Hydrothermal synthesis of CdWO₄ nanorods and their photoluminescence properties

Bin Gao, Huiqing Fan and Xiaojun Zhang

ABSTRACT
CdWO₄ nanorods with wolframite structure were synthesized in the presence of the surfactant SDBS by a hydrothermal method, and characterized by a variety of techniques. The obtained products are CdWO₄ nanorods with length of 0.8–2.5 µm and width of 50–250 nm. The surfactant SDBS plays a key role in the formation of the CdWO₄ nanorods. The pH value impacts on crystallinity of the products. The PL properties of the CdWO₄ nanorods prepared under different conditions were studied. The intensity of the PL emissions of the samples increases with crystallinity and aspect ratio of the CdWO₄ nanorods.

KEYWORDS
CdWO₄ nanorods, photoluminescence, hydrothermal method.

1. Introduction
Tungstates, with high luminescence efficiency, great density, strong resistance to radiation damage, no deliquescence etc., have good application prospects in many fields. One phase of CdWO₄ belonging to the monoclinic crystallographic system, has a wolframite structure. The lattice constants are a = 0.5029 nm, b = 0.5859 nm, c = 0.5074 nm, β = 91.47°, respectively.

CdWO₄ has a high refractive index, a high X-ray absorption coefficient, low radiation damage, high luminescence intensity and low afterglow to luminescence, and as such is considered a promising light-emitting material. One application of CdWO₄ is that it is used as a popular X-ray scintillator at room temperature. CdWO₄ scintillators, with high efficiency, short decay time, high stopping power and high chemical stability, etc., are difficult to replace by other scintillators in this field.

As an important luminescent material, CdWO₄ crystals were synthesized and their luminescence properties have been studied by many research groups. Up to now, the synthesis methods of CdWO₄ mainly include Czochralski’s method, molten salt whisker growth technology, high temperature solid state reaction method, laser pulse ablation, spray pyrolysis, sol-gel method and hydrothermal process. Most of the aforementioned synthesis methods can only obtain macro-size CdWO₄, and these synthesis processes require high temperature and, hence, are difficult to control. Photoluminescence properties of solid materials are closely associated with size, morphology and micro-structure of the solid light-emitting particles. Therefore, exploring the synthesis of CdWO₄ nanocrystals with a special morphology is of important significance to investigating its photoluminescence properties and applications. Compared with other synthetic methods, the hydrothermal approach needs a low reaction temperature, simple operation and facile control composition. This paper reports the synthesis of CdWO₄ nanorods through a hydrothermal treatment process using Na₂WO₄·2H₂O and CdCl₂·2.5H₂O as main raw materials in the presence of sodium dodecyl benzene sulfonate (SDBS) surfactant. The formation mechanism and photoluminescence properties of the synthesized CdWO₄ nanorods were studied.

2. Experimental
All the chemical reagents used were of analytical grade (Xi’an Chemical Reagent Co. Ltd) and used without further purification. A typical experimental process is described as follows: 2 mmol (0.66 g) of sodium tungstate dihydrate (Na₂WO₄·2H₂O) was dissolved in 20 mL de-ionized water in a glass beaker and stirred with a glass rod until the formation of a saturated solution. A certain amount of sodium dodecyl benzenesulfonate (SDBS) was added to the saturated solution under vigorous magnetic stirring. Stirring was continued until a homogeneous solution was formed. 20 mL of a 0.1 mol L⁻¹ solution of cadmium dichloride (CdCl₂·2.5H₂O) was added, drop-wise, to the above-mentioned mixed homogeneous solution while stirring vigorously. The solution immediately became a white opaque suspension. The pH value of the suspension was adjusted with 1 M hydrochloric acid or sodium hydroxide.

The pH value was measured using a pH meter. The final concentrations of SDBS in the solution were 0.005, 0.01 and 0.015 mol L⁻¹, respectively. After 60 min of stirring, the final non-transparent suspension was transferred to a 100 mL Teflon-lined stainless steel autoclave to about 80% of its capacity. The autoclave was sealed and maintained at 180 °C for 24 h and then cooled to room temperature naturally. After the hydrothermal treatment a white precipitate formed at the bottom of the autoclave. The precipitate was centrifuged, filtered, and rinsed with distilled water and absolute alcohol several times to remove any ions possibly remaining in the final products. Finally, the products were dried at 80 °C for 6 h in air to give pale yellow powders.

The crystal structures of the obtained products were recorded on an X-ray powder diffractometer (XRD; D/Max-2400, Rigaku, Tokyo, Japan) with CuKα radiation (λ = 0.15418 nm). The XRD data were collected over a 2θ range from 15° to 80° at a scanning rate of 5° min⁻¹. The morphologies and microstructures of the synthesized samples were characterized using high-resolution transmission electron microscopy (HRTEM; JEM-3000F, JEOL, Tokyo, Japan), equipped with selected area electron diffraction (SAED) and energy dispersive X-ray spectrometer (EDX; X-Max, Oxford Instruments, Oxfordshire, UK) and operated at 200 kV. 
diffraction peaks indicate that well-crystallized CdWO\(_4\) crystals indicating that the products were highly pure phases. The sharp characteristic peaks from impurities were detected by XRD.

3. Results and Discussion

X-ray powder diffraction analysis was employed to determine the crystal structure of the synthesized CdWO\(_4\) nanorods. Figure 1 shows the XRD patterns of the CdWO\(_4\) nanorods prepared in 0.01 mol L\(^{-1}\) SDBS at pH values of 5, 7 and 9. In three cases all the diffraction peaks could be indexed to a pure monoclinic phase of crystallized CdWO\(_4\) with a wolframite structure. The calculated cell parameters were \(a = 0.5021\) nm, \(b = 0.5872\) nm and \(c = 0.5076\) nm, which is consistent with the standard values for monoclinic phase CdWO\(_4\) (JCPDS, No. 14-0676, \(a = 0.5029\) nm, \(b = 0.5859\) nm, \(c = 0.5074\) nm). No characteristic peaks from impurities were detected by XRD, indicating that the products were highly pure phases. The sharp diffraction peaks indicate that well-crystallized CdWO\(_4\) crystals can be obtained under current synthetic conditions.

XRD analysis also showed that the intensity of XRD diffraction peaks of the CdWO\(_4\) nanorods obtained at pH of 7 reached a maximum value, suggesting that this condition is the optimal condition for synthesis of crystalline CdWO\(_4\) nanorods. The relatively broad peaks probably arise from the small width of the synthesized CdWO\(_4\) nanorods.

The morphology of the products was characterized by transmission electron microscopy (TEM). TEM images of samples prepared at 180 °C for 24 h with an SDBS concentration of 0.005, 0.01 or 0.015 mol L\(^{-1}\), are shown in Fig. 2a-c (pH = 7). The TEM images indicate that the products are composed of large-scale nanorods. The TEM observations also demonstrate that an almost 100% yield of CdWO\(_4\) nanorods can be easily obtained using this simple method. The nanorods synthesized with an SDBS concentration of 0.005 mol L\(^{-1}\) exhibit a narrow distribution of widths ranging from 50 to 80 nm. The lengths of the nanorods are in the order of 800–1300 nm. The nanorods are straight and have smooth, round tips (Fig. 2a). The products obtained with the SDBS concentration of 0.01 mol L\(^{-1}\) are shown in Fig. 2b. While the widths of the nanorods are independent of the SDBS concentration, the lengths increase to 1.5–2 \(\mu\)m. At an SDBS concentration of 0.015 mol L\(^{-1}\), both the widths and lengths of the nanorods increased compared to the first two products (Fig. 2c). In this case, the widths ranged from 130 to 250 nm and the lengths up to 2.5 \(\mu\)m. It can be seen from the aspect ratio that the CdWO\(_4\) nanorods accrete with an increase in the SDBS concentration from 0.005 to 0.01 mol L\(^{-1}\), but decreases when the SDBS concentration further raises to 0.015 mol L\(^{-1}\). The aspect ratio of the CdWO\(_4\) nanorods prepared in 0.01 mol L\(^{-1}\) SDBS is approximately 40. Figure 2d is a selected area, electronic diffraction (SAED) pattern, of a CdWO\(_4\) nanorod. The diagram shows clear diffraction spots, indicating that well-crystallized CdWO\(_4\) nanorods are single crystals. The surfactant, SDBS, plays an important role in the formation of the CdWO\(_4\) nanorods. In the reaction system, the concentration of the SDBS is larger than its critical micelle concentration (CMC, 1.48 mmol L\(^{-1}\)) and so is present in the form of rod-like micelle. There is water in the rod-like micelles and these can be seen as nano-reactors. In the beginning, the ion of WO\(_4^{2-}\) is mainly located in the inner surface of the micelle. After adding CdCl\(_2\)-2.5H\(_2\)O solution to the mixture, the Cd\(^{2+}\) ions combine with WO\(_4^{2-}\) to form CdWO\(_4\) crystal. The micelle wrapping limit the crystallization of CdWO\(_4\) in a relatively small spatial scale and then inhibit the crystal growth. The micellar shape changes with the SDBS concentration, consequently, CdWO\(_4\) nanorods with different morphology are obtained. In addition, the SDBS can be ionized to form dodecylbenzene sulfonic ions (DBS) with a different spatial structure. The DBS can selectively adsorb onto certain crystal faces of the CdWO\(_4\), and thereby decrease the surface energy and growth velocity of these planes in the hydrothermal process. In this way, the CdWO\(_4\) crystal nucleus orients growth along a certain direction to form a rod-like structure. The inhibition of the crystal face growth along a particular directions enhances with concentration of SDBS and therefore the growth trend of the grain in a certain direction is more obvious. Thus the aspect ratio of the CdWO\(_4\) nanorods increases with SDBS concentration. However, the growth of the CdWO\(_4\) crystal in all directions is simultaneously suppressed when the concentration of the SDBS exceeds a certain value. It decreases the aspect ratio of the CdWO\(_4\) nanorods. The analysis shows that the surfactant of SDBS in the formation of the CdWO\(_4\) nanorods mainly plays the roles of a soft template and an adsorbent.

The photoluminescence (PL) spectra were measured at room temperature on a steady-state fluorescence and phosphorescence lifetime spectrometer (FLSP 920, Edinburgh Instruments Ltd, Livingston, UK) with an excitation wavelength of 320 nm. The excitation source was a steady-state Xe-arc lamp with an output power of 450 W. The photoluminescence (PL) spectra were measured at room temperature on a steady-state fluorescence and phosphorescence lifetime spectrometer (FLSP 920, Edinburgh Instruments Ltd, Livingston, UK) with an excitation wavelength of 320 nm. The excitation source was a steady-state Xe-arc lamp with an output power of 450 W.

The morphology of the products was characterized by transmission electron microscopy (TEM). TEM images of samples prepared at 180 °C for 24 h with an SDBS concentration of 0.005, 0.01 or 0.015 mol L\(^{-1}\), are shown in Fig. 2a-c (pH = 7). The TEM images indicate that the products are composed of large-scale nanorods. The TEM observations also demonstrate that an almost 100% yield of CdWO\(_4\) nanorods can be easily obtained using this simple method. The nanorods synthesized with an SDBS concentration of 0.005 mol L\(^{-1}\) exhibit a narrow distribution of widths ranging from 50 to 80 nm. The lengths of the nanorods are in the order of 800–1300 nm. The nanorods are straight and have smooth, round tips (Fig. 2a). The products obtained with the SDBS concentration of 0.01 mol L\(^{-1}\) are shown in Fig. 2b. While the widths of the nanorods are independent of the SDBS concentration, the lengths increase to 1.5–2 \(\mu\)m. At an SDBS concentration of 0.015 mol L\(^{-1}\), both the widths and lengths of the nanorods increased compared to the first two products (Fig. 2c). In this case, the widths ranged from 130 to 250 nm and the lengths up to 2.5 \(\mu\)m. It can be seen from the aspect ratio that the CdWO\(_4\) nanorods accrete with an increase in the SDBS concentration from 0.005 to 0.01 mol L\(^{-1}\), but decreases when the SDBS concentration further raises to 0.015 mol L\(^{-1}\). The aspect ratio of the CdWO\(_4\) nanorods prepared in 0.01 mol L\(^{-1}\) SDBS is approximately 40. Figure 2d is a selected area, electronic diffraction (SAED) pattern, of a CdWO\(_4\) nanorod. The diagram shows clear diffraction spots, indicating that well-crystallized CdWO\(_4\) nanorods are single crystals. The surfactant, SDBS, plays an important role in the formation of the CdWO\(_4\) nanorods. In the reaction system, the concentration of the SDBS is larger than its critical micelle concentration (CMC, 1.48 mmol L\(^{-1}\)) and so is present in the form of rod-like micelle. There is water in the rod-like micelles and these can be seen as nano-reactors. In the beginning, the ion of WO\(_4^{2-}\) is mainly located in the inner surface of the micelle. After adding CdCl\(_2\)-2.5H\(_2\)O solution to the mixture, the Cd\(^{2+}\) ions combine with WO\(_4^{2-}\) to form CdWO\(_4\) crystal. The micelle wrapping limit the crystallization of CdWO\(_4\) in a relatively small spatial scale and then inhibit the crystal growth. The micellar shape changes with the SDBS concentration, consequently, CdWO\(_4\) nanorods with different morphology are obtained. In addition, the SDBS can be ionized to form dodecylbenzene sulfonic ions (DBS) with a different spatial structure. The DBS can selectively adsorb onto certain crystal faces of the CdWO\(_4\), and thereby decrease the surface energy and growth velocity of these planes in the hydrothermal process. In this way, the CdWO\(_4\) crystal nucleus orients growth along a certain direction to form a rod-like structure. The inhibition of the crystal face growth along a particular directions enhances with concentration of SDBS and therefore the growth trend of the grain in a certain direction is more obvious. Thus the aspect ratio of the CdWO\(_4\) nanorods increases with SDBS concentration. However, the growth of the CdWO\(_4\) crystal in all directions is simultaneously suppressed when the concentration of the SDBS exceeds a certain value. It decreases the aspect ratio of the CdWO\(_4\) nanorods. The analysis shows that the surfactant of SDBS in the formation of the CdWO\(_4\) nanorods mainly plays the roles of a soft template and an adsorbent.
The TEM images of a single CdWO₄ nanorod synthesized at pH value of 5, 7 and 9, respectively, are shown in Figs. 3a, 3b and 3c (0.01 mol L⁻¹ SDBS). The inset of each image is the HRTEM lattice diagram of a part of the nanorod. The widths of the CdWO₄ nanorods synthesized at three different pH values are all about 55 nm, which implies that pH does not bring about significant changes in the morphology of the CdWO₄ nanorods. However, the pH value does impacts on crystallinity of the CdWO₄ nanorods. It can be seen from the insets that the CdWO₄ nanorod synthesized with at a pH of 7 has the best crystallinity and almost no lattice defects. The nanorods obtained at pH = 5 and 9 have relatively poor crystallinity, with many line defects (the white arrows in the insets in Figs. 3a and 3c). The crystallinity of CdWO₄ nanorod prepared in acidic environment (pH = 5) is poorer than that in alkaline (pH = 9) and neutral (pH = 7) solutions. This is consistent with the XRD results.

The elemental identification of the synthesized product was obtained with an energy dispersive X-ray spectrometer (EDX) attached to the TEM system. Figure 4 is the EDX spectrum of an individual CdWO₄ nanorod.

It can be seen from the diagram, in addition to signals of Cd, W and O, Signal C originates from the TEM grid. EDX spectrum of an optional individual CdWO₄ nanorod at 180 °C for 24 h with the SDBS concentration of 0.01 mol L⁻¹ (pH = 7). The C signal comes from the TEM grid. Quantitative analysis shows that atomic number ratio of the elements of Cd, W and O is approximately 1:1:4 and is consistent with the composition of CdWO₄, indicating that the synthetic products are CdWO₄ crystal.

PL spectra were measured at room temperature on a steady-state fluorescence and a phosphorescence lifetime spectrometer with an excitation wavelength of 320 nm. A steady-state Xe-arc lamp with an output power of 450 W was employed as excitation source. The PL spectra of the CdWO₄ nanorods at pH = 5, 7 and 9 (0.01 mol L⁻¹ SDBS) are shown in Fig. 5. A strong blue-green emission band is present in the 400–600 nm range in all three spectra in which there is a strong emission peak at 485 nm and a shoulder at 460 nm. Compared to the PL emission (460 nm) of a massive CdWO₄ single crystal, the strongest emission peak position of the CdWO₄ nanorods has a red shift of 25 nm. Here, it is noteworthy that the emission peak is also influenced by the excited wavelength, size and aspect ratio of the CdWO₄ nanorods. The PL spectra also demonstrate that the intensities of the PL emissions of the CdWO₄ nanorods prepared at different pH values are variable. The intensity of the CdWO₄ nanorods prepared with pH7 is highest and at pH5 is lowest. By comparing the TEM results, we can see a transformation of the lumines-
cence intensity of the CdWO₄ nanorods synthesized at different pH values. This indicates that the PL emission intensity of the CdWO₄ nanorods is associated with the crystallinity of the products. Fluorescence emission originates from a recombination of electron-holes. Low emission intensity means that light-emitting material has a low recombination rate of electron-holes and a high separation rate of electron-holes. Consequently, the fluorescence intensity of the CdWO₄ nanorods increases with the crystallinity of the samples. At the same time, the high-energy peak at 322 nm, in the UV light zone, is present.

Figure 3 TEM images of a randomly chosen CdWO₄ nanorod synthesized with PH = 5, 7 and 9, respectively. The inset in each image is the HRTEM lattice diagram of a part of the nanorod.

Figure 4 EDX spectrum of an optional individual CdWO₄ nanorod at 180 °C for 24 h with the SDBS concentration of 0.01 mol L⁻¹ (pH = 7). The C signal comes from the TEM grid.
in the PL spectrum of the CdWO₄ nanorods obtained at pH 7 due to its good crystallinity. The peak is possibly a band edge ultra-violet emission. The visible emission is usually ascribed to structural defects (surface oxygen vacancies). The UV emission is attributed to the near-band-edge emission and arises from the recombination of free excitons through an exciton-exciton collision process. Chen and coworkers attribute the band edge UV emission to the radiative recombination of excitons bound to neutral donor.

The PL spectra of the CdWO₄ nanorods prepared with an SDBS concentration of 0.005, 0.01 and 0.015 mol L⁻¹, respectively, are shown in Fig. 6 (pH = 7). The ranges of fluorescence emission band (400–600 nm), as well as the positions of the strong emission (485 nm) and shoulder peaks (460 nm), are almost identical in all three spectra. The high-energy peaks at 322 nm, in the UV light zone, are present in the three spectra. The results indicate that the PL spectra of the well-crystallized CdWO₄ nanorods show, not only a strong blue-green emission band, but a band edge UV emission. Meanwhile, it can be seen from Fig. 6 that the intensity of the PL emission of the CdWO₄ nanorods synthesized with an SDBS concentration of 0.01 mol L⁻¹, is a maximum.

The change in PL emission intensity can be attributed to a one-dimensional confinement effect, and be caused by the differences in morphology of the CdWO₄ nanorods. The trend is in agreement with the change in aspect ratio of the CdWO₄ nanorods. These results suggest that the intensity of PL emission is strongly bound up with the morphology of the CdWO₄ nanorod powders.

From the above results, we can see that the pH value and concentration of surfactant SDBS do not affect the position of blue-green band in the 400–600 nm range. However, the luminescence intensity of blue-green emission bands of the CdWO₄ nanorods varies with pH and SDBS concentration. Previously, this luminescence was attributed to electronic transition within the coordination anion of WO₆⁶⁻. The PL emission bands were ascribed to the ¹A₁ → ³T₁ transition within the WO₆⁶⁻ complex. We believe that the photoluminescence properties depend strongly on the morphology and crystallinity of the CdWO₄ nanorods.

Figure 5 Room temperature PL spectra of the CdWO₄ nanorods synthesized at different pH values.

Figure 6 PL spectra of the CdWO₄ nanorods prepared with an SDBS concentration of (a) 0.005 (b) 0.015 and (c) 0.01 mol L⁻¹, respectively.
4. Conclusions
CdWO₄ nanorods were synthesized by a hydrothermal method using Na₂WO₄·2H₂O and CdCl₂·2.5H₂O as raw materials in the presence of the surfactant SDS. The lengths and widths of the CdWO₄ nanorods fall into the range of 0.8–2.5 µm and 50–250 nm, respectively. The results show that the surfactant plays the roles of a soft template and an adsorbent of crystal face oriented growth in the formation of the nanorods. The surfactant concentration and pH value impact on the morphology and crystallinity of the CdWO₄ nanorods. The intensity of photoluminescence increases with the crystallinity and aspect ratio of the CdWO₄ nanorods.

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