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Research Article

Fast Microwave-Assisted Synthesis and Photoluminescence of $CaWO_4$ Nanocrystals

Quanguo Li, Yanhua Shen, and Taohai Li

College of Chemistry, Key Lab of Environment Friendly Chemistry and Application of Ministry of Education, Xiangtan University, Xiangtan 411105, China

Correspondence should be addressed to Taohai Li; hnlth@xtu.edu.cn

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In this work, $CaWO_4$ nanoparticles have been synthesized by microwave-assisted method at a low temperature of 120°C. The as-prepared powders were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), and Fourier transform infrared spectroscopy (FT-IR). It is found that the reaction time played an important role in the morphology controlling and crystallinity level of $CaWO_4$ crystals. The effects of photoluminescent properties have a great relationship with crystallinity.

1. Introduction

In recent years, with the advance of nanoscale materials science and technology, the synthesis of nanoscale materials with unique properties is becoming more and more important for studying the variation of materials' properties with size and morphology [1–5]. Nanomaterials based on the scheelite-type have attracted considerable interest because of their luminescent property approved use in electrooptic applications [6–8]. $SrWO_4$, $CaWO_4$, $PbWO_4$, and $BaWO_4$ were considered to be typical oxides structure of scheelite-type. Locating within tetrahedral O-ion cages, W ions are isolated from each other in the scheelite structure, while Ca, Ba, Sr, and Pb ions are surrounded by eight oxygen ions [9].

$CaWO_4$ with a scheelite structure is an important optical material, which has attracted particular interest because of its applications [10] in quantum electronics or scintillators as laser host material [11, 12]. $CaWO_4$ powders are usually prepared by traditional solid-state reactions which require high temperature and harsh reaction conditions [13]. Recently, $CaWO_4$ nanoparticles have been prepared by various wet chemical methods [14–18], which needs long reaction time, or nonaqueous solvents, such as hydrothermal method, citrate complex method, combustion process, coprecipitation, microwave-hydrothermal methods, polymeric precursor method, and microwave-solvothermal methods [19–22]. Therefore, to synthesize $CaWO_4$ nanoparticles with a mild method (e.g., low temperature and/or quick reaction time) is of significance in both fundamental and applied studies [23].

In this paper, we report the synthesis, crystal structure, and fluorescence property of $CaWO_4$ nanocrystals, which is prepared from the reaction of $CaCl_2$ and $Na_2WO_4{\cdot}2H_2O$ in the presence of PEG1000 by fast microwave-assisted method. By controlling the different reaction time, the degree of crystallinity of $CaWO_4$ can be controlled. It means that we can obtain $CaWO_4$ with higher crystallinity target structure by adjusting the reaction time, which is important for the preparation of aimed productions in the system of Ca–W–O.

2. Experimental Section

2.1. Synthesis. $CaCl_2$ (AR), $Na_2WO_4{\cdot}2H_2O$ (AR), and PEG1000 (AR) were used as the starting materials, and all of them were of analytical grade without any further purification. $CaWO_4$ nanocrystals were prepared by microwave-assisted method in the absence of any organic additives. In a typical procedure, 0.1093 g $CaCl_2$ 0.1003 g $Na_2WO_4{\cdot}2H_2O$, and 0.1409 g PEG1000 were put into quartz tube and dissolved in 10 mL distilled water, and the mixture was vigorously stirred for 10 min to ensure that all reagents were dispersed homogeneously. And then put the sealed quartz

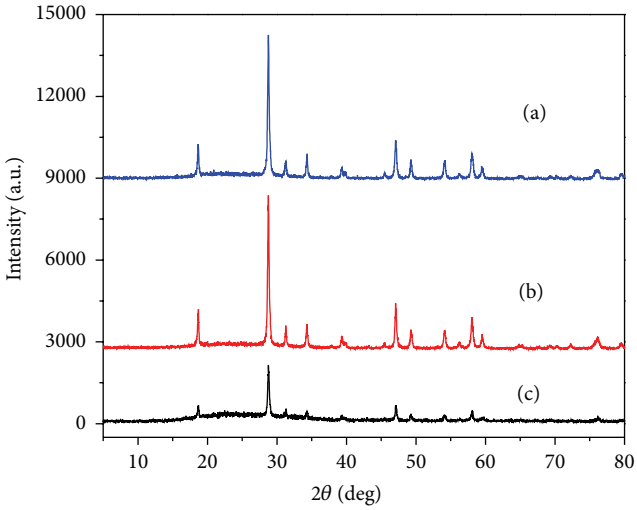


Figure 1: XRD patterns of the as-prepared $CaWO_4$ samples synthesized by microwave-assisted method at 120°C for different reaction times: (a) 15 min, (b) 10 min, and (c) 5 min, respectively.

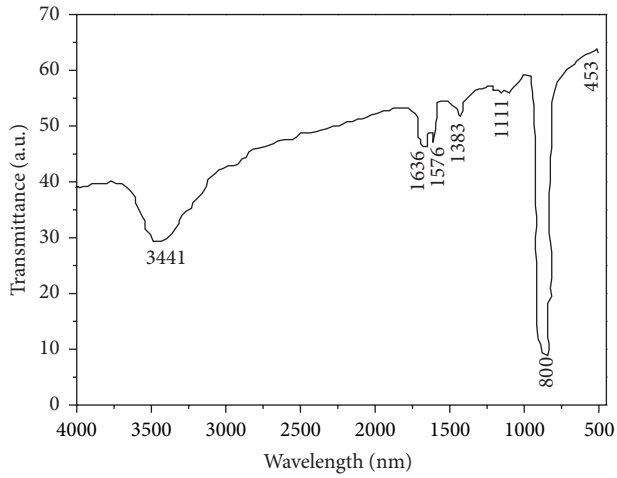


Figure 2: The FT-IR spectrum of $CaWO_4$ nanocrystals synthesized under 120°C, for 15 min.

tube into the microwave reactor. Reaction temperature and time, pressure, and microwave power output were adjusted according to the parameters of the reactor. After cooling to room temperature naturally, the precipitates were collected, washed with distilled water and absolute ethanol for several times, and then dried in a vacuum oven at about 60°C for 24 h.

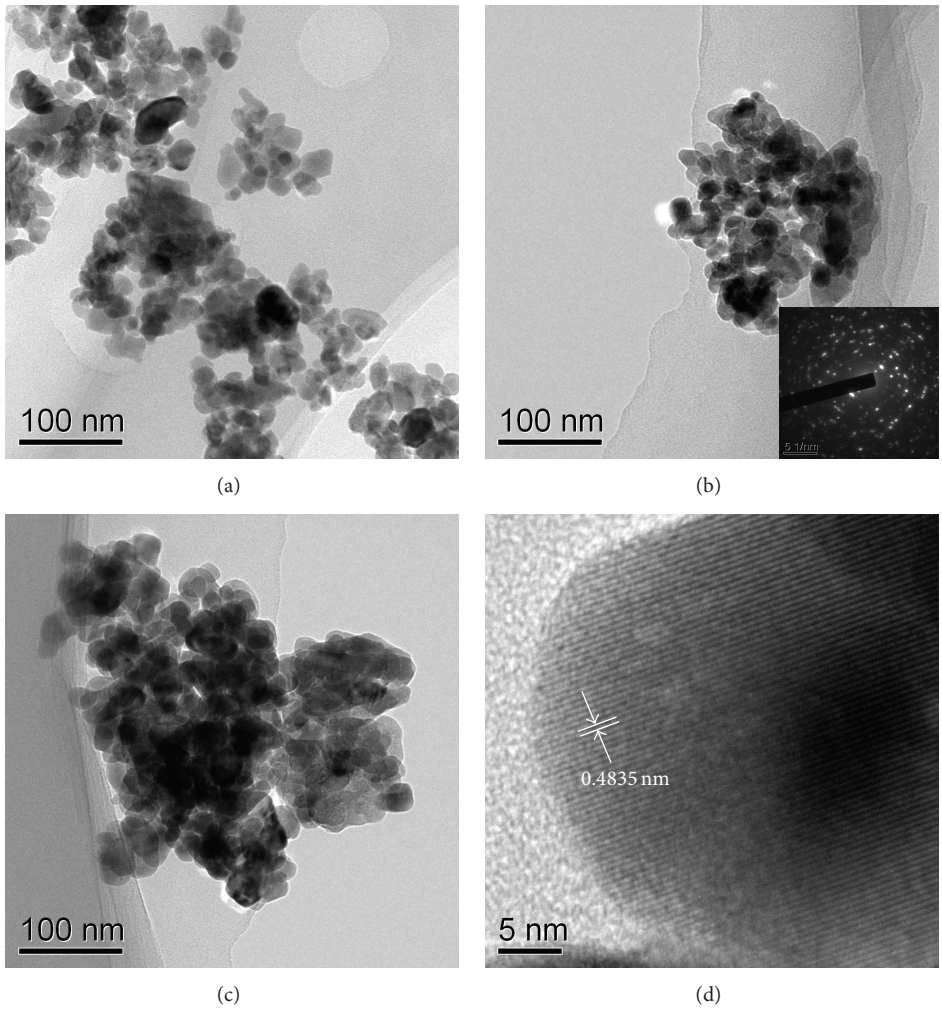
2.2. Characterization. The morphologies of $CaWO_4$ samples were examined by transmission electron microscopy (TEM) (JEM-2010, JEOL, Japan). The FT-IR spectra (Nicolet-380, Nicolet Instrument Co., USA) were recorded in the region of 4000–400 cm^{-1}. X-ray diffraction (XRD) patterns were measured on a MiniFlex2 goniometer. Employing a scanning rate of 0.02°s^{-1} in the 2θ range from 5° to 70°, the operating voltage and current were maintained at 30 kV and 15 mA, respectively. Photoluminescence (PL) spectra were recorded by a Hitachi 850 fluorescence spectrometer with a Xe lamp at room temperature. Fourier transform infrared spectroscopic (FT-IR) analysis was carried out using pressed KBr disks in the region of 4000–400 cm^{-1} by using a Perkin Elmer spectrometer instrument.

3. Results and Discussion

3.1. Structural Analysis. The phase identification of all the products was performed by XRD. To investigate the effect of reaction time on the crystallinity, $CaWO_4$ was prepared with different reaction time. The products synthesized at 120 degrees in 5 min, 10 min, and 15 min show similar patterns, which are in good agreement with the standard values for the tetragonal phase $CaWO_4$ (*Fm3hm*, JCPDS No. 41-1431). Figure 1 shows the XRD patterns of the products obtained via microwave-assisted method. When reaction time is 5 min, the crystallinity of as-prepared product is considerably low, and there are few peaks that cannot be observed. Therefore, a longer time supports the formation of the thermodynamically stable, well-crystallized, and uniform products. It is very clear that the crystallinity of obtained products increase with the increasing of reaction time for 15 min (Figure 1(a)). In a word, the reaction time of the reaction systems was found to play an important role in determining the crystallinity of the $CaWO_4$ nanocrystals.

To further confirm the formation of the $CaWO_4$ crystal structure, Fourier transform infrared (FT-IR) spectroscopy was performed on the as-prepared $CaWO_4$ nanocrystals (Figure 2). The bands at 1383 cm^{-1}, 1576 cm^{-1}, 1636 cm^{-1}, and 3441 cm^{-1} are assigned to O–H stretching vibration and H–O–H bending vibration [24], respectively. The two bands are the characteristic vibrations of water from air absorbed on the sample surface physically which is completely different from coordinated water in compounds. The 111 cm^{-1} band is the characteristic vibrations of CO_2 in the air. A strong absorption band around 800 cm^{-1} is related to O–W–O stretches of the WO_4 tetrahedron, because the AWO_4-type sheelite oxides, having S4 site symmetry for the WO_4 groups, which show the main absorption bands in the region of 400–1000 cm^{-1}, centered around 911, 405, and 833 cm^{-1} based on the v1, v2, and v3 modes of the WO4 groups, respectively [25]. The 453 cm^{-1} band is attributed to the v2 stretching vibration of W–O on the same grounds.

3.2. Morphology Control. Figure 3 shows the typical TEM images of $CaWO_4$ samples synthesized via microwave-assisted method at 120°C with different reaction time. It is very remarkable that $CaWO_4$ nanocrystals are 63 nm in diameter, when reaction time is 15 min (Figure 3(c)). But the diameter of as-prepared $CaWO_4$ is 46 nm and 62 nm, when reaction time is 5 min and 10 min (Figures 3(a) and 3(b)), respectively, which are in good agreement with the XRD results. This result further confirms that longer heating time would promote the crystallization of $CaWO_4$ nanocrystals. Figure 3(c) shows that the spacing of the lattice fringe is



(a) (b) (c) (d)

Figure 3: TEM images of the as-prepared $CaWO_4$ samples synthesized at 120°C for different reaction times: (a) 5 min, (b) 10 min, and (c) 15 min. (d) A typical higher magnification TEM image of the obtained $CaWO_4$ crystals.

0.4835 nm and in consonance with the (101) face. Thus, it indicates that $CaWO_4$ nanocrystals were synthesized by directional connection and self-assembly.

At room temperature, PL property of the $CaWO_4$ nanoparticles was initially studied. Figure 4 shows the representative PL spectrum of the $CaWO_4$ nanoparticles synthesized at 120°C for 5 min (a), 10 min (b), and 15 min (c), respectively. With the excited wavelength at 250 nm, the corresponding broad emission peak at 420 nm was observed. Further studies on PL property of the as-prepared $CaWO_4$ nanoparticles were in progress. With the increasing of the reaction time, the emission peak value increases constantly, which has the same change with morphology and crystallinity. These results strongly indicate that the PL properties of $CaWO_4$ are sensitive to the degree of structural order-disorder (crystallinity) and the relatively weak variations in the atomic arrangements which was basically in agreement with the analysis of Orhan et al. [21]. In general, the possible reasons are associated with the charge-transfer transitions within the $[WO_4]^{2-}$ complexes [26–29] or due to the vacancies as $[WO_3 \cdot V_O^z]$ [30] and $[CaO_7 \cdot V_O^z]$ [31].

4. Conclusions

$CaWO_4$ nanocrystals have been successfully prepared by microwave-assisted method at a low reaction temperature of 120°C with different time. Experimental results indicated that the crystallinity of as-synthesized $CaWO_4$ was affected by the reaction time. With the prolonging of the reaction time, the crystallinity of the sample got higher, and the average diameter of particles got bigger. The $CaWO_4$ nanocrystal obtained by this preparation method has favourable luminance, which receives emissive wavelength at 420 nm with the excitation wavelength at 250 nm. It indicated that the kernel became bigger, the crystallinity was higher, and the intensity of fluorescence changed to become stronger as time went on.

Acknowledgments

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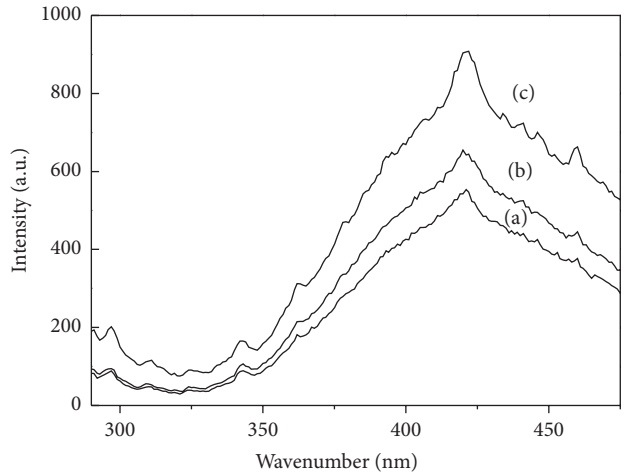

Figure 4: PL spectra of the $CaWO_4$ nanoparticles synthesized at 120°C for (a) 5 min, (b) 10 min, and (c) 15 min.

Conflict of Interests

The authors declared that they have no conflict of interests to this work.

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