Nonaqueous sol-gel synthesis of metal oxide nanostructures

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Metal complexes reacting in common organic solvents at a relatively low temperature can generate homogenous structures in a large variety of controlled shapes and sizes.

Nanotechnology provides solution-based routes to synthesizing—at high yield, high purity, and crystallinity—metal oxide particles that are single phase and nanosize. Often, the synthesized particles show a narrow size distribution, and controllable growth can eventually be achieved. Numerous materials have been synthesized, characterized in detail, and demonstrated or suggested for applications in various fields, including catalysis, energy storage, gas sensing, medicine, and photonics. In general, the high surface area and small size of the oxide particles open new opportunities for fundamental research and applications. Furthermore, shape tuning, surface modification, and doping (introducing impurities) modify the chemical and physical properties of the particles, thereby allowing the production of materials with tunable optical and magnetic properties.

Compared to aqueous sol-gel chemistry and surfactant-assisted routes, simpler approaches use a solvent that acts as a ligand and controls the growth of the nanoparticles without additional ligands. For example, the benzyl alcohol route can synthesize oxide nanoparticles and nanostructured hybrid materials. Although the precipitates from this route are usually not directly redispersible in a polar or apolar solvent, post-functionalization with small quantities of organic molecules often leads to a clear dispersion in different solvents. Moreover, the simple precursors allow exploration of the chemistry taking place during particle formation. In fact, these reaction mechanisms are more complex than the simple thermal decompositions claimed for nonaqueous surfactant-assisted routes. Despite that complexity, the knowledge acquired in the past few years permits a rational idea of a specific reaction’s results.

As one example of this synthesis route, we used a nonaqueous sol-gel approach in benzyl alcohol to create manganese (Mn)- and chromium (Cr)-doped zirconium oxide (ZrO$_2$) and hafnium oxide (HfO$_2$) nanoparticles. The synthesis led to high quality nanocrystals of uniform size (3–4nm) and shape, presenting a homogeneous distribution of the magnetic ion. Transmission electron micrographs (TEMs) reveal structures of Mn-doped and undoped zirconia nanoparticles (see Figure 1). Tuning the reactivity of the molecular precursors allowed homogeneous and high doping efficiency. We obtained the largest effective doping concentration—17% Mn—for HfO$_2$ from Mn(acac)$_3$. A combination of several characterization techniques

Figure 1. (A) Transmission electron micrograph (TEM) of an agglomeration of 4.38% manganese-doped zirconium oxide (Mn-ZrO$_2$) particles created with the benzyl alcohol route. (B) Higher resolution TEM of a Mn-ZrO$_2$ particle in the [110] orientation, and the power spectrum (inset). (C) TEM of pure zirconia sample. (D) Higher resolution TEM of a zirconium particle in the [110] orientation, and the power spectrum (inset).
correlated the synthesis conditions to the doping efficiency and behavior, as well as the magnetic properties of the as-synthesized nanocrystals. Indeed, researchers recently predicted that both oxides would be ferromagnetic above room temperature when doped with transition metal ions. The magnetic measurements, however, revealed a paramagnetic state for doped samples of ZrO$_2$ and HfO$_2$ for all manganese metal contents. This behavior—in apparent disagreement with the calculations—comes from the manganese oxidation state, which varies from (II) to (III) for low and high doping content, respectively. A ferromagnetic state requires Mn(IV), which could not be stabilized into zirconium and hafnium oxide.

In a second example, placing a rare-earth (RE) alkoxide and benzyl alcohol—or a derivative, such as biphenyl alcohol—in an autoclave at 250–300 $^\circ$C for a few days created materials that are ordered, lamellar, and organic-inorganic hybrids. The material consists of very thin crystalline oxide layers of the general formula RF$_2$O$_3$, which are regularly separated from each other by organic layers of intercalated benzoates or biphenolate molecules. TEMs of various benzoate and biphenolate hybrid materials reveal lamellar structure (see Figure 2). In the images, the alternate contrast of the lamellar phase produces the typical fringes and the ordered structure extends over several lamellae. The dark layers come from the oxide part, which strongly scatters incident electrons. The organic material between the oxide layers stays practically invisible. Interestingly, all RE-based materials prepared in benzyl alcohol exhibit common structural features, such as a similar interlamellar distance of about 1.8nm. The hybrid materials synthesized in 4-biphenylmethanol also show a typical lamellar structure, but with an interlamellar distance of 2.6nm because of the larger size of the intercalated biphenolate molecules. The morphology also differs. For instance, the gadolinium oxide layers are less extended compared to the ones synthesized in benzyl alcohol: see Figure 2(C). The neodymium oxide sheets extend over a larger area, forming nanowires several micrometers long with the lamellar periodicity perpendicular to the long axis: see Figure 2(D). Several characterization techniques—powder x-ray and electron diffraction, vibrational spectroscopy, solid-state nuclear magnetic resonance, and elemental analysis—revealed the structure of the hybrid materials. The oxide layers consist of three monolayers about 0.6nm thick of crystalline rare-earth oxide alternating with a double layer of benzoate or biphenolate species, which bridges to the oxide nanosheets, forming the ordered nanostructure by $\pi - \pi$ interactions.

The peculiar organic-inorganic nanostructure creates interesting optical properties in hybrid materials made of gadolinium and yttrium oxide doped with a lanthanide—europium ($\text{Eu}^{3+}$), neodymium ($\text{Nd}^{3+}$), or terbium ($\text{ Tb}^{3+}$)—and undoped neodymium and erbium oxide. For instance, the main deexcitation pathway leading to the emission of the lanthanide (Ln) ions takes place via an energy transfer from the phenyl rings of the organic molecules in between the layers to the Ln$^{3+}$ centers (i.e., the antenna effect). In comparison with standard phosphors, these materials exhibit higher radiance and luminance values, a larger excitation range with the maximum shifted toward the red, and the possibility to tune the emission chromaticity by varying the excitation wavelength.

In the past few years, researchers have developed many approaches to making synthetic metal-oxide nanoparticles. In spite of these efforts, few general synthesis routes exist. Nevertheless, we used the benzyl alcohol route to synthesize a large variety of oxide nanoparticles and hybrid materials. Unfortunately, various effect such as metal oxide formation mechanisms (e.g., condensation), intermediate products formed during the reaction, side reactions, and catalytic effects of the metal centers prevent us from predicting the reactivity of metal complexes in a particular solvent. The elucidation of these effects is the basis for developing future approaches to synthesizing multi-metal and doped-metal oxide nanoparticles, as well as hybrid materials.
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References