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Hydrothermal Preparation and Characterization of Luminescent $CdWO_4$ Nanorods

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Nanometer-sized inorganic low-dimensional systems exhibit a wide range of optical and electrical properties[1,2] that rely sensitively on both size and shape.[3,4] Low-dimensional systems represent one of the important frontiers in advanced materials research. Quantum confinement of electrons in low-dimensional systems provides a powerful tool for manipulating their optical, electrical, and thermoelectrical properties.[5−7] Recently, the preparation and properties of one-dimensional (1D) nanomaterials have received considerable attention.[8−10] The template method is proved to be a very effective method for the fabrication of the 1D desired materials.[10−12] However, it is interesting to explore the solution-based synthesis of 1D nanomaterials without the presence of preformed templates.

Because of its intriguing luminescence and structure properties,[13] tungstate is an attractive material and has received much intense research interest. Cadmium tungstate ($CdWO_4$) crystals with a monoclinic wolframite structure[14] are considered to be highly functional materials because of their high average refractive index,[15] low radiation damage, low aftergrow to luminescence and high X-ray absorption coefficient. At room temperature, $CdWO_4$ shows photoluminescence (PL) whose peak is about 460 nm and has been used as an X-ray scintillator.[16] As a scintillator, its advantages, such as high efficiency, short decay time, high chemical stability, and high stopping power, make $CdWO_4$ irreplaceable.[17] Recently, because of its potential use as an advanced medical X-ray detector in computerized

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tomography,[18] it has attracted special interest.

Because of their different faults and their effects on spectral-kinetic and scintillation characteristics,[19] the $CdWO_4$ crystals as well as other tungstates are unstable. This instability relates primarily to impurities and structural defects, different kinds of nonuniformities, and microinclusions in the crystals. It is important to synthesize high-quality luminescent materials with special morphology. Various preparation methods have been developed to synthesize tungstates, such as a high-temperature solid-state reaction for powders,[20] a flux method for whisker growth,[21] the Czochralski method for single-crystal growth,[22] and pulsed laser ablation for growth of thin films of $CdWO_4$ using PL less targets.[23] Nevertheless, control of the crystalline structure with a fine monomorphology has not yet been achieved.

Cadmium tungstate nanorods with different sizes were synthesized by the reaction of cadmium chloride ($CdCl_2$) and sodium tungstate ($NaWO_4$) at 130 °C under pressure in an autoclave with the pH ranging from 3.0 to 14.0. Next, 0.005 mol of sodium tungstate (99.5%) was put into a Teflon-lined stainless steel autoclave of 100 mL capacity, and then the autoclave was filled with distilled water up to 60−70% of the total volume. The pH of the solution was adjusted to more than 3 with NaOH and HCl. Then 0.005 mol of $CdCl_2$ (98%) was put into the above solution. The pH value of the solution was readjusted to the previous value. The autoclave was maintained at 130 °C for 5 h without shaking or stirring during the heating period and then was allowed to cool to room temperature naturally. A white precipitate was collected and washed with distilled water to remove the residue of the reactants. The final product was dried in a vacuum at 60 °C for 2 h.

$CdWO_4$ is a monoclinic crystal structure with intermediate divalent cations and has been described as an ABX_4 structure, whose crystals are of the wolframite structure and not the scheelite structure. The monoclinic cell contains two $CdWO_4$ units. The divalent Cd has the usual octahedron configuration whose distances are close to the standard one. W has a very distorted coordination polyhedron: four O atoms are at the same distance and two are at different distances. The two distant O atoms were usually excluded from the first coordination sphere of W and were assigned to that of Cd.[14]

The samples obtained were characterized by X-ray powder diffraction (XRD). The XRD measurements were carried out with a Japan Rigaku D/max-rA rotation anode X-ray diffractometer, using Ni-filtered Cu Kα radiation. A scan rate of 0.05°/s was applied to record the patterns in the 2θ range 10−70°. The XRD patterns of the samples are shown in Figure 1. Figure 1a is the sample prepared at pH 4. In the XRD pattern all of the reflections, to within experimental error, can be indexed to the monoclinic cell of $CdWO_4$ with lattice constants $a = 5.027$ Å, $b = 5.858$ Å, and $c = 5.072$ Å (equal to the values of JCPDS 14-676). Figure 1b is the sample at pH 6. Figure 1c is the sample at pH 8. Figure 1d is the sample at pH 12, which shows that there exist some impurities in the sample in addition to $CdWO_4$. As we can see from the XRD patterns, the intensity and sharpness of the XRD peaks decreased when the pH value increased. This fact implied that the particle size and the crystallinity increase as the pH value decreases. When pH < 3, the XRD pattern shows that the product was pure H_2WO_4, and when pH ≥ 12, the XRD pattern shows that there are some impurities in addition to cadmium tungstate. So, the initial pH value is an important factor for the synthesis of $CdWO_4$. The optimal range of the initial pH value is 3−8.

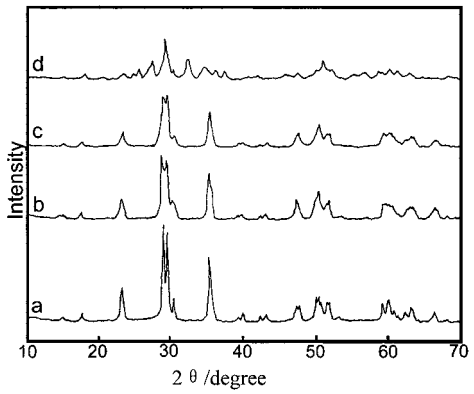

Figure 1. XRD patterns of the $CdWO_4$ nanocrystallites prepared at different pH values: (a) 4; (b) 6; (c) 8; (d) 12.

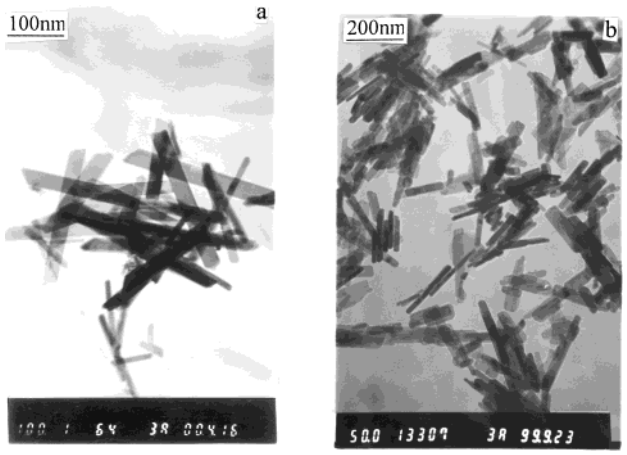

Figure 2. TEM images of $CdWO_4$ prepared at different pH values: (a) 4; (b) 8.

The morphology and particle sizes of the samples were investigated by transmission electron microscopy (TEM), using an accelerating voltage of 200 kV. Figure 2b shows the TEM image of $CdWO_4$ nanocrystallites prepared at pH 8. As shown in Figure 2b, the cadmium tungstate crystallites appear to display rodlike monomorphology with lengths of 80−280 nm and widths of 20−40 nm. Figure 2a display the TEM image of the sample prepared at pH 4. For comparison, we have carried out analogous experiments with $CdMoO_4$ and $CaWO_4$, and both are simple inorganic materials like $CdWO_4$. Under the same reaction conditions, we found that the $CdMoO_4$ nanoparticles that were obtained are spherical and the $CaWO_4$ that was formed is platelike. Although there is no template such as a micellar template in our aqueous system, the nanorods were, nevertheless, formed.

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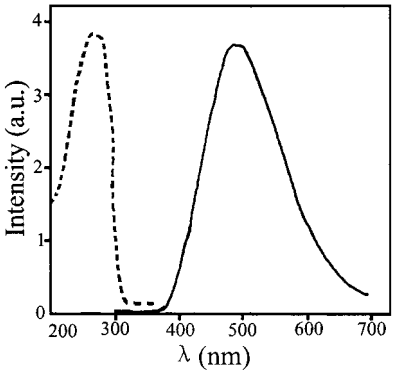

Figure 3. Excitation (dashed line) and PL (solid line) spectra of $CdWO_4$ nanorods prepared at pH 4. The excitation wavelength for the emission spectrum was 253 nm, and the monitoring wavelength for the excitation spectrum was 486 nm.

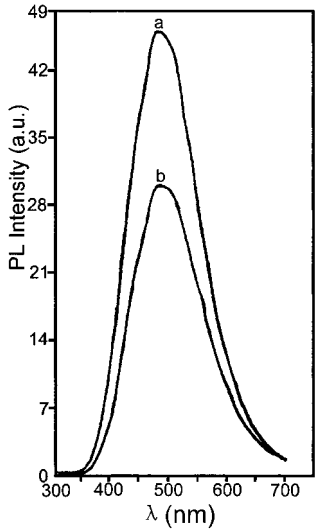

Figure 4. PL spectra (with the excitation wavelength 253 nm) of $CdWO_4$ prepared at different pH values: (a) 6; (b) 8.

These results indicate that, in our aqueous system, the crystal habits of inorganic materials play an important role in the formation of the final morphology of the materials. With regard to the formation of nanorods, the nanorods formation is probably facilitated by the acicular habit of the $CdWO_4$ crystal.[19]

The luminescence and excitation spectra of the samples were determined by a Hitachi 850 fluorescence spectrometer with a Xe lamp at room temperature. Figure 3 is the room temperature PL and excitation spectra of the rodlike cadmium nanocrystallite hydrothermally prepared at pH 4. The spectra exhibited only one blue-green PL emission peak at 486 nm and one excitation peak at 266 nm. Here, we assume that the excitation and PL of the rodlike cadmium tungstate are based on the $^1A_1-^3T_1$ transition. Compared to the PL emission (460 nm) of a single crystal at room temperature, the PL emission is red shifted by about 25 nm, which may be caused by the oriented growth of the nanocrystallites of cadmium tungstate. Parts a and b of Figure 4 are the PL emissions of the $CdWO_4$ samples hydrothermally prepared at pH 6 and 8, respectively. Their PL emission peaks both are at 486 nm, the same as that of the sample prepared at pH 4. This suggested that the blue emission apparently originated from the WO_4^{2-} complex.[24] We observed that the drastic variations in the intensities of the PL emissions and the intensity of the PL emission itself are much stronger than that of the sample prepared at pH 4, which shows that the intensities of the PL emission depended strongly on the preparation conditions. However, the PL intensity does not directly relate to the crystallinity of $CdWO_4$.

In summary, $CdWO_4$ nanorods with diameters of 20−40 nm and lengths ranging from 80 to 280 nm have been prepared starting from a normal inorganic salt under hydrothermal conditions. The products show a very strong PL peak at 486 nm with the excitation wavelength 253 nm. Further studies of the formation and growth mechanism of the nanorods are underway.

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