Asian Journal of Chemistry; Vol. 23, No. 4 (2011), 1531-1534

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Controlled Synthesis of Calcium Tungstate Microstructures with Different Morphologies in an AOT/TEA/H_2O System

KEYAN BAO*, GE GUO, HONGXIAN SUN, JIAWEI YAN, WENRU XING and CHENGHUA DING

College of Chemistry and Pharmacy Engineering, Nanyang Normal University, Nanyang 473061, Henan Province, P.R. China

*Corresponding author: E-mail: bkeyan@mail.ustc.edu.cn

(*Received*: 3 May 2010; *Accepted*: 2 December 2010) AJC-9351

Calcium tungstate micro-crystallites with dumbbell-like morphologies were prepared in triethanolamine-water mixed solution system, employing AOT as surfactant. It is found that the morphologies of $CaWO_4$ are mostly affected by the concentration of AOT and the volume ratio of triethanolamine-water. For example, by adjusting the volume ratio of triethanolamine-water and the concentration of AOT, ellipsoid- and orange-like $CaWO_4$ micro-crystallites could be controlled synthesized. Room-temperature photoluminescence measurements showed that the prepared $CaWO_4$ micro-crystallite had a strong dark blue peak at 429 nm or blue emission peak at 448 nm, which indicated their potential application as electro-optic devices.

Key Words: Triethanolamine-water, Dumbbell, Ellipsoid, Orange, Calcium tungstate.

INTRODUCTION

Calcium tungstate ($CaWO_4$) is an important optical material with potential application in various fields, for example photoluminescence[1-3], electro-optic applications[4-7], medicine, ceramics, pigments, cosmetics[8-10]. In the past years, there are many approaches to prepare $CaWO_4$ crystallites, such as Czochralski method[11], traditional solid state reaction[12], spray pyrolysis route[13], molten salt method[14]. But $CaWO_4$ crystallites prepared by these methods are always with irregular and inhomogeneous morphologies, because of the tendency of $[WO_4]^{2-}$ to vapourize at high temperature. So many efforts have been made to develop alternative synthesis methods to $CaWO_4$, *e.g.*, microwave irradiation method[15] and wet chemical method[16-19]. It was reported that $CaWO_4$ spherical nanoparticles was synthesized by a solvothermal route[16] and $CaWO_4$ nanocrystals was prepared by cationic surfactant CTAB micro-emulsion mediated hydrothermal procedure[17].

In this paper, $CaWO_4$ crystallites with dumbbell-like morphologies self-assembled with nanobundles were large-scale synthesized in triethanolamine-water mixed solution system, employing AOT as surfactant at 120 ºC for 6 h. Further study shows that the concentration of AOT and the volume ratio of triethanolamine-water have great influence on the shapes of the products. By controlling experimental conditions, $CaWO_4$ micro-crystallites with different morphologies such as ellipsoid and orange structures were prepared.

EXPERIMENTAL

All the reagents used in the experiment were analytically pure, purchased from Shanghai Chemical Reagent Company and used without further purification.

Synthesis of $CaWO_4$ micro-crystallites: $CaWO_4$ micro-crystallites with dumbbell-like morphologies were prepared in an triethanolamine/water mixed solution system following the reported procedure: 5 mL of 0.4 mol L^{-1} $Ca(NO_3)_2$ solution was added into 35 mL triethanolamine which including 0.5 mmol AOT under vigorous stirring. After stirring for 10 min, 5 mL of 0.4 mol L^{-1} $Na_2WO_4 \cdot 2H_2O$ solution was added into the above solution. After continuing stirring for 10 min, the final solution was transferred into a 50 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and maintained at 120 ºC for 6 h before being cooled down to room temperature. The white precipitate was collected and washed with absolute ethanol and distilled water several times and dried in a vacuum at 60 ºC for 4 h.

Characterization: Powder X-ray diffraction (XRD) measurements were carried out with a Philips X'Pert diffractmeter (CuK_α λ = 1.541874 Å; nickel filter; 40 kV, 40 mA). Field emission scanning electron microscope (FESEM) images were taken on a Jeol JSM-6300F SEM. PL emission spectra of the as-prepared samples with different morphologies were measured using a 255 nm excitation line at room temperature. The Raman spectrum was recorded on a LABRAM-HR Confocal Laser MicroRaman spectrometer at ambient temperature.

RESULTS AND DISCUSSION

The XRD pattern of $CaWO_4$ with dumbbell-like morphology is shown in Fig. 1. All the peaks can be perfectly indexed to the tetragonal phase of $CaWO_4$ (a = 5.246 Å and c = 11.379 Å), which is in good agreement with the literature (JCPDS No. 85-0443). No other impurities were detected in the product. The homogeneity of this sample was also confirmed using Raman system. A typical Raman spectrum of $CaWO_4$ was obtained for this sample, as shown in Fig. 2. All grains indicate only Raman spectra of the tetragonal $CaWO_4$ phase exists in the product.

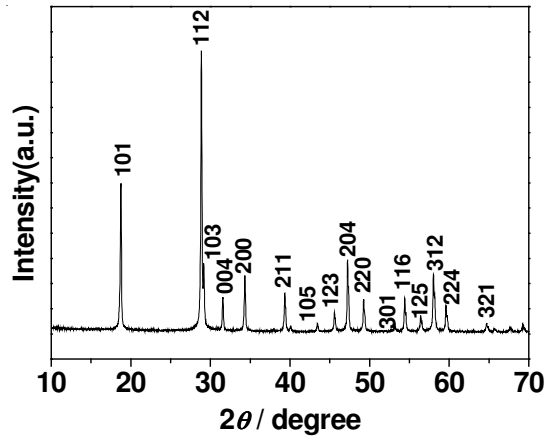

Fig. 1. XRD pattern of dumbbell-like $CaWO_4$

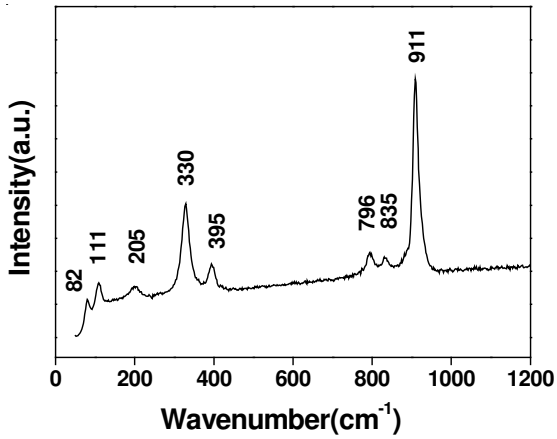

Fig. 2. Raman spectra of dumbbell-like $CaWO_4$

The morphology of the synthesized product was examined by FESEM. Fig. 3(a) is the low magnification FESEM image of $CaWO_4$, which is clearly demonstrates that the product is composed of dumbbells with the length of about 3-4 μm. A detailed observation of the dumbbell reveals that the dumbbell consists of many nanobundles and the nanobundles assembled by small nanoparticles, look like the surface of a cauliflower. The high magnification image shown in Fig. 3(b) reveals that there are lots of holes in the surface of the dumbbell.

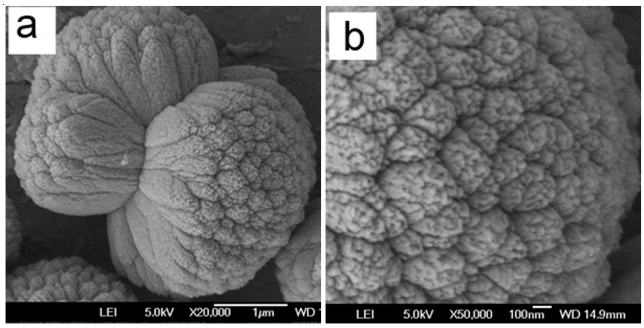

Fig. 3. FESEM images of dumbbell-like $CaWO_4$ at (a) low and (b) high magnification

Fig. 4 present FESEM images of $CaWO_4$ micro-crystallites with different morphologies such as ellipsoids and spheres were obtained by changing the ratio of TEA/H_2O and the concentration of AOT. When the ratio of TEA/H_2O was increased to 7:2, $CaWO_4$ ellipsoid with average length of the minor axis of the ellipsoids of about 1 μm and major axis in the ranges of 2-3 μm were obtained, as shown in Fig. 4(a-b). When the concentration of AOT was increased to 0.33 mol/L, orange-like $CaWO_4$ with diameters in the ranges of 5.0-6.5 μm were obtained [Fig. 4(c)]. Careful observation from the high magnification image [Fig. 4(d)] indicate that the surfaces of $CaWO_4$ are composed of nanobundles, but they are connected very closely and no gap between them.

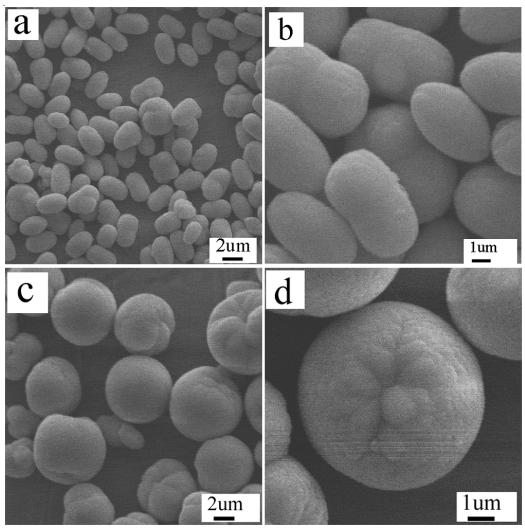

Fig. 4. Products were prepared at different experiment condition at 120 ºC: (a-b) FESEM images of ellipsoid-like $CaWO_4$, (c-d) FESEM images of orange-like $CaWO_4$

To understand the growth mechanism of $CaWO_4$ dumbbells, several experiments are carried and the intermediates at different reaction time were collected. Fig. 5 show the FESEM images of the products obtained at various reaction times, which indicate the $CaWO_4$ dumbbells grow from small nanoparticles. At the first stage (120 ºC, 0.5 h), there are lots of small nanoparticles with sizes in the range of 50-100 nm in the products, as shown in Fig. 5(a). When the reaction time was prolonged to 1 h, many small nanoparticles and a few dumbbells crystallites self-assembled with thin nanobundles appears in the products [Fig. 5(b)]. As the reaction time increased to 2 h, the product mostly consists of dumbbells crystallites, which surfaces covered with a lot of small nanoparticles, as shown in Fig. 5(c-d). When the reaction was performed at 120 ºC for 4 h, the product consists of dumbbells was obtained (Fig. 5e). A detailed observation from the image of Fig. 5(f) exhibits that there are many small

nanoparticles remaining on the tip of the dumbbells. When the reaction time was further extended to 6 h, the morphology of the product changes a little compared with that obtained at 120 ºC for 4 h, as shown in Fig. 5(g). But the magnification FESEM image in Fig. 5(h) indicates that there are no nanoparticles remaining on the tip of the dumbbell crystallites.

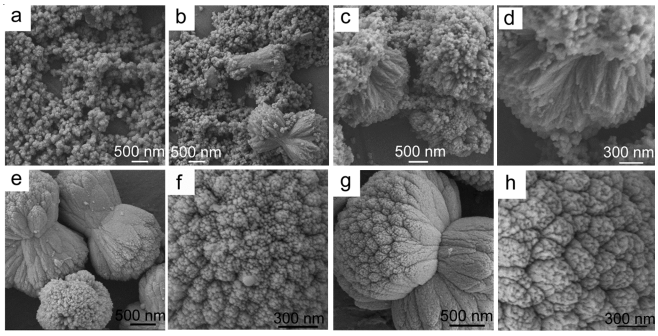

Fig. 5. FESEM images of $CaWO_4$ dumbbells prepared at 120 ºC with different reaction time: (a) 0.5 h, (b) 1 h, (c-d) 2 h, (e-f) 4 h, (g-h) 6 h

In principle, crystal growth and crystal morphology are influenced by the degree of super saturation, the diffusion of the species, the surface and interfacial energy and the structure of the crystals; that is to say extrinsic and intrinsic factors, the crystal structure and the growth surroundings are accounted for the final morphology. Cheon *et al.*[20] have reported that there are four different parameters, kinetic energy barrier, temperature, time and capping molecules, that can influence the growth pattern of nanocrystals under non-equilibrium kinetic growth conditions in the solution-based approach.

According to the literature[21,22], AOT is an anionic surfactant with a twin-tailed surfactant. It tends to self-assemble, which results in the desired structure micelle by controlling its concentration. Sugimoto and co-workers[23,24] synthesized of peanut-like hematite (α-Fe_2O_3) crystals from a gel-sol method in the presence of sulfate ions, where they disclosed that the bidentate-specific adsorption of sulfate ions to the growing surfaces parallel to the c axis resulted in the formation of hematite nanorods[25]. The mechanism for the formation of the peanut-like shape has been explained in terms of the formation of the gradual outward bending of the dense rod-like subcrystals or nanorods on both ends of ellipsoidal particles by the growth of new crystalline nanorods in the spaces between the existing subcrystals[24].

The growth mechanism of $CaWO_4$ dumbbell is similar with the literatures. The formation mechanism $CaWO_4$ dumbbell was suggested as following: the sulfonic acid groups of AOT could be preferentially adsorbed on the growing surfaces parallel to a certain crystallographic direction of $CaWO_4$, resulting in rod-like nanostructures. The dumbbell-like nanostructures could be formed through outward bending of adjoining small crystals by nucleation. Meanwhile, the presence of a double-tailed hydrophobic group in AOT would play the role of a spacer, which is present between the grow in small crystals jostling one another and so would enhance the outward bending of the crystals, favouring the formation of dumbbell-like microstructures.

Optical property: Room temperature photoluminescence properties of $CaWO_4$ with different morphologies were also investigated. Fig. 6 shows that $CaWO_4$ micro-crystallites exhibited a blue or dark blue emission peak about 448 nm or 429 nm with the excited wavelength at 255 nm. The products of ellipsoid-like and orange-like $CaWO_4$ exhibit blue emission peaks about 448 nm, while the product of dumbbell-like $CaWO_4$ exhibits a dark blue emission peak about 429 nm. The photoluminescence emissions intensity of dumbbell-like $CaWO_4$ is much stronger than of ellipsoid-like and orange-like $CaWO_4$, which indicate that the photoluminescence emissions intensity of $CaWO_4$ depended on the morphologies and sizes of the products. As we know that red, yellow and blue are very important light sources for electro-optic devices. Room temperature photoluminescence measurements showed the as-prepared $CaWO_4$ micro-crystallite had a strong dark blue or blue emission peak, which indicated their potential application as electro-optic devices.

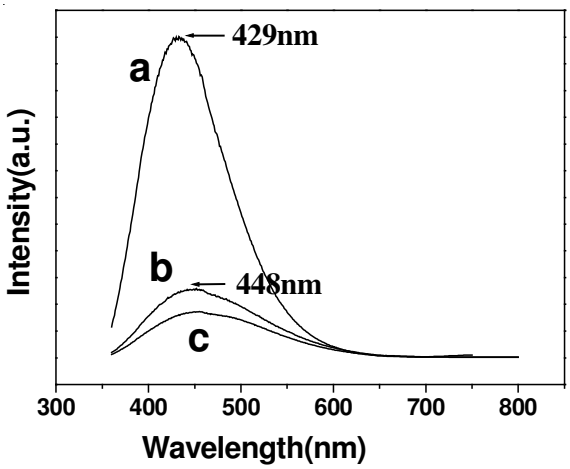

Fig. 6. Photoluminescence spectra of the products: (a) dumbbell-like $CaWO_4$, (b) ellipsoid-like $CaWO_4$ and (c) orange-like $CaWO_4$

Conclusion

In summary, $CaWO_4$ micro-crystallites with different morphologies such as dumbbell, ellipsoid and orange structures were successfully synthesized in triethanolamine-water mixed solution system, employing AOT as surfactant at 120 ºC for 6 h. The products were characterized by XRD, FESEM, photoluminescence spectra and Raman spectra. Room-temperature photoluminescence measurements showed that the products of ellipsoid-like and orange-like $CaWO_4$ exhibit blue emission peaks about 448 nm, while dumbbell-like $CaWO_4$ exhibits a dark blue emission peak about 429 nm. Red, yellow and blue are very important light sources for electro-optic devices. Room temperature photoluminescence measurements of $CaWO_4$ micro-crystallites have strong dark blue or blue emission peaks, which indicated their potential application as electro-optic devices.

ACKNOWLEDGEMENTS

This work was supported by the Key Scientific and Technological Project of Henan Province (092102210021) and Special Foundation of Nanyang Normal University (No. Nytc2004k02).

REFERENCES

1. V. Murk, M. Nikl, E. Mihokova and K. Nitsch, *J. Phys.: Condens. Mat*., **9**, 249 (1997).
2. R. Grasser, E. Pitt, A. Scharmann and G. Zimmerer, *Phys. Status Solidi B*, **69**, 359 (1975).
3. W.S. Cho, M. Yashima, M. Kakihana, A. Kudo, T. Sakata and M. Yoshimura, *Appl. Phys. Lett*,. **66**, 1027 (1995).
4. M. Nikl, P. Bohacek, P. Mihokova, N. Solovieva, A. Vedda, M. Martini, G.P. Pazzi, P. Fabeni, M. Kobayashi and M. Ishii, *J. Appl. Phys*., **91**, 5041 (2002).
5. M. Nikl, P. Bohacek, P. Mihokova, M. Kobayashi, M. Ishi, Y. Usuki, V. Babin, A. Stolovich, S. Zazubovich and M. Bacci, *J. Lumi*., **87-89**, 1136 (2000).
6. M. Kobayashi, M. Ishii, Y. Usuki and H. Yahagi, *Nucl. Instrum. Methods Phys. Res. A*, **333**, 429 (1993).
7. S.H. Yu, B. Liu, M.S. Mo, J.H. Huang, X.M. Liu and Y.T. Qian, *Adv. Funct. Mater*., **13**, 639 (2003).
8. Z.L. Zhang, Q.S. Wu and Y.P. Ding, *Inorg. Chem. Commun*., **6**, 1393 (2003).
9. Z.P. Liu, Z.K. Hu, J.B. Liang, S. Li, Y. Yang, S. Peng and Y.T. Qian, *Langmuir*, **20**, 214 (2004).
10. X.L. Hu and Y.J. Zhu, *Langmuir*, **20**, 1521 (2004).
11. S.P.S. Porto and J.F. Scott, *Phys. Rev*., **157**, 716 (1967).
12. G. Blasse and L.H. Brixner, *Chem. Phys. Lett*., **173**, 409 (1990).
13. Z. Lou and M. Cocivera, *Mater. Res. Bull*., **37**, 1573 (2002).
14. Y.G. Wang, G.T. Tao and J.F. Ma, *Mater. Lett*., **60**, 291 (2006).
15. J.H. Ryu, J.W. Yoon and K.B. Shim, *Electrochem. Solid-State Lett*., **8**, 15 (2005).
16. S.J. Chen, J. Li, X.T. Chen and X.Z.You, *J. Crystal Growth*, **253**, 361 (2003).
17. L.N. Sun, G.B. Sun and C.W. Hu, *J. Crystal Growth*, **289**, 231 (2006).
18. H.W. Liao, Y.F. Wang, X.M. Liu, Y.D. Li and Y.T. Qian, *Chem. Mater*., **12**, 2819 (2000).
19. D. Chen, G.Z. Shen, K.B. Tang, H.G. Zheng and Y.T. Qian, *Mater. Res. Bull*., **38**, 1783 (2003).
20. S.M. Lee and Cho. S.N. Cheon, *J. W. Adv. Mater*., **15**, 441 (2003).
21. J.H. Fendler, *Chem. Rev*., **87**, 877 (1987).
22. J. Tanori and M.P. Pileni, *Langmuir*, **13**, 639 (1997).
23. T. Sugimoto, M.M. Khan and A. Muramatsu, *Colloids Surf. A*, **70**, 167 (1993).
24. D. Shindo, G.S. Park, W. Waseda and T. Sugimoto, *J. Colloid Interf. Sci*., **168**, 478 (1994).
25. T. Sugimoto and Y. Wang, *J. Colloid Interf. Sci*., **207**, 137 (1998).