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In Situ One-Pot Synthesis of 1-Dimensional Transition Metal Oxide Nanocrystals

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One-dimensional colloidal metal oxide nanocrystals are of great importance in materials chemistry, but reports on these materials are rare due to lack of well-defined synthetic protocols. In this paper, we present a general and highly effective one-pot synthetic protocol to produce 1-dimensional nanostructures of transition metal oxide (e.g., $W_{18}O_{49}$, TiO_2, Mn_3O_4, and V_2O_5) through thermally induced crystal growth processes from a mixture of metal chloride and surfactants.

The development of general synthetic methods to produce colloidal inorganic nanocrystals with a controlled size and dimensionality is an important subject in materials chemistry. They exhibit unique size and shape dependent optical, magnetic, and electronic properties and therefore can be utilized as building blocks for the next generation nanodevices.[1−3] Especially, recent studies have been focused on the synthesis of 1-dimensional (1-D) nanostructures[4−7] including nanorods and nanowires with their advantages of exceptional anisotropic electronic properties as well as facile applicability for the construction of 2-terminal circuit devices.[8,9]

Until now, most of these 1-D nanostructures are based on II−VI semiconductors such as CdSe[4,6] and ZnO.[10] Despite their technological importance of transition metal oxide materials, solution based studies on the collidal metal oxide nanocrystal synthesis have been limited on the 0-D structures[11−18] and the report of 1-D metal oxide nanocrystal[19−24] is rare. Recently, a multistep approach that includes the metallic nanocrystal formation and subsequent oxidation processes with additional oxidants has been developed for the synthesis of $BaTiO_3$,[7] MnO,[19] and WO_{3-x}[21,22] nanocrystals. However, such a method, in general, includes complicated or delicate synthetic procedures and therefore has some difficulty in being extended to other metal oxide systems. Peng et al.[15] and Hyeon et al.[18] independently utilized two step fabrication procedures, which required a precursor synthesis of metal−fatty acid complex to generate magnetic metal oxide nanocrystals. This protocol is very useful for the 0-D nanostructures, but the yield for nanorods is relatively low and also this fabrication method is mostly focused on the magnetic metal oxide systems.

In this paper, we report a general and highly effective one-pot synthetic protocol to produce 1-D nanostructures of transition metal oxide which include $W_{18}O_{49}$, TiO_2, Mn_3O_4, and V_2O_5.

From the previous studies on the shape controlled synthesis of semiconductor[25−27] and magnetic nanocrystals,[28,29] it has been known that the synthetic approach for 1-D nanocrystals must fulfill the following requirements: the development of a well-defined precursor system that can generate stable monomers, sufficiently high monomer concentration to maintain the kinetically controlled growth regime, and the proper choice of surfactants that can modulate the energy of specific crystal faces. Here we present that the simple reaction of metal chloride, one of the most basic compounds of the transition metals, with a mixture of oleic acid and oleylamine surfactants can satisfy the requirements and efficiently yield 1-D transition metal oxide nanocrystals with high crystallinity and narrow size distribution.

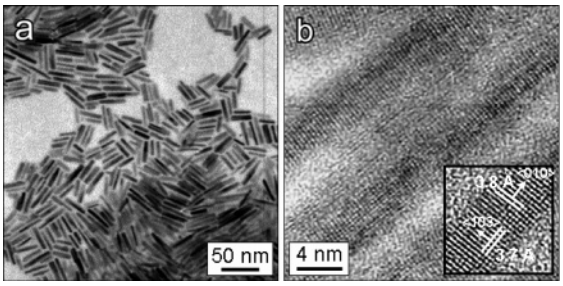

Figure 1. TEM (a) and HRTEM (b) of tungsten oxide nanorods. Inset: magnified HRTEM image showing lattice fringes of $W_{18}O_{49}$ nanorods.

In a typical synthesis, WCl_4 (0.1 mmol) was dissolved in oleic acid (5.5 mmol) and oleylamine (1.8 mmol) and the resulting solution was heated to 350 °C at a heating rate of 10 °C/min under an argon atmosphere. After 60 min, the reaction was quenched by the addition of cold toluene (4 mL) and treated with acetone to precipitate dark blue colored flocculates that were separated by centrifugation. The resulting powder is well dispersed in hydrophobic solvent such as toluene and dichloromethane. Transmission electron microscopic (TEM) analysis (Figure 1a) shows well-defined rod shaped nanocrystals of 4.5 ± 0.6 nm in width and 28.3 ± 5.1 nm in length. The control of aspect ratio of nanorods is also possible by changing the growth time and the concentration of oleylamine. When the nanocrystals were aged for 2 h, the nanocrystals elongated further along their long axis to 37.2 ± 5.4 nm whereas the width of nanorods was almost identical (see Supporting Information). An intense and sharp ⟨010⟩ peak in X-ray diffraction (XRD) patterns (see Supporting Information) also reveals that the nanorods anisotropically are grown along the *b*-axis of the monoclinic structure of $W_{18}O_{49}$.[30] Consistently, a high-resolution TEM study (Figure 1b) indicates that the $W_{18}O_{49}$ nanorods have

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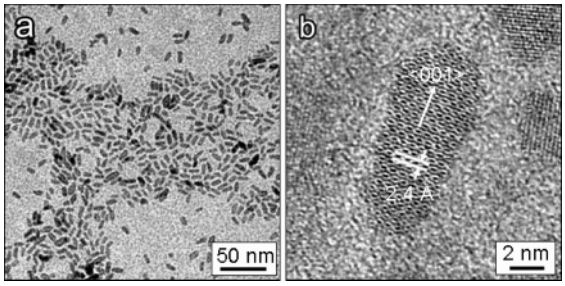

Figure 2. TEM (a) and HRTEM (b) of manganese oxide nanorods.

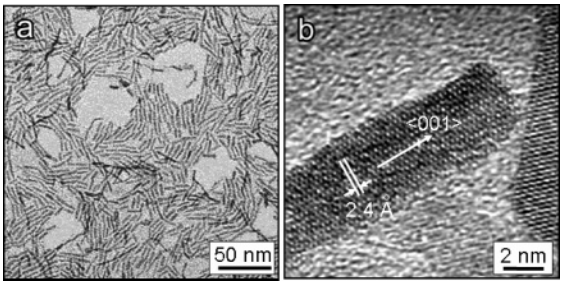

Figure 3. TEM (a) and HRTEM (b) of titanium dioxide nanorods.

single crystallinity in the monoclinic structure and the lattice fringes that orient in the ⟨010⟩ direction with an interplanar distance of 3.78 Å reveal the nanorod is elongated along the ⟨010⟩ direction.

To test whether the synthetic protocol used for the tungsten oxide nanorod synthesis could be applicable for other metal oxide nanocrystals, we utilized manganese chloride as a precursor for the manganese oxide nanocrystal synthesis. The reaction procedure is very similar to that of tungsten oxide nanorod synthesis. $MnCl_2$ (0.5 mmol) was dissolved in oleic acid (0.5 mmol) and oleylamine (6.5 mmol) and the resulting solution was heated to 270 °C at a heating rate of 10 °C/min under argon atmosphere. After 20 min, the reaction was quenched by the addition of cold toluene (4 mL) and treated with acetone to precipitate dark brown flocculates that were separated by centrifugation. The resulting powder is very soluble in typical hydrophobic solvents. Figure 2 shows the TEM and HRTEM images of nanocrystals obtained. Similar to the case of tungsten oxide nanocrystals, 1-D structures of manganese nanocrystals with 3.1 ± 0.3 nm in width and 8.4 ± 1.2 nm in length were observed with the aspect ratio of ~3. The control of aspect ratio is also possible by changing the growth temperature. The nanocrystals grown at 350 °C are rice shapes with 6.9 ± 1.4 nm in width and 14.8 ± 2.4 nm (aspect ratio: ~2). XRD (see Supporting Information) and HRTEM (Figure 2b) analyses of the nanocrystals obtained reveal that these nanocrystals are high-quality single crystalline Mn_3O_4 nanocrystals with the tetragonal symmetry.[30] The nanocrystals are elongated along the ⟨001⟩ direction with an interplanar distance of 2.4 Å that is well matched with the known value of the tetragonal Mn_3O_4 structure.

The reaction of metal halide with a mixture of oleic acid and oleylamine can be further applicable for the titanium dioxide where titanium chloride was used as a titanium precursor. $TiCl_4$ (0.5 mmol) was mixed with oleic acid (1 mmol) and oleylamine (6.5 mmol). The reaction mixture was heated to 290 °C at a heating rate of 10 °C/min under argon. After 2 min, the reaction was quenched by the addition of 6 mL toluene and then the reaction mixture was allowed to cool to room temperature. White TiO_2 nanocrystals were isolated by the addition of an excess amount of acetone followed by centrifugation. The resulting powder obtained was redissolved in 10 mL of toluene and reprecipitated with 40 mL of ethanol. The TEM and HRTEM analyses of TiO_2 nanocrystals are represented in Figure 3. TiO_2 nanocrystals are highly anisotropic with the aspect ratio of ~7. According to the XRD analysis, these nanocrystals have a tetragonal anatase structure.[30] The HRTEM image (Figure 3b) of the nanorods also shows that these nanocrystals have single crystallinity and are preferentially grown along the ⟨001⟩ direction with an interplanar distance of 2.4 Å, which is consistent with the known value of the anatase TiO_2 structure.

In general, several parameters including the crystalline phase of nucleating seeds, surface energy, kinetic vs thermodynamic growth, and selective adhesion processes of capping ligands are known to be related to anisotropic growth of nanocrystals.[31] Especially, because our metal oxide nanorods have crystallographically anisotropic structures, surface energy can play a crucial factor. Both tetragonal TiO_2 and Mn_3O_4 nanocrystals have a {001} surface with higher energy, whereas monoclinic $W_{18}O_{49}$ nanocrystals possess a {010} surface with higher energy.[32] Because the growth rate is exponentially proportional to the surface energy under the kinetic growth process, the energy difference between the higher energy surface and other lower energy surfaces can promote preferential growth along the ⟨001⟩ directions of TiO_2 and Mn_3O_4, and the ⟨010⟩ direction of $W_{18}O_{49}$, respectively. This kind of kinetically driven growth process can be facilitated by efficient and stable metal oxide monomer formation from the reaction of metal halide and oleic acid. Presumably, the crystal growth process involves in situ formation of metal chloride−oleate complex and a subsequent acyl halide elimination process,[33] which results in stable metal oxide monomers and drives the anisotropic growth of the metal oxide nanocrystals along the high energy crystallographic direction.

In addition to $W_{18}O_{49}$, Mn_3O_4, and TiO_2, we further tested the general applicability of the synthetic protocol to V_2O_5 nanocrystals where 1-D shaped nanocrystals could also be obtained although the growth condition to produce 1-D structures of these materials is not fully optimized yet (See Supporting Information). In summary, the method developed here is versatile, reproducible, and simple, and therefore, it can be used as a new protocol for a variety of 1-D metal oxide nanocrystals in a potentially large synthetic scale.

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Supporting Information Available: Experimental procedures, TEM images, XRD, and absorption spectra analyses of $W_{18}O_{49}$, Mn_3O_4, TiO_2, and V_2O_5 nanocrystals. This material is available free of charge via the Internet at http:// pubs.acs.org.

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