

Benzyl Alcohol and Transition Metal Chlorides as a Versatile Reaction System for the Nonaqueous and Low-Temperature Synthesis of Crystalline Nano-Objects with Controlled Dimensionality

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The development of general pathways for the synthesis of nanoparticles with reduced dimensionality is a main objective of nanochemistry. The anisotropy inherent in one- and two-dimensional systems is the crucial factor in determining the unique properties that these nanomaterials exhibit.¹ Consequently, the control over particle size and shape, and hence over the dimensionality, is of great interest with regard to specific applications of such materials as nanodevices. Low-dimensional systems include quantum dots (zero-dimensional), nanowires, nanorods, and nanotubes (one-dimensional), as well as layerlike entities (two-dimensional).²

Because general methods for the preparation of nanostructures with reduced dimensionality are not yet available, we focused our investigations on that objective. The synthesis approach must fulfill other requirements such as good yields and high crystallinity of the products. Non-hydrolytic sol-gel routes using alcohols and halides have been reported for the synthesis of monolithic titania³ and silica gels.⁴ We found that benzyl alcohol and TiCl_4 provide an unprecedentedly versatile reaction system for the preparation of spherical, "quasi" zero-dimensional titania nanoparticles.⁵ It allows excellent control over particle size, phase, and crystallinity. By choosing the appropriate thermal conditions and relative amounts of benzyl alcohol and titanium tetrachloride, the particle size can be adjusted in the range of 4–8 nm in small steps.⁵ In contrast to most of the sol-gel processes that lead to amorphous materials, the as-synthesized anatase particles are highly crystalline even at a reaction temperature of 40 °C.

To prove whether the use of benzyl alcohol and transition metal chlorides could be applied as a general route to nanosized, low-dimensional transition metal oxides, we also investigated VOCl_3 and WCl_6 in addition to TiCl_4 . All of these metal oxides have been intensively studied because of their outstanding chemical and physical properties. Titanium oxides are of interest for applications as gas sensors,⁶ catalysts,⁷ photocatalysts,⁸ and photovoltaic cells.⁹ Vanadium oxides are applied in catalysis¹⁰ and electrochemistry,¹¹ and tungsten oxides have been investigated for electrochromic device technology.¹²

In a typical synthesis procedure, the transition metal chloride (either 0.5 mL of TiCl_4 , 0.5 mL of VOCl_3 , or 400 mg of WCl_6) was slowly added to 20 mL of benzyl alcohol under vigorous stirring at room temperature. The reaction vessel was covered, and the sol was heated to either 40 °C (TiCl_4), 100 °C (WCl_6), or 120 °C (VOCl_3), respectively. The aging time differed depending on the precursor. For the vanadium and tungsten oxide, the aging time was 48 h. The titania needed between 7 and 14 days to react at 40 °C.⁵ The resulting suspensions were centrifuged, and the precipitate was thoroughly washed with either ethanol or tetrahydrofuran. The

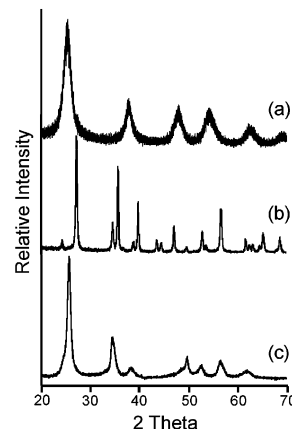


Figure 1. XRD powder patterns: (a) titanium oxide (anatase), (b) vanadium oxide, (c) tungsten oxide (tungstite).

collected material was left to dry in air overnight and finally ground into a powder. For the optical measurements, the tungsten oxide-benzyl alcohol reaction mixture was centrifuged, and the precipitate was redispersed in ethanol. After another centrifugation process, the supernatant and transparent ethanol solution was used for the luminescence and quantum yield measurement.

A general drawback of sol-gel processes is the amorphous nature of the precipitate and the need for subsequent heat treatment to induce crystallization. In our case, all of the as-synthesized products are highly crystalline. Powder X-ray diffraction (XRD) patterns of the obtained materials are shown in Figure 1. The white titania sample consists of the anatase phase TiO_2 without indication of other crystalline byproducts (Figure 1a). The peaks are relatively broad, corresponding to a particle size of 4.9 nm by Debye-Scherrer analysis.⁵ The vanadium oxide powder pattern (Figure 1b) has not yet been assigned to a known vanadium oxide phase. However, the black color of the sample points to a mixed valent oxide, and further investigations are in progress. According to EDX measurements, no elements other than vanadium and chlorine are present (V to Cl atomic ratio is about 12 to 1). Calcination at 450 °C leads to single-phase V_2O_5 . The XRD powder pattern of the yellow tungsten oxide shows broad peaks that match well with tungstite $\text{WO}_3 \cdot \text{H}_2\text{O}$ (Figure 1c).

Representative transmission electron microscope (TEM) images reveal the unique morphology differences of the oxides (Figure 2). The "quasi" zero-dimensional titania particles have diameters ranging from 4 to 5 nm (Figure 2a). The vanadium oxide sample exclusively consists of isolated particles with an ellipsoidal, "quasi" one-dimensional shape (Figure 2b). Their lengths range from 150 to 250 nm, and their diameters vary between 25 and 50 nm. These dimensions are considerably smaller than those reported

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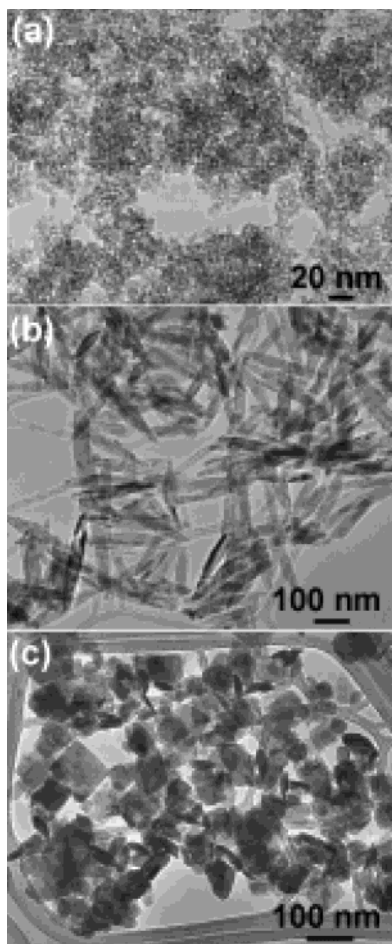


Figure 2. Representative TEM images: (a) titanium oxide nanoparticles, (b) vanadium oxide nanorods, (c) tungsten oxide nanoplatelets.

for vanadium oxide nanorods obtained using carbon nanotubes as templates (diameters of 20–55 nm, length up to 3 μm),¹³ and for vanadium oxide nanotubes synthesized with long-chain alkylamines as templates (outer diameters of 50–150 nm, length up to 15 μm).^{14,15} The tungsten oxide forms nearly square, “quasi” two-dimensional platelets (Figure 2c). The discrete, nonagglomerated particles have sides ranging from 30 to 100 nm. Side views on particles that are oriented vertically to the TEM copper grid reveal that the thickness is between 5 and 10 nm.

Illumination of an ethanol solution containing tungsten oxide particles at 365 nm (UV lamp) gives a strong blue luminescence at room temperature. Only little is reported in the literature on photoluminescence (PL) of WO_3 ,^{16–18} and, to the best of our knowledge, this is the first observation of blue PL of WO_3 nanoparticles at room temperature. The PL emission and excitation spectra of this sample are shown in Figure 3. Excitation of the sample at 380 nm (in the center of the excitation peak) results in a broad emission peak centered at around 425 nm (Figure 3B), which we assign to a band-to-band transition¹⁷ within the crystalline WO_3 nanoparticles. The PL quantum efficiency was estimated to 5% by comparing the integrated emission of the sample with that of the standard quinine sulfate in sulfuric acid. The excitation spectrum of the emission at 425 nm (Figure 3A) exhibits a

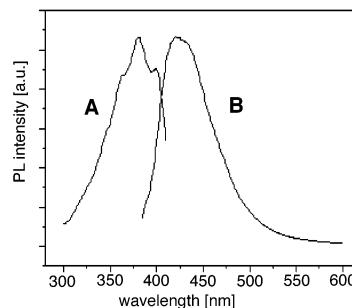


Figure 3. Photoluminescence excitation (A) and emission (B) spectra of tungsten oxide nanoparticles.

maximum at 380 nm (3.26 eV) and two shoulder peaks at 364 nm (3.41 eV) and 396 nm (3.13 eV). These results are in the range of reported band gap energies;^{16,19} however, a detailed study of the photophysical properties of the WO_3 sample is in progress.

This study illustrates the successful synthesis of high-quality transition metal oxide nanoparticles via a nonaqueous sol–gel route at low temperatures. The reaction between transition metal chlorides and benzyl alcohol leads to low-dimensional particle shapes such as nearly spherical titania nanoparticles, vanadium oxide nanorods, and tungsten oxide nanoplatelets. The process is simple, allows a scale-up in gram quantities, and leads to highly crystalline materials with novel optical properties.

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