Communication

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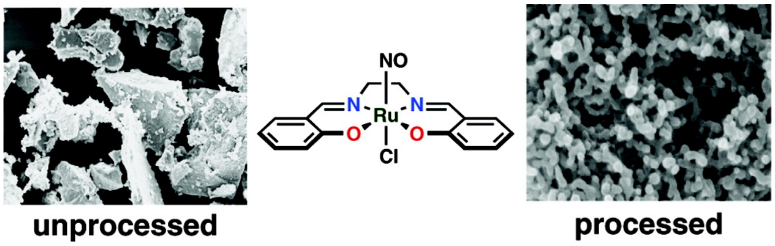

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Nanoparticulate Metal Complexes Prepared with Compressed Carbon Dioxide: Correlation of Particle Morphology with Precursor Structure

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The physical and chemical properties of nanomaterials are governed in part by size, shape, and surface morphology.[1] For example, metallic nanoclusters of sizes ranging from 1 to 10 nm have properties vastly different from their bulk forms. Few, if any, studies have reported about the characteristics of nanomaterials composed entirely of metal complexes because limited preparative methods have hindered production.[2] Herein, we report the creation of nanoparticles of metal complexes using precipitation with compressed antisolvent (PCA) technology.[3] We demonstrate that PCA is a convenient method for the preparation of metal complex-based nanostructures whose morphologies show a dependence on the structures of the molecular precursors.

The PCA technique is a semicontinuous method that regularly utilizes supercritical carbon dioxide (*sc*CO_2) as the precipitant.[4] During processing, carbon dioxide dissolves into a solution of the desired compound, as solvent diffuses out.[5] Because of the greater precipitant−solvent ratio and efficient mass transfer, substantial supersaturation is achieved, resulting in the production of small particles of the dissolved compound. Therefore, PCA technology yields relatively uniform particles with sizes ranging from nanometers to micrometers. Furthermore, this methodology offers the possibility of a one-step route to nearly residue-free and dry particles, under relatively mild operating conditions.

Various nanomaterials prepared by PCA methods have been reported, nearly all of which use organic compounds as the molecular precursors.[6] The generality of this methodology toward organic systems suggested to us that it could also be employed to make nanoparticulate metal complexes. We have investigated particle formation using complexes containing salen ligands [salen, *N,N′*-salicylidiene)-1,2-ethylene-di-aminato(2-)]; the molecular forms of these complexes have varied functions, ranging from reversible gas binders[7] to enantioselective catalysts.[8] In addition, the molecular structures of metal salen complexes can be easily modulated to probe the effects of precursor structure on nanoparticle morphology.

We have investigated the preparation of nanoparticles from neutral metal−salen complexes having different coordination geometries (Figure 1). The four-coordinate M^{II}salen (M^{II} = Ni and Co) complexes have essentially planar molecular structures that can be altered by additions of substituents onto the aromatic rings or changes to the ethylene linker, as in the optically pure [Ni^{II}salen*] complex. Further deviations from planarity were realized using [Ru(salen)(NO)(Cl)], a six-coordinate complex known for its photolytic release of nitric oxide.[9]

Details of the apparatus used to prepare the nanoparticles have been described previously.[10] The procedure, in brief, involved spraying CH_2Cl_2 solutions of the complexes and *sc*CO_2 simultaneously through a coaxial nozzle (150-μm ID for the inner tube), causing instantaneous precipitation of the complexes as processed particles.[11] Collection of the particles was achieved via a 0.2-μm filter.[12]

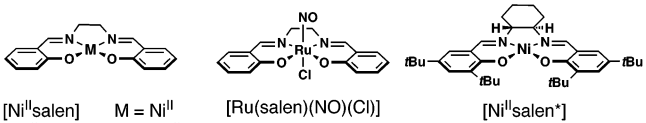

Figure 1. Precursor complexes used to prepare nanoparticles.

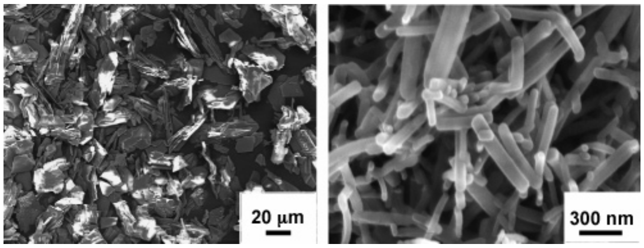

Figure 2. SEM images of unprocessed [Ni^{II}salen] (left) and the rodlike primary particles obtained from the PCA process (right).

Results from analytical and spectroscopic studies indicate that the metal complexes remain intact after being processed into particles.[12] Elemental percentages of the particles obtained from combustion and inductively coupled plasma analyses are in agreement with the ratio calculated for their corresponding parent complexes. Electronic absorbance and electron paramagnetic resonance (EPR) measurements of the processed particles are similar to those found for their molecular precursors. For instance, particles of [Co^{II}salen] have an axial X-band EPR spectrum that is similar to that of the unprocessed complex.

Scanning electron microscopy (SEM) was used to characterize the structures of the processed particles. A representative SEM image of the processed [Ni^{II}salen] complex (Figure 2) shows aggregates of primary particles having rodlike structures, with average diameter and length of 85 and 700 nm, respectively. In contrast, the SEM image of the unprocessed [Ni^{II}salen] depicted flat irregular shards with sizes ranging from micrometer to millimeter (Figure 2). Magnification of these shards did not reveal the presence of discrete primary particles; rather, only amorphous surfaces were observed. PCA-processed particles of the related cobalt complex, [Co^{II}salen], are also rods with dimensions nearly identical to those observed for the [Ni^{II}salen] particles (Figure S1).

The primary particles produced from [Ni^{II}salen*], the complex having a nonplanar, optically pure salen ligand, are shown in Figure 3. Rather than rodlike structures, the primary particles of [Ni^{II}salen*] have irregular shapes that are elongated with micrometer-sized lengths and diameters of ∼200 nm. Figure 3 also shows the SEM

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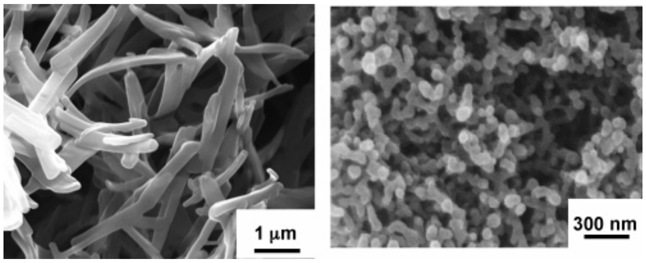

Figure 3. SEM images of PCA-processed [Ni^{II}salen*] (left) and [Ru(salen)(NO)Cl)] (right).

image of the particles obtained for [Ru(salen)(NO)(Cl)]. Unlike the previous metal salen complexes, this precursor complex has additional ligands in the axial positions, affording a nonplanar molecular structure (Figure 1). The resulting primary nanoparticles have spherical morphology with an average particle diameter of 50 nm. As with the planar salen complexes, the unprocessed [Ru(salen)(NO)(Cl)] gave amorphous shards of varied sizes and shapes (Figure S2).

Studies show that changes in PCA processing variables, such as temperature, pressure, and CO_2 flow rate, affect the size of the nanoparticles.[6] To our knowledge the possibility of manipulating particle morphology by altering the initial molecular geometry of the compound being precipitated has not been reported. Our results suggest that there indeed may be a correlation between the molecular structure of the precursor and the final morphology of PCA-processed particles *when prepared under conditions nearly identical to the other operating variables*. The planar precursors, [M^{II}salen], give rise to primary particles with rodlike structures with submicrometer-length scales and diameters of less than 100 nm. Deviations from planarity of the precursors produce substantial changes in particle structure, as illustrated by the 50-nm spherical particles prepared with [Ru(salen)(NO)(Cl)].

Analysis of previously reported particles prepared by PCA methods lends support to the importance of precursor structure. A large majority of PCA-processed particles have spherical-like morphologies; these particles always consist of compounds with nonplanar molecular structures. Conversely, rodlike structures are observed for the few cases when nearly planar organic compounds are used in processing. For instance, griseofulvin[6b] and carbamazepine,[13] two organic pharmaceuticals having basically planar molecular structures, afforded elongated micrometer-sized rods after PCA processing.

Particle formation using PCA technology is undoubtedly a complex process with several processing variables contributing to the final morphology of the particles. Our finding that one controlling variable is the molecular structure of the precursor compounds could lead to new and possibly enabling methods for manipulating the structures of molecule-based nanoparticles. This bottom-up approach would then yield particles whose structures can be varied to enhance applications in absorption and catalysis. Studies to test this idea are ongoing.

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Supporting Information Available: Full synthetic and spectroscopic details of all complexes and particles, and the SEM images of processed [Co^{II}salen] and unprocessed [Ru(salen)(NO)(Cl)]. This material is available free of charge via the Internet at http://pubs.acs.org.

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