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Short communication

Low temperature synthesis of $CaMoO_4$ nanoparticles

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Abstract

$CaMoO_4$ nanoparticles were successfully synthesized by a molten salt method at a temperature as low as 270 °C. The as-prepared powders, characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM), exhibited a pure $CaMoO_4$ phase about 70 nm in particle size and uniform nearly-spherical particle shape. The room temperature luminescent spectra were performed on a Fluorolog-3 spectrofluorometer; the powders exhibited green emission peaks of 508 nm. The molten salt medium could speed up the diffusion rates of the reaction ions, and thus decrease greatly the synthesis temperature of $CaMoO_4$ nanoparticles.

Keywords: Molten salt method; $CaMoO_4$ nanoparticles; Low temperature

1. Introduction

$CaMoO_4$ with a scheelite type structure has been of practical interest for a long time because of its attractive luminescence [1]. It provides green emission as an available solid-state laser material. Various techniques, which need high temperature and harsh reaction conditions, have been developed to synthesize $CaMoO_4$, such as the Czochralski method [2], and coprecipitation [3], combustion [4] and conventional solid-state reaction [5]. $CaMoO_4$ powders prepared by these processes are relatively large in particle size with irregular morphology, and of inhomogeneous composition due to MoO_3 tendency to vaporize at high temperatures [6]. To overcome these disadvantages, the citrate complex method [7] has been successfully used to synthesize $CaMoO_4$ nanoparticles, but this method is complex, and involves the use of large amounts of organic solvents, and still needs a relatively high calcination temperature of 600 °C. Therefore, it is far from being environmentally friendly and low-cost.

In this paper, we report the synthesis of $CaMoO_4$ nanoparticles with perfectly crystalline morphology and homogeneously chemical composition by a simple method at a relatively low temperature of 270 °C without any organic additives. This method has advantages of simple instrumentation, easy manipulation, low temperature, and short synthesis time. It also is friendly to the environment and available to a large-scale production. To our knowledge, no such study has ever been reported.

2. Experimental

In a typical synthesis, appropriate amounts of reagent grade $Ca(NO_3)_2$, Na_2MoO_4, and $LiNO_3$ (molar ratio 1:1:10 and 1:1:20, respectively) were directly put into an alumina crucible without any mixing step, and then calcined for 3 and 7 h at 270 °C. The resultant products were thoroughly washed with distilled water and absolute ethanol for several times, and then dried at 70 °C for 3 h. The XRD patterns of the samples were recorded on a X-ray powder diffractometer (XRD, D/max, Rigaku, Japan). All TEM images were taken with a JEM-1200EX transmission electron microscope (JEOL Ltd, Tokyo, Japan), operating at 60 KV. The room temperature luminescent spectra were performed on a Fluorolog-3 spectrofluorometer (USA).

3. Results and discussion

The effect of calcination time on the formation of $CaMoO_4$ was investigated. Fig. 1a and b shows the XRD patterns of the as-prepared powders, with $Ca(NO_3)_2$, Na_2MoO_4, and $LiNO_3$

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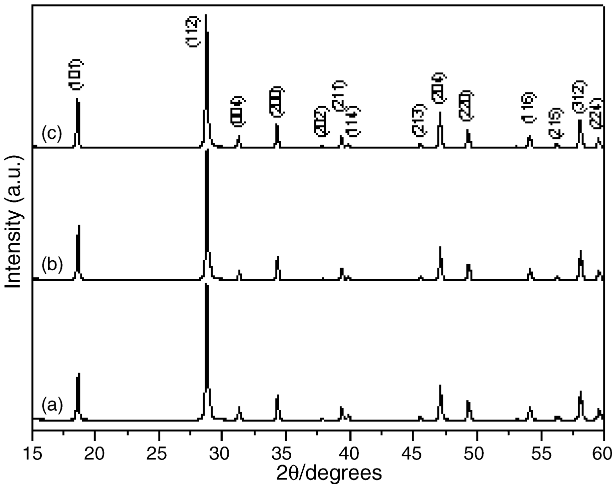

Fig. 1. XRD patterns of the $CaMoO_4$ nanoparticles synthesized by calcining at 270 °C for (a) 3 h, (b) 7 h, respectively, both with $Ca(NO_3)_2$, Na_2MoO_4, and $LiNO_3$ molar ratio 1:1:10, and for (c) 7 h with $Ca(NO_3)_2$, Na_2MoO_4, and $LiNO_3$ molar ratio 1:1:20.

molar ratio 1:1:10, calcined at 270 °C for (a) 3 h, (b) 7 h, respectively. All peaks in a and b patterns can be indexed as a tetragonal phase $CaMoO_4$ with a scheelite type structure, well consistent with the previous reported data. Unreacted or additional phases are not detected. It means that a pure tetragonal phase $CaMoO_4$ can be obtained at 270 °C. Furthermore, $LiNO_3$, which melting point is 253 °C [8], just provides a reaction medium for the formation of $CaMoO_4$ phase to increase diffusion rates of reaction ions, and can be washed away by distilled water. One can find that the diffraction peaks become stronger and sharper with prolonged calcination time, a condition which would favor the crystallization and evolution of $CaMoO_4$ nanoparticles. The mean particle size of $CaMoO_4$ powders varies from 48 to 72 nm, as calculated by the Scherrer equation, corresponding to the calcination times of 3 and 7 h, respectively.

The effect of $Ca(NO_3)_2$, Na_2MoO_4, and $LiNO_3$ molar ratio on the formation of $CaMoO_4$ was also studied in the present paper. Fig. 1b and c presents the XRD patterns of the $CaMoO_4$ powders prepared at 270 °C for 7 h, with $Ca(NO_3)_2$, Na_2MoO_4, and $LiNO_3$ molar ratio 1:1:10 (Fig. 1b) and 1:1:20 (Fig. 1c), respectively. The different molar ratios did not bring about significant changes in the XRD patterns, implying that $CaMoO_4$ crystallites did not grow up significantly by altering $Ca(NO_3)_2$, Na_2MoO_4, and $LiNO_3$ molar ratio. The mean particle sizes of the powders corresponding to a and b patterns, as calculated by Scherrer equation, are both 72 nm. No any other impurities and secondary phases can be observed in both XRD patterns.

Figs. 2 and 3 display the TEM micrographs of the $CaMoO_4$ powders synthesized at 270 °C for different calcination times and molar ratios. All samples (Figs. 2a, b and 3a) but one (Fig. 3b) were prepared with the same $Ca(NO_3)_2$, Na_2MoO_4, and $LiNO_3$ molar ratio 1:1:10; the powder corresponding to Fig. 3b was prepared with $Ca(NO_3)_2$, Na_2MoO_4, and $LiNO_3$ molar ratio 1:1:20. As shown in Fig. 2, the as-prepared powders consist of uniform and nearly-spherical nanoscale size particles. When the calcination time increases from 3 to 7 h, the mean particle sizes of $CaMoO_4$ powders increase from 50 to 70 nm, as shown in Fig. 2a and b, which are in a good agreement with the results from XRD. Fig. 3a and b also confirm that no significant changes in particle size took place when $Ca(NO_3)_2$, Na_2MoO_4, and $LiNO_3$ molar ratio increased from 1:1:10 to 1:1:20. The mean particle size in both cases is approximately 70 nm, well consistent with the XRD results.

Room-temperature photoluminescence properties of the as-prepared $CaMoO_4$ nanoparticles were studied. As shown in Fig. 4, with the excited wavelength at 356 nm, the powders exhibit green emission peak at 508 nm, which is about 30 nm

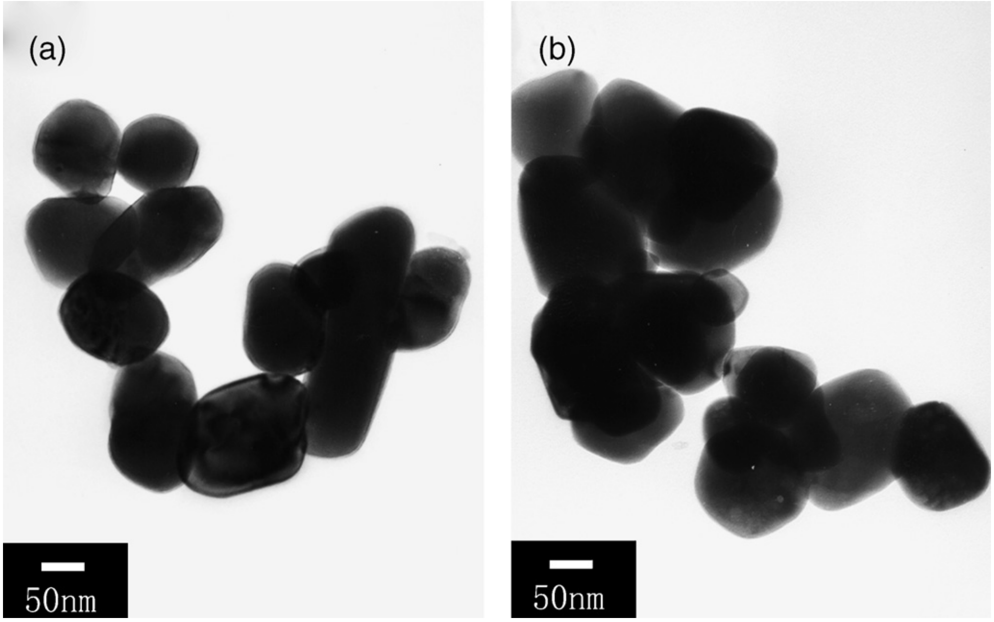

Fig. 2. TEM images of the $CaMoO_4$ nanoparticles synthesized by calcining at 270 °C for (a) 3 h and (b) 7 h, respectively, with $Ca(NO_3)_2$, Na_2MoO_4, and $LiNO_3$ molar ratio 1:1:10.

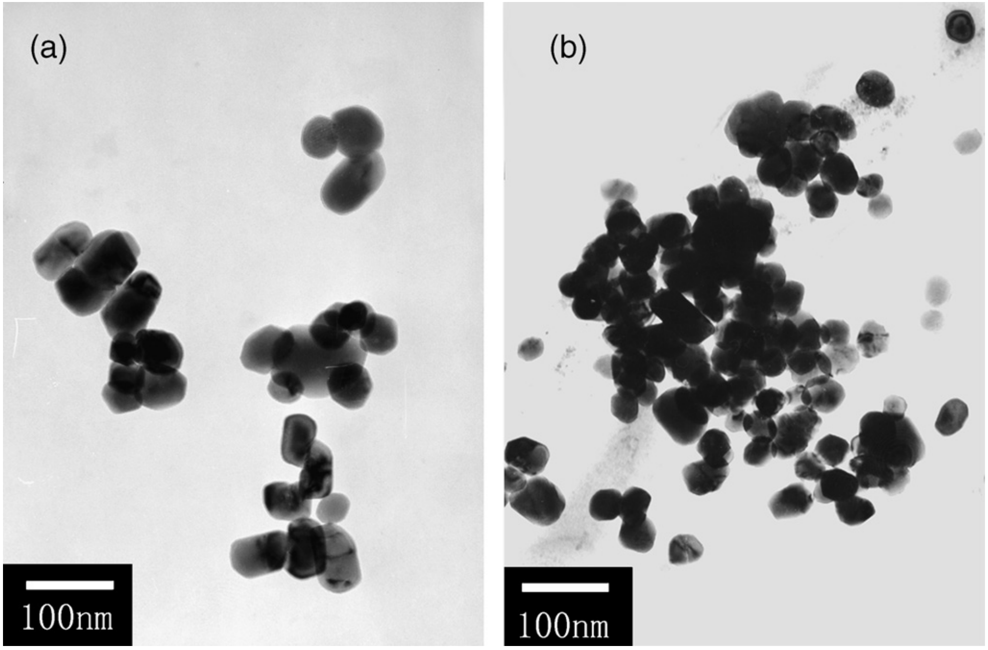

Fig. 3. TEM images of the $CaMoO_4$ nanoparticles synthesized by calcining at 270 °C for 7 h with $Ca(NO_3)_2$, Na_2MoO_4, and $LiNO_3$ molar ratio (a) 1:1:10 and (b) 1:1:20, respectively.

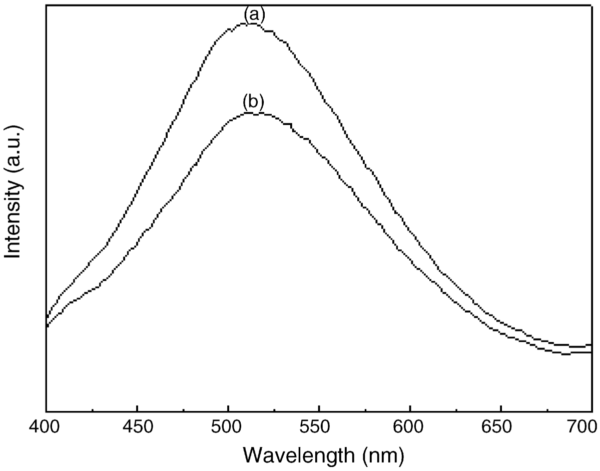

Fig. 4. PL spectra of the $CaMoO_4$ nanoparticles synthesized by calcining at 270 °C, with $Ca(NO_3)_2$, Na_2MoO_4, and $LiNO_3$ molar ratio both 1:1:10, for (a) 3 h and (b) 7 h, respectively.

lower than formerly reported for $CaMoO_4$ film (536 nm [1]). In addition, PL emission intensity of the $CaMoO_4$ nanocrystalline powders prepared at 270 °C for 3 h is noticeably stronger than that for 7 h, indicating the large dependence of the PL properties on the particle size of the $CaMoO_4$ powders.

4. Conclusion

$CaMoO_4$ nanoparticles, possessing good PL properties, were successfully synthesized at a relatively low temperature of 270 °C. This method is simple, environmentally friendly, low-cost, and not involving special requirements for high temperature and/or high pressure conditions. It is expected that some other nanoscale materials, which easily vaporize at high temperature, may be synthesized by this method.

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