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Growth of $CdWO_4$ Nanorods and Nanowires by a Surfactant Directed Adsorption Mechanism

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$CdWO_4$ nanorods and nanowires were obtained from surfactant directed adsorption of cetyltrimethylammonium bromide (CTAB) and sodium dodecylbenzenesulfonate (SDBS), respectively, under hydrothermal conditions. The products were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), and high-resolution transmission electron microscopy (HRTEM). TEM and HRTEM analyses confirm that the $CdWO_4$ nanorods synthesized in the presence of the cationic surfactant CTAB have an average diameter of 36 nm and lengths of up to 1 μm, with a preferential growth direction along [100], and the $CdWO_4$ nanowires grown in the presence of the anionic surfactant SDBS are around 12 nm in diameter and several micrometers in length, with a growth direction along [110]. Their luminescent properties measured at room temperature show that the nanorod-like $CdWO_4$ has a stronger PL peak at 460 nm than the nanowire-like structures. A surfactant directing adsorption mechanism has been proposed.

One-dimensional (1D) nanostructures, such as nanorods, nanowires, nanotubes, and nanobelts, have attracted intense interest over the past decade because of their distinctive geometries, novel physical and chemical properties, and potential applications in nanodevices.[1] At present, a variety of efficient synthetic strategies for 1D nanostructures, such as the vapor–liquid–solid (VLS) method,[2] vapor–solid (VS) growth,[3] supercritical fluid–liquid–solid (SFLS) process,[4] template-directed growth and diverse solution-based methods,[5] have been developed. Xia et al.[6a] and Rao et al.[6b] have recently published comprehensive reviews on the synthesis of 1D nanostructures. As well, low-temperature solution-phase synthesis has been proposed as an attractive approach toward 1D nanosized materials with high crystallinity.[4a,6a,7] Controlling the diameter and length of 1D objects is a challenging goal of contemporary materials science.[8] On the other hand, the reaction conditions that affect the growth of 1D materials also provide information about the growth mechanism for 1D materials.

Among metal tungstates, cadmium tungstate ($CdWO_4$) nanocrystals, which have a monoclinic wolframite structure,[9] are considered to be highly functional materials because of their high average refractive index,[10] low radiation damage, low after-grow to luminescence and high X-ray absorption coefficient.[11] They can be used, for instance, as an X-ray Scintillator,[12] and have the potential to be used as an advanced medical X-ray detector in computerized-tomography.[13] Various preparation methods have been developed to synthesize cadmium tungstate, such as a high-temperature solid-state reaction for powders,[14] a flux method for whisker growth,[15] the Czochralski method for single-crystal growth,[16] and pulsed laser ablation for growth of thin films of $CdWO_4$ using PL less targets.[17] In addition, the procedures that have been reported concerning the preparation of nanostructured $CdWO_4$ in solution have mainly involved hydrothermal processes affording $CdWO_4$ nanorods,[18] a polymer-controlled route to 1D and 2D very thin nanocrystals[19] and a route using lamellar inorganic-surfactant precursors which affords $CdWO_4$ nanowires.[20] However, the detailed mechanism concerning morphology control of $CdWO_4$ has seldom been systematically investigated.

Up to now, there have been a few reports describing how ions or molecules in solution can affect the shape of a nanocrystal.[21] Pileni et al. reported[21a] that the formation of nanorods and cubes are explained in terms of anion adsorption on the (111) and (100) faces, respectively. By replacing chloride with other ions, the morphology of copper nanocrystals drastically changes. Selective adsorption of SO_4^{2-} onto different crystal facets causes nanoparticles to grow with NaV_6O_{15} and $Na_2V_6O_{16}\cdot 3H_2O$ ultimate nanowire morphology.[21b] Nanorods with well-controlled diameters and lengths can also be produced by employing various surfactants in the synthetic system.[21c] This indicates that preferential adsorption of molecules and ions in solution onto different crystal facets directs the growth of nanoparticles by controlling the growth rates along different crystal axes.

A crystallographic study on $CdWO_4$ indicated that the charge densities on the (001), (010), and (100) planes are different from each other. The projected structures of the different crystal planes in $CdWO_4$ are shown in Fig. 1. Figure 1a is the atom distribution in the (001) plane, which shows that Cd, W, and O atoms are exposed on the surface of the plane. Figure 1b depicts the atom distributing of the (010) plane, also indicating that Cd, W, and O atoms are exposed. Figure 1c shows the

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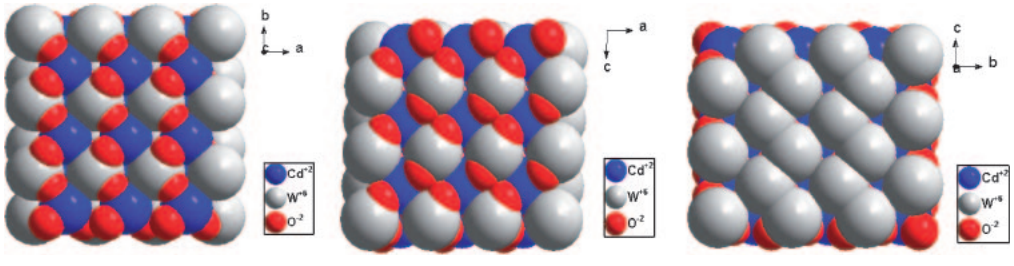

(a) (b) (c)

Fig. 1. Structures of $CdWO_4$ projected along different planes (3 × 3 × 3 lattices). (a) (001) plane; (b) (010) plane; (c) (100) plane.

atom distributing of the (100) plane, and in this case, W atoms are mainly exposed. The crystal planes (001) and (010) should, therefore, have different charge densities than the (100) plane has. The (100) crystal plane has a positive charge aggregation, which is consistent with reported results.[22] Thus, the crystal facets should selectively interact with species having different charges during crystal nucleation and growth, which may change the way that the crystal grows, i.e., causing an oriented growth of $CdWO_4$ crystals. Therefore, if one selects a species (molecules or ions) that can selectively adsorb onto a specific crystal face of $CdWO_4$, the morphology of $CdWO_4$ can be controlled. To test this strategy, we selected two different surfactants CTAB and SDBS as directing adsorption agents, which produce CTA^+ cations and DBS^- anions in solution, respectively, and studied the hydrothermal synthesis of $CdWO_4$ crystals. As a result, single-crystal $CdWO_4$ nanorods were obtained using the cationic surfactant CTAB, and single-crystal $CdWO_4$ nanowires were prepared using the anionic surfactant SDBS. As well, it was determined that the nanorods and nanowires have different growth directions.

Experimental

Synthesis of $CdWO_4$ Nanorods and Nanowires. All analytical grade reagents were purchased from Shanghai Chemical Company and used without further purification.

In a typical procedure, 1 mmol of sodium tungstate bihydrate ($Na_2WO_4 \cdot 2H_2O$) and 1 mmol of cadmium chloride ($CdCl_2$) were put into a Teflon-lined stainless steel autoclave with a 60 mL capacity, and then were dissolved in 5 mL of distilled water, followed by the addition 45 mL of *n*-octanol. Finally, 0.5 mmol of cetyltrimethylammonium bromide (CTAB) or sodium dodecylbenzenesulfonate (SDBS) was added to the mixture. The autoclave was sealed and maintained at 180 °C for 16 h. The system was then allowed to cool to room temperature. The grey-white precipitate was collected by filtration and washed several times with distilled water and absolute ethanol. The final products were dried under vacuum at 60 °C for 2 h. $CdWO_4$ nanoparticles were obtained when no surfactant was used.

Characterization of $CdWO_4$ Nanorods and Nanowires. X-ray powder diffraction (XRD) patterns were recorded on a Philips X′ Pert PRO SUPER X-ray diffractometer using Cu Kα radiation ($\lambda = 1.5418$ Å). Transmission electron microscopy (TEM) images were taken using a Hitachi Model H-800 transmission electron microscope. High-resolution transmission electron microscopy (HRTEM) images were taken using a JEOL-2010F high-resolution transmission microscope operated at 200 kV. Luminescence spectra were acquired by using a Hitachi 850 fluorescence spectrometer with a Xe lamp at room temperature.

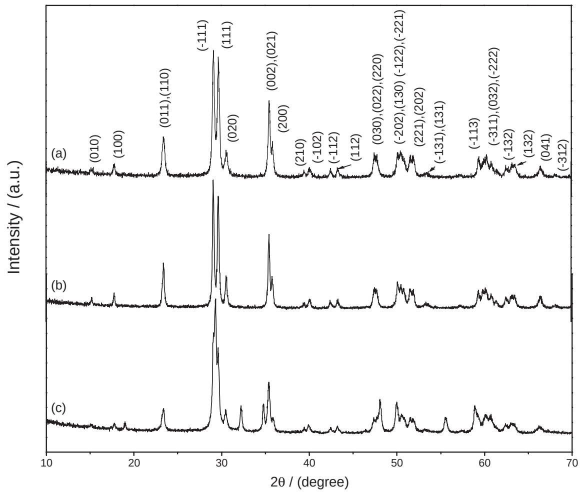

Fig. 2. XRD patterns of $CdWO_4$. (a) Nanorods; (b) nanowires; (c) nanoparticles.

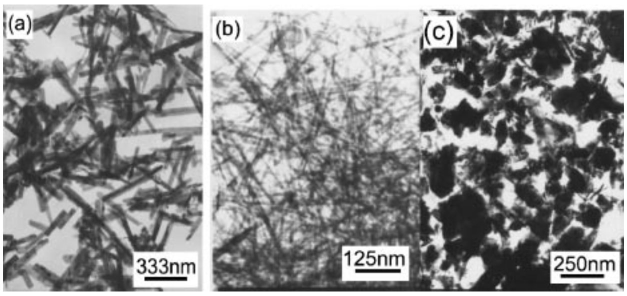

Fig. 3. TEM images of $CdWO_4$. (a) Nanorods; (b) nanowires; (c) nanoparticles.

Results and Discussion

XRD patterns of the $CdWO_4$ nanorods and nanowires obtained with different surfactants are shown in Figs. 2a and 2b. Figure 2c shows XRD pattern of the $CdWO_4$ nanoparticles synthesized in the absence of a surfactant. All of the diffraction peaks in Fig. 2 could be indexed to a monoclinic phase of $CdWO_4$ [space group: $P2/c$ (No. 13)], which is in agreement with the literature results (JCPDS No. 80-0140). No characteristic peaks due to impurities in Figs. 2a and 2b were observed, indicating that the 1D $CdWO_4$ nanostructures were pure. However, a few unknown peaks were observed in Fig. 2c, and we speculate that they are due to CdO and $Cd(OH)_2$.

Figure 3 shows TEM images of the $CdWO_4$ products ob-

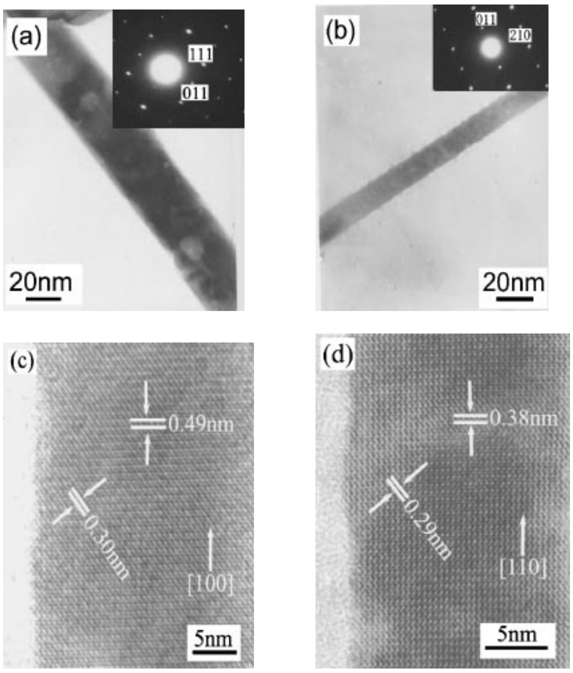

Fig. 4. TEM and HRTEM images of $CdWO_4$. (a, c) Single nanorod; (b, d) single nanowire.

tained under different conditions. From Fig. 3a, the $CdWO_4$ products that were synthesized using the CTAB surfactant have a rod-like morphology. The nanorods have diameters of 36 nm and lengths of up to 1 µm. The inset of Fig. 4a is a selected area electron diffraction (SAED) pattern taken from the single $CdWO_4$ nanorod, and it consists of many spots. All of the spots were determined to arise from monoclinic $CdWO_4$, i.e., the $CdWO_4$ nanorods appear to be single crystals. The structure of these nanorods was further examined by HRTEM, Fig. 4c. Based on the micrographs, the lattice fringes in the nanorod are structurally uniform, and the interplanar spacings are about 0.49 and 0.30 nm, which correspond to the (100) and (111) planes of $CdWO_4$, respectively, further confirming the single-crystalline nature of the $CdWO_4$ nanorods. In addition from Fig. 4c, the nanorods preferentially grow in the [100] direction. From Fig. 3b, the $CdWO_4$ products synthesized in the presence of the anionic surfactant SDBS have wire-like nanostructures, and they have diameters of 12 nm and lengths of up to several micrometers. The inset in Fig. 4b is the SAED pattern for a single $CdWO_4$ nanowire. The SAED pattern consists of many spots, which were identified as arising from monoclinic $CdWO_4$. In other words, the $CdWO_4$ nanowires also appear to be single crystals. The structure of these nanowires was also examined by HRTEM, Fig. 4d. The lattice fringes in the nanowire are structurally uniform, and interplanar spacings are about 0.38 and 0.29 nm, which correspond to the (110) and (020) plane lattice spacings of $CdWO_4$, respectively, further confirming the single-crystalline nature of $CdWO_4$ nanowires. Figure 4d also shows that these nanowires grow preferentially in the [110] direction. However, in the absence of any surfactants, the $CdWO_4$ products are mainly irregular particles, and only minor rod-like structures exist in the products, Fig. 3c.

Based on the above experiment results, the $CdWO_4$ nanorods and nanowires can be obtained when CTAB and SDBS, respectively, are used. In the absence of any surfactants, irregular $CdWO_4$ particles, including minor rod-like particles, are obtained. The presence of the minor nanorods produced in the absence of surfactants may be attributed to the anisotropic nature of monoclinic $CdWO_4$.

As for cationic surfactant CTAB or anion surfactant SDBS, our experimental results indicate that CTA^+ cations preferentially adsorb onto or bind to the (010) and (001) planes of $CdWO_4$ crystals and weakly adsorb onto or bind to the (100) plane because the positive charge density on the (010) and (001) faces are lower than that on the (100) plane. Wang et al.[22] have suggested that the zigzag orientation of W octahedral anions in the (100) plane makes it unfavorable for CTA^+ cations to adsorb onto this plane. Therefore, the surface energy of the (010) and (001) faces are lower than that of (100) face, which would make the growth rates on the (010) and (001) faces slower than that of the (100) face. As a result, it is possible to form $CdWO_4$ nanorods along [100] direction. In contrast, DBS^- anions preferentially adsorb onto or bind to the (100) plane of $CdWO_4$ crystals and weakly adsorb onto or bind to the (010) and (001) faces because of relative high positive charge density of the (100) plane. It is also possible that CTA^+ would prefer to adsorb onto the (010) face because of the high density of oxygen atoms on this face.[22] So, the surface energy of the (100) face is significantly lower than that of the (010) and (001) faces, and therefore, the growth rate of the (010) and (001) faces is faster than that of the (100) face. Even so, however, the different growth rates between the (010) and (001) planes are due to their inherent difference in charge density. This implies that the interaction of the anionic surfactant SDBS with (010) or (001) plane may be different, and as a consequence, in the presence of SDBS, $CdWO_4$ crystals grow into 1D nanowires, rather than 2D nanoplates. The $CdWO_4$ nanowires grow in the [110] direction, which is different from that of the nanorods synthesized in the presence of cationic surfactant CTAB.

In addition, the surfactants may form micelles in solution under the current conditions. The micelles with positive or negative charges may still interact with specific facets of the crystals, and, therefore, cause the crystals to grow in different directions.

At present, the consensus is that the preferential adsorption of ions or molecules from solution onto different crystal faces directs the growth of nanoparticles into various shapes,[21] and the adsorption interaction strongly relies on the nature of the adsorbed species and the properties of the specific crystal faces. It appears that the interaction of the surfactants CTAB and SDBS with the specific facets of $CdWO_4$ is different under our experimental conditions. As a result, $CdWO_4$ nanorods can be obtained in the presence of the cationic surfactant CTAB, while nanowires form in the presence of the anionic surfactant SDBS.

Figure 5 shows the room temperature PL spectra of the $CdWO_4$ nanorods, nanowires, and nanoparticles. The spectra of the $CdWO_4$ 1D nanostructures and the $CdWO_4$ nanoparticles synthesized in the absence of a surfactant have a very strong blue emission band in the range 400–550 nm, and the emission peaks are all at about 460 nm with excitation at 253 nm. These results are in agreement with the data for single

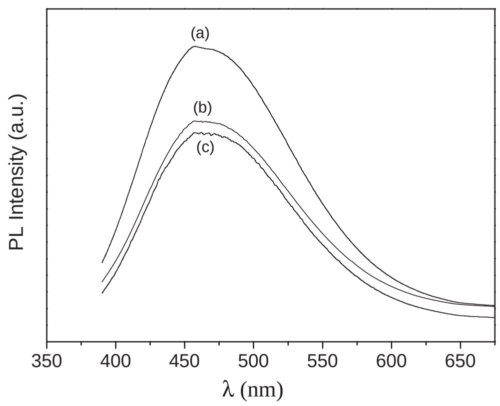

Fig. 5. Room temperature PL spectra of $CdWO_4$ nanostructures. (a) Nanorods; (b) nanowires; (c) nanoparticles.

crystals obtained at high temperatures but are blue-shifted compared to the reported “intrinsic luminescence” (480–490 nm).[12,23] The PL emission is caused by an ${}^1A_1 \rightarrow {}^3T_1$ transition within a $WO_4{}^{2-}$ complex.[24] However, the PL intensity of the $CdWO_4$ nanostructures decreases in the sequence of $CdWO_4$ nanorods, nanowires, and nanoparticles. In other words, the difference in the PL intensity of the nanorods, nanowires, and nanoparticles depends strongly on the nanostructured morphology, which is attributed to the difference in the growth directions and the crystallinity of these nano-sized materials.

Conclusion

In summary, single-crystal $CdWO_4$ nanorods were obtained using the cationic surfactant CTAB, and single-crystal $CdWO_4$ nanowires were prepared using the anionic surfactant SDBS. In our experimental system, CTA^+ cations preferentially adsorb onto or bind to the (010) and (001) planes, which led to the formation of $CdWO_4$ nanorods with a growth direction along [100], and the DBS^- anions adsorbed onto the (100) plane, leading to the formation of $CdWO_4$ nanowires with a growth direction along [110]. The difference in PL intensities of the $CdWO_4$ nanorods, nanowires, and nanoparticles is attributed to the different morphologies and crystallinities of these nanostructures. This growth mechanism for 1D nanostructures is also expected to apply to the synthesis of other metal tungstate 1D nanostructures.

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