

Fabrication of Size and Shape Controlled Cadmium Oxide Nanocrystals

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Metal oxide nanocrystals have attracted considerable attention owing to their specific properties and potential application in various fields. For instance, metal oxide nanocrystals are used as catalysts¹ and MR contrast agents² as well as in the treatment of hyperthermia;³ they are also used in bioseparation⁴ and in the preparation of transparent conducting oxide materials.⁵

For use in scientific applications, metal oxide nanocrystals were entirely synthesized uniform size and shape because nanocrystals properties depend on their size and shape, which were different nature their bulk counterpart. For instance, in the case of CdSe quantum dots, the emission color changes from red to blue depending on the nanocrystals size.⁶ The surface plasmon resonance of octahedral gold nanocrystals is red-shifted to a greater extent as compared to that of spherical gold nanocrystals, when the nanocrystal size is the same in both cases.⁷ Therefore, precise control of the nanocrystal size and shape is very important.

Cadmium oxide is a II-VI binary oxide semiconductor with a direct bandgap of 2.27 eV and an indirect bandgap of 0.55 eV in the bulk state.⁸ CdO is a promising candidate for a transparent conducting oxide material because it has a simple rock-salt crystal structure, high carrier mobility, and high conductivity, which is due to the nonstoichiometric property which resulted from oxygen vacancies⁹ in cadmium oxides.

Although CdO nanocrystals have numerous potential applications, very less research has been carried out on the synthesis and characterization of these nanocrystals. Recently, their importance as a transparent conducting oxide material has been increased gradually, they have been synthesized and studied by a few research groups. Ghoshal et al. synthesized micro-octahedral CdO crystals and measured their electrical resistivity,⁹ and the Zhang group synthesized hexagonal CdO nanodisks with a nanoporous structure.¹⁰

Herein, we report the synthesis of colloidal CdO nanocrystals with various sizes and shapes. CdO nanocrystals were synthesized by thermal decomposition of the precursor, cadmium(II) acetylacetonate ($\text{Cd}(\text{acac})_2$). Size and shape control was achieved by adjusting the thermal decomposition temperature and the surfactant ratio (the oleic acid/oleylamine ratio). The detailed procedure for the synthesis of CdO nanocrystals using oleic acid is as below.

$\text{Cd}(\text{acac})_2$ (93 mg, 0.3 mmol; Strem), oleic acid (254 mg, 0.9 mmol; TCI), and 1-octadecene (10 mL, Aldrich) were loaded in a 50-mL three-necked flask, and the mixture was

degassed under vacuum at 100 °C for 2 h. Subsequently, the temperature was raised to 300 °C, and the mixture was stirred at this temperature for 30 min under N_2 atmosphere. CdO nanocrystals were precipitated from the reaction solution by adding isopropanol and separated by centrifugation.

Figure 1(a) shows the transmission electron microscopy (TEM) images of the synthesized CdO nanocrystals; the nanocrystals are octahedral and the length of octahedron corner is 70 nm. Figure 1(b) shows the tilted TEM image of the nanocrystals shown in Figure 1(a). The three-dimensional octahedral structure in the inset matches well with the TEM image, confirming that the as-synthesized CdO nanocrystals are octahedral in shape. The powder X-ray diffraction (XRD) pattern of the CdO nanocrystals shows five prominent peaks, which are indexed to the (111), (200), (220), (331), and (222) planes of a cubic rock-salt structure (Figure 1(d)). The abnormally high intensity of the (111) plane peak indicates that the as-synthesized CdO nanocrystals are octahedral in shape. Cubic and octahedral crystals are defined by the R value, which is the ratio of (100) and (111) peak intensities, as proposed by Wang.¹¹ The R value of the as-synthesized CdO nanocrystals [2.37] is larger than that of a perfect octahedron [1.73], indicating that the distance between the horizontal edges in an octahedral

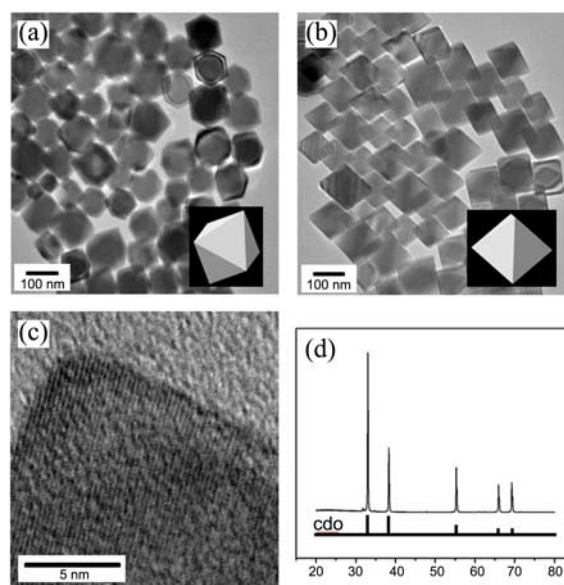


Figure 1. TEM image of CdO; (a) octahedral CdO, (b) tilted TEM image of Figure 1(a), and (c) high-resolution TEM images of Figure 1(a). (d) X-ray diffraction patterns of octahedral CdO.

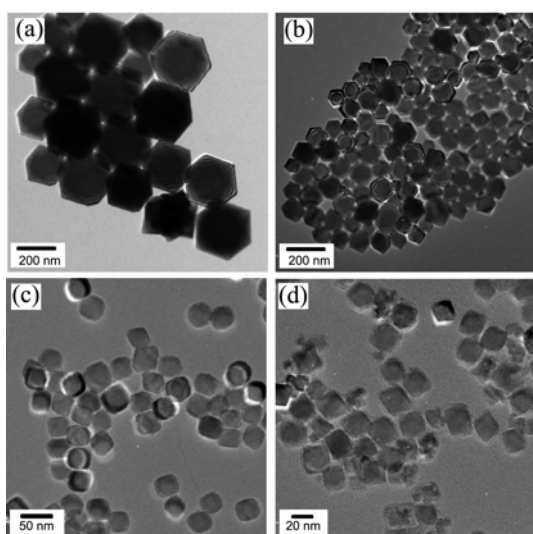


Figure 2. TEM image of CdO nanocrystals which aged at (a) 290 °C, (b) 300 °C, (c) 310 °C, and (d) 320 °C, respectively.

CdO crystal is much different from that between the vertical edges.

The CdO nanocrystals were grown by controlled heating at 290 °C, 300 °C, 310 °C, and 320 °C (Figure 2). At high temperatures, 20 nm sized nanocrystals were formed, while at low temperatures, 200 nm octahedral nanocrystals were formed. It could be easily hypothesized that the aforementioned size difference is due to the difference in the number of nuclei generated at different reaction temperatures. Because of the larger number of nuclei generated under high-temperature conditions at constant reactant concentration, nuclei growth was restricted. The effect of surfactant concentration on the crystal size was found to be similar to that of temperature: the nanocrystal size was inversely proportional to the surfactant concentration.¹²

To control the size and shape of the CdO nanocrystals, the synthetic reaction was carried out using various oleic acid/oleylamine mole ratios, 2:1, 1:2, and 0:3. An increase in the oleylamine amount in the surfactant not only led to the formation of small CdO nanocrystals but also changed the nanocrystal shape from octahedral to spherical. The changes resulted from the different binding abilities on the nanocrystals between oleic acid and oleylamine.¹³ In addition, it was thought that oleic acid preferentially adsorb on (111) plane of the CdO nanocrystal and that the restricted growth in this plane led to the formation of octahedral CdO nanocrystals. On the other hand, oleylamine did not show preferential coordination in any plane of the nanocrystals, and therefore, spherical nanocrystals were formed (Figure 3). The XRD data for the CdO nanocrystals synthesized using oleylamine revealed that the nanocrystals were mixture of CdO and Cd nanocrystals, which were formed by the reduction of oleylamine. Oxygen atoms in CdO nanocrystal are originated from CO₂ molecules which are generated by thermal decomposition of acetylacetonate ligand in the Cd(acac)₂ precursor.¹³

In summary, size- and shape-controlled CdO nanocrystals

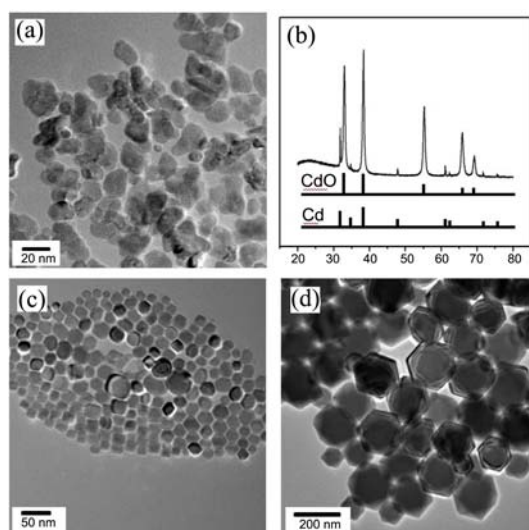


Figure 3. TEM images of CdO nanocrystals using (a) oleylamine only, oleic acid to oleylamine ratio (c) 1/2 and (d) 2/1. (d) X-ray diffraction pattern of (a).

were obtained *via* a simple thermal decomposition method in which the decomposition temperature and surfactant composition (oleic acid/oleylamine ratio) were appropriately adjusted. Oleic acid facilitated the formation of octahedral CdO nanocrystals by effecting growth rate control in a given crystal plane through selective binding. Further research must be carried out to clarify the applications of the synthesized CdO nanocrystals.

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