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# Room-temperature Synthesis of $CdMoO_4$ Nanooctahedra in the Hemline Length of 30 nm

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Uniform single-crystal $CdMoO_4$ nanooctahedra in the hemline regime of 30 nm have been synthesized via a reverse-microemulsion route at room temperature. The as-prepared products were characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), and selected area electron diffraction (SAED). Room-temperature photoluminescence (PL) measurement exhibited a blue emission peaking at 438 nm under the 360 nm excitation, which is mainly attributed to the existence of intrinsic distortions into the $[MoO_4]$ tetrahedron moiety in the lattices.

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Recently, metal molybdates have received increasing interest due to photoluminescence, usefulness as industrial catalysts, unique structures, and so forth.[1] Particularly, the controlled preparation of metal molybdate particles with different sizes and morphologies has been an exciting field because of the influence of particle size and morphology on the properties of materials. Under these circumstances, metal molybdate particles with different sizes and morphologies have been prepared, including $SrMoO_4$ nanowires and flower-like mesocrystals,[2,3] thin $BaMoO_4$ film[4] and flower-like nanostructures,[5] $PbMoO_4$ dendrites,[6] and doughnut-shaped $CaMoO_4$ microstructures.[7] As an important metal molybdate, cadmium molybdate ($CdMoO_4$) has attracted considerable attention owing to its excellent optical, chemical, and electronic structural properties.[8] A few efforts have been devoted to the exploration of approaches for the fabrication of $CdMoO_4$ micro/nanostructures. For example, Qian et al. have successfully synthesized octahedral $CdMoO_4$ microparticles via a microemulsion-mediated hydrothermal route.[9] Zhen and co-workers have prepared hollow $CdMoO_4$ microspheres by a surfactant-free aqueous solution route at room temperature.[10] However, these methods need higher temperature or complicated manipulations. Moreover, these $CdMoO_4$ particles are mostly microcrystals. Nanosized $CdMoO_4$ crystals have been rarely studied. Thus, it is significant to explore appropriate methods to synthesize $CdMoO_4$ in nanoscale and control their morphology under milder conditions.

As we all know, simple chemical reactions in reverse micelles and microemulsions have been shown to be powerful in controlling the size and shape of inorganic nanocrystals.[11] Reverse microemulsions are colloidal "nanodispersions" of water in oil stabilized by a surfactant and cosurfactant film.[12] The morphology and size of water pool can be rationally controlled by adjusting the experimental conditions. Subsequently, these nanoscale water pools can provide ideal spatially constrained microreactors for the formation of controlled size and morphology of inorganic nanoparticles. Specifically, various inorganic nanocrystals, including metal, semiconductors, and inorganic salt have been synthesized in reverse-microemulsion media.[13] We also prepared $BaMoO_4$ nanooctahedra by microemulsion approach.[14] Herein, we further report single-crystal octahedra of tetragonal $CdMoO_4$ with hemline length of 30 nm by a reverse-microemulsion method, and its luminescent properties are also presented.

Typically, two 13.20-mL portions of microemulsion solutions were prepared by adding 1.20 mL of 0.1 M aqueous $Cd(NO_3)_2$ and $Na_2MoO_4$ solutions into a *n*-octanol/Triton X-100 (OP)/cyclohexane system (*n*-octanol/OP = 3.90, water contents ($\omega$) = water/OP = 20), respectively. After 30 min of stirring, the above two different microemulsion solutions with equivalent volume were mixed slowly and stirred for another 10 min. The resulting mixture was aged without stirring for 48 h at room temperature. The precipitate was washed with acetone, deionized water, and absolute ethanol to remove surfactant or other impurities.

Figure 1a shows the XRD patterns of the as-prepared samples. All the reflections can be readily indexed to a pure tetragonal structure of $CdMoO_4$, which are well consistent with the standard data (JCPDS Card No. 07-0209). The energy-dispersive X-ray (EDX) spectra (Figure 1b) indicate that the samples mainly contained O, Si, Mo, and Cd. The Si signals are from the Si substrate, the other three elements come from the sample.

Figure 2a is typical FESEM image of $CdMoO_4$ particles, which are composed of high yield uniform polyhedral crystals. To examine the morphology of the polyhedral crystals, low-magnification TEM image was recorded (Figure 2b), it can be seen that the structures are uniform octahedral with edge length of 30 nm, which can be further confirmed from the high-magnification TEM image (Figure 2c). The high-resolution TEM (HRTEM) image (Figure 2d) shows lattice planes with spacing of 3.05 and 2.58 Å, corresponding to the (112) and (200) planes, respectively. The SAED pattern (Figure 2e) can be indexed as tetragonal $CdMoO_4$ nanooctahedra. The clear lattice fringes and perfect diffraction pattern indicate that the nanooctahedra are single crystals.

Figure 3 lists PL spectra of the octahedral $CdMoO_4$ nanoparticles. It is clear that $CdMoO_4$ samples exhibit a strong and

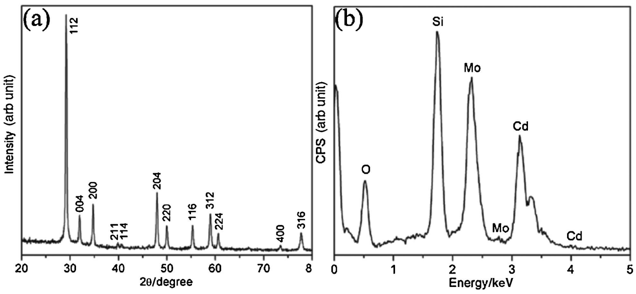

**Figure 1.** (a) XRD pattern and (b) EDX spectra of $CdMoO_4$ nanooctahedra.

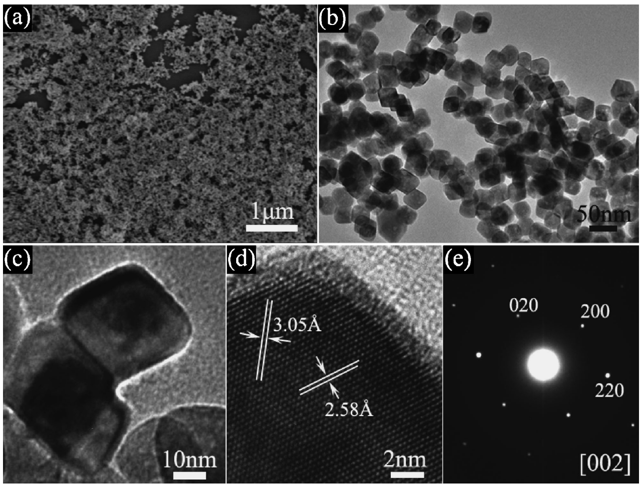

**Figure 2.** (a) FESEM, (b) low-magnification and (c) high-magnification TEM, (d) HRTEM and (e) the corresponding SAED of $CdMoO_4$ synthesized at room temperature for 48 h.

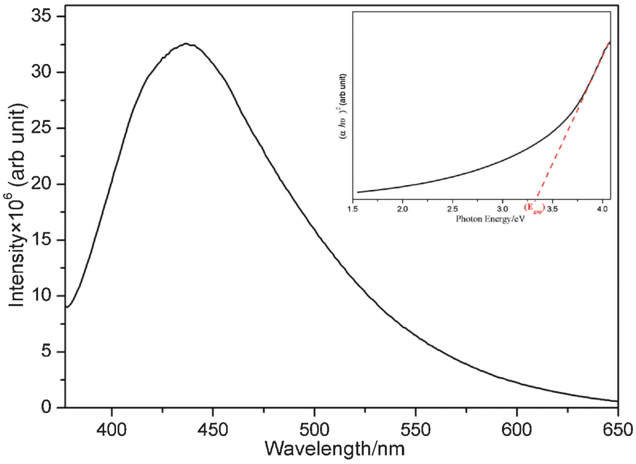

**Figure 3.** PL spectra and inset plots the band gap of $CdMoO_4$ octahedra.

broad emission peak centered at 438 nm with an excited wavelength of 360 nm (3.34 eV, inset in Figure 3). These emissions are different from the results of the earlier reports.[10,15] Generally, the measured emission spectra of metal molybdate are mainly attributed to the charge-transfer transitions with the $MoO_4{}^{2-}$ complex.[16] In addition, according to the previous researches, the PL properties of metal molybdate greatly depend on their particle size or morphology.[2,17] Therefore, we may infer that the PL pattern of the as-grown $CdMoO_4$ octahedra is chiefly ascribed to intrinsic distortions on the $[MoO_4]$ tetrahedron groups, particle sizes, and morphology. A more detailed investigation on the properties of $CdMoO_4$ octahedra with different sizes is currently in progress.

To better understand the formation of $CdMoO_4$ nanooctahedra, many experiments have been carried out under different conditions. Although the exact mechanism of the formation is not clear yet, it is reasonable to believe that the intrinsic anisotropy of crystals, the surfactant OP, and the water content as well as the reagent concentration play vital roles in the final formation process. For instance, when the water content was set at 5 or the reagent concentration changed to 0.05 M, the hemline regimes of the octahedral particles are 200 and 70 nm (not shown here), respectively. Further studies on the growth of the $CdMoO_4$ nanooctahedra are underway.

In summary, well-shaped $CdMoO_4$ nanooctahedra have been successfully prepared by a reverse-microemulsion method. The surfactant OP, $\omega$, and the reagent concentration show significant effects on the sizes and morphologies of the products. XRD, SEM, TEM, and SAED were employed to demonstrate the high purity and good crystallinity of the $CdMoO_4$ octahedra. The $CdMoO_4$ octahedra exhibit strong emission, which is mainly attributed to intrinsic distortions on the $[MoO_4]$ tetrahedron groups, particle sizes, and morphology.

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