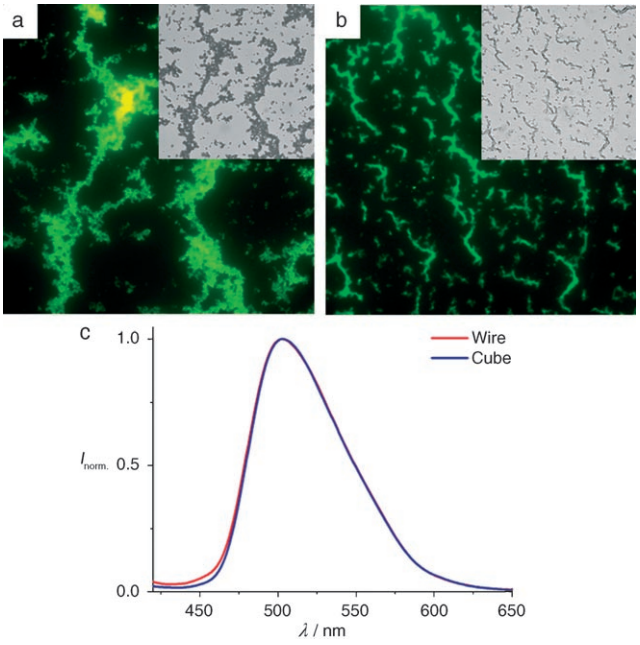

Figure 2. OM and FM images of a) the fully formed Zn-MS-Zn nanocubes and b) the initial Zn-MS-Zn nanowires. c) Emission spectra of Zn-MS-Zn nanowires and nanocubes.

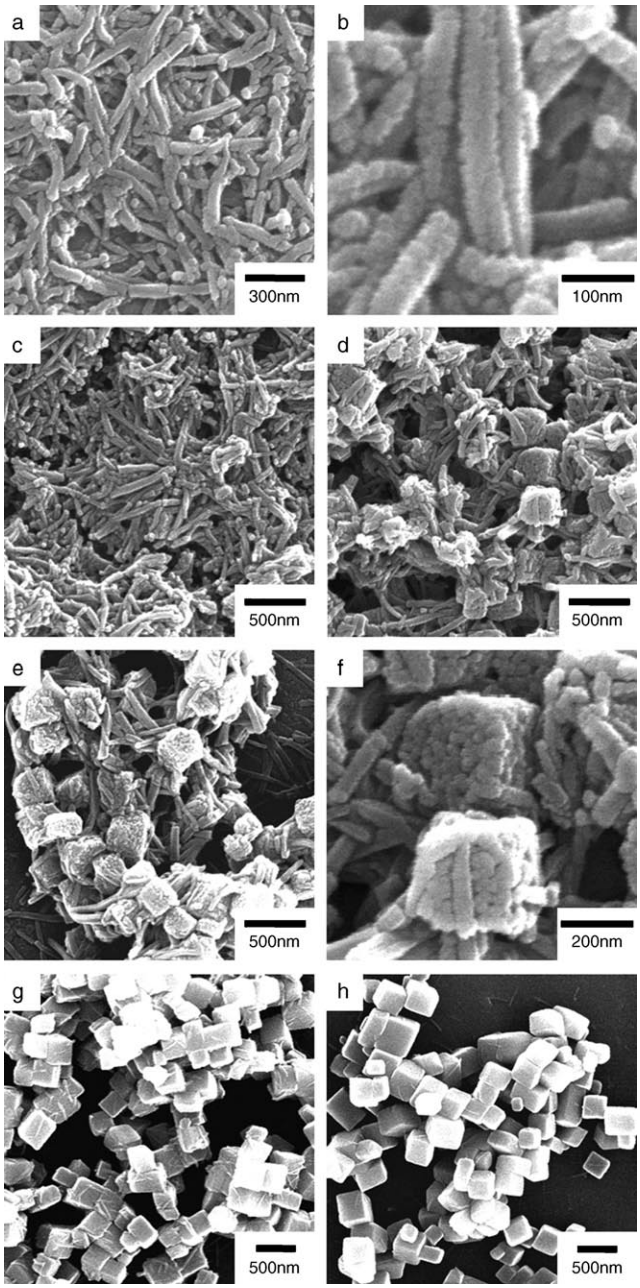

Figure 3. SEM images monitoring the process of transformation of Zn-MS-Zn nanowires into Zn-MS-Zn nanocubes. a) Low-magnification and b) high-magnification images of the initial nanowires, c) image showing initiation of nanowire aggregation, d) and e) intermediates at the later stages, showing cubic clusters, f) high-magnification image of the cubic clusters, g) image showing surface annealing at the latest stage, and h) image of the fully formed nanocubes.

(Figure 3a and b). The nanowires begin to aggregate into a cubic shape in the next stage (Figure 3c). Over time, the number of aggregates with a cubic shape increases (Figure 3d–f). The aggregated nanowires slowly anneal into single particles with smooth surfaces (Figure 3g) and ultimately form uniform cubic particles (Figure 3h). These observations reveal a unique wire-to-cube transformation in which nanowire aggregation into cube-shaped clusters precedes intrastructural fusion to afford cubic CPPs.

We also investigated the effect of varying the reaction temperature and solvent on the formation of particles. The reaction temperature was found to be important for the generation of particles and manipulation of their size. Smaller cubes were generated at lower reaction temperatures. Figure 4a shows an SEM image of Zn-MS-Zn particles with an average size of (166 ± 15) nm obtained at 80 °C under otherwise identical conditions as described above. This value can be compared to the particle size of (308 ± 36) nm for the products obtained at 120 °C. When DMSO/DMF (1:1, 3 mL) was used instead of DMSO/DMF (1:2, 3 mL, see above), bigger cubes with an average particle size of (600 ± 94) nm were formed (Figure 4b). In DMSO/DMF (2:1), microcubes with an average particle size of (4.86 ± 0.78) μm were obtained (Figure 4c). The ultimate size of the cubes reflects the number of nanowires involved in the aggregation process, which in turn is likely affected by the solubility of nanowires. The SEM images indicated that the nanowires initially formed in the early stages of all reactions have similar dimensions regardless of the size of the final cubic products (see the Supporting Information). Thus, the size of the CPPs can be controlled by limiting the number of nanowires in the aggregated intermediates. At low temperature, the aggregation process likely commences at a large number of sites and thus results in a relatively large number of nanocubes of small size. However, under conditions of good solubility, such as high temperature or in a mixed solvent system having a large portion of DMSO, the attendant smaller number of aggregation sites translates into a smaller number of particles of larger average size.

In conclusion, nano- and microsized fluorescent cubic CPPs consisting of metalloligand building blocks and metal nodes can be easily synthesized in high yield by a simple solvothermal approach. Fluorescent CPPs containing metalated salen complexes have potential for applications in heterogeneous catalysis and as contrast agents for bioimaging. Formation of CPPs is accompanied by a morphological transformation from nanowires to nanocubes. The nanowires are formed initially and then aggregate into cube-shaped clusters which undergo intrastructural fusion to produce cubic particles. A strategy based on this transformation process has been developed for the controlled formation of CPPs, the key to which is management of the number of aggregated nanowires by variation of the reaction conditions. The particle growth demonstrated here should be of significant general assistance in understanding the factors controlling CPP size and morphology. In this way, the goal of rational control of the chemical and physical properties of CPPs may become a reality.

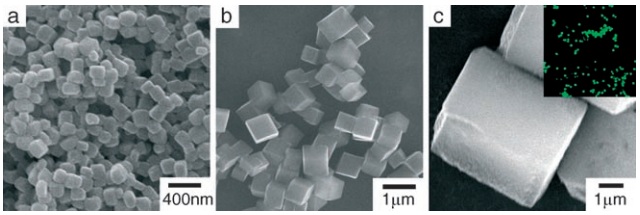

Figure 4. SEM images of the nano- and microcubes prepared under different reaction conditions. a) Zn-MS-Zn nanocubes with an average diameter of (166 ± 15) nm (s.d., $n = 100$), b) Zn-MS-Zn nanocubes with an average diameter of (600 ± 94) nm (s.d., $n = 100$), and c) Zn-MS-Zn microcubes with an average diameter of (4.86 ± 0.78) μm (s.d., $n = 100$); inset in d) is an FM image.

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[14] The nanowires seem to be flexible and can be folded; therefore, the size of the cubic particles can be smaller than the length of the wires.

