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Short communication

Facile electrochemical synthesis of $PbWO_4$ dendrites

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Abstract

$PbWO_4$ dendrites have been successfully synthesized by a simple sonochemical method without any surfactants at room temperature. The as-prepared powders were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), electron diffraction (ED), and high-resolution transmission electron microscopy (HRTEM). The effect of pH value, molar ratio of $[WO_4^{2-}]/[Pb^{2+}]$, reaction time, and the initial concentration of the starting solution on the formation of $PbWO_4$ dendrites was investigated. Experimental results indicate that the molar ratio of $[WO_4^{2-}]/[Pb^{2+}]$ played a crucial role in the formation of $PbWO_4$ dendrites. A growth mechanism of $PbWO_4$ dendrites was also discussed. The present process is proved to be environment-friendly, and can be extended to the controllable synthesis of other tungstates.

Keywords: $PbWO_4$ dendrites; Sonochemical synthesis

1. Introduction

Recently, much attention has been focused on dendritic structures, which display distinct structures and may open new opportunities for wide applications in future nanodevices [1,2]. Lead tungstate ($PbWO_4$) nano- and macrocrystals with a tetragonal scheelite-type structure are of technological importance due to their excitonic luminescence, thermoluminescence and stimulated Raman scattering (SRS) behavior [3,4]. In previous studies, $PbWO_4$ dendrites have been synthesized by the microemulsion-based solvothermal method, surfactant-assisted hydrothermal process, and the surfactant-assisted solution chemical method [5–7]. However, all these methods required the assistance of surfactants and the procedure was complex.

The sonochemical method is a novel method for the preparation of nanoparticles, and has advantages of rapid formation, narrow size distributions, and high purities [8,9]. In this paper, we first report the controlled synthesis of $PbWO_4$ dendrites by a facile sonochemical route without any surfactants, which is of fundamental importance in investigating the correlation between morphology and basic physical properties.

2. Experimental procedure

All the chemicals were of analytical grade purity. In a typical experiment, Na_2WO_4 and $Pb(NO_3)_2$ were used as starting materials. The effect of molar ratio of $[WO_4^{2-}]/[Pb^{2+}]$ on the formation of $PbWO_4$ was investigated. Appropriate amounts of Na_2WO_4 and $Pb(NO_3)_2$, such as 0.002 M Na_2WO_4 and 0.010 M $Pb(NO_3)_2$ (1:5), 0.002 M Na_2WO_4 and 0.002 M $Pb(NO_3)_2$ (1:1), 0.010 M Na_2WO_4 and 0.002 M $Pb(NO_3)_2$ (5:1), were separately dissolved in 20 ml distilled water to form aqueous solutions, and then were mixed together with strongly magnetic stirring at room temperature. Next, the solutions were irradiated with a high-intensity ultrasonic horn for some time under ambient air. Finally, the resultant precipitates were centrifuged, washed with distilled water, and dried naturally for characterization. The effect of the initial concentration of the starting solution on the formation of $PbWO_4$ was also investigated. When the molar ratio of $[WO_4^{2-}]/[Pb^{2+}]$ was kept 5:1, the solution concentrations were adjusted to 0.0125 M, 0.025 M, 0.05 M, and 0.1 M.

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X-ray diffraction was performed on an X-ray diffractometer (D8 Focus, Germany) using CuKα radiation. Transmission electron microscope (TEM) images were taken with a JEOL, 200CX TEM by using an acceleration voltage of 160 kV. The samples used for TEM observations were prepared by dispersing some powder products in ethanol followed by ultrasonic vibrations for 10 min, then placing a drop of the dispersion onto a copper grid coated with a layer of amorphous carbon.

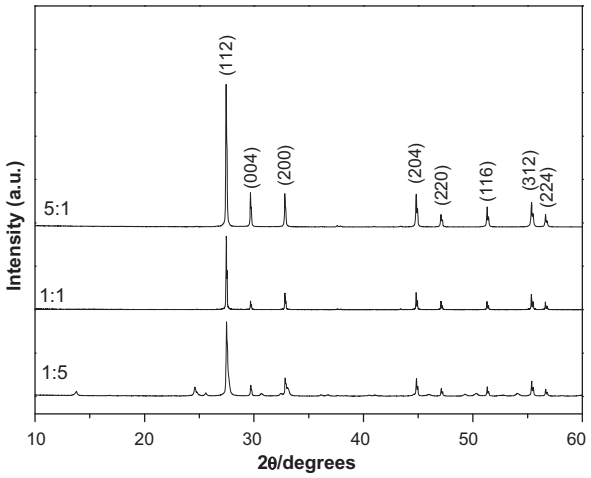

Fig. 1. Powder X-Ray diffraction patterns of the as-prepared $PbWO_4$ samples synthesized by the sonochemical process for ultrasonic time 1 h with different $[WO_4^{2-}]/[Pb^{2+}]$ molar ratios: (a) 1:5, (b) 1:1 and (c) 5:1.

3. Results and discussion

The effect of molar ratio of $[WO_4^{2-}]/[Pb^{2+}]$ on the formation of $PbWO_4$ crystals was investigated. Fig. 1 shows the XRD patterns of the as-prepared $PbWO_4$ samples prepared by the sonochemical process with different molar ratios. When the molar ratio of $[WO_4^{2-}]/[Pb^{2+}]$ was 1:5, the strong XRD patterns can be indexed to a pure tetragonal phase of well-crystallized $PbWO_4$, well consistent with the reported data (JCPDS: 85-1857). In addition, small quantities of monoclinic phase of $PbWO_4$ were detected in the XRD patterns. When the molar ratio of $[WO_4^{2-}]/[Pb^{2+}]$ was 1:1 and 5:1, all the diffraction peaks can be indexed to a tetragonal phase $PbWO_4$ with a scheelite structure, matching well with the reported data (JCPDS no. 85-1857). No other impurities and secondary phases can be detected in the XRD patterns. Based on the above results, it can be concluded that well-crystallized $PbWO_4$ crystals can be successfully obtained when the molar ratio of $[WO_4^{2-}]/[Pb^{2+}]$ was 1:1 and 5:1. The yield of $PbWO_4$ crystals produced by the sonochemical method is higher than 95%.

Fig. 2 shows the TEM images of the as-prepared $PbWO_4$ samples synthesized at pH 7 by the sonochemical process. When the molar ratio of $[WO_4^{2-}]/[Pb^{2+}]$ was 1:1, the obtained $PbWO_4$ powders were composed of irregular crystallites with the particle size about 500 nm. However, when the molar ratio of $[WO_4^{2-}]/[Pb^{2+}]$ was increased to 5:1, it is interesting to find that the obtained $PbWO_4$ products consisted of a majority of dendritic nanostructures. A higher

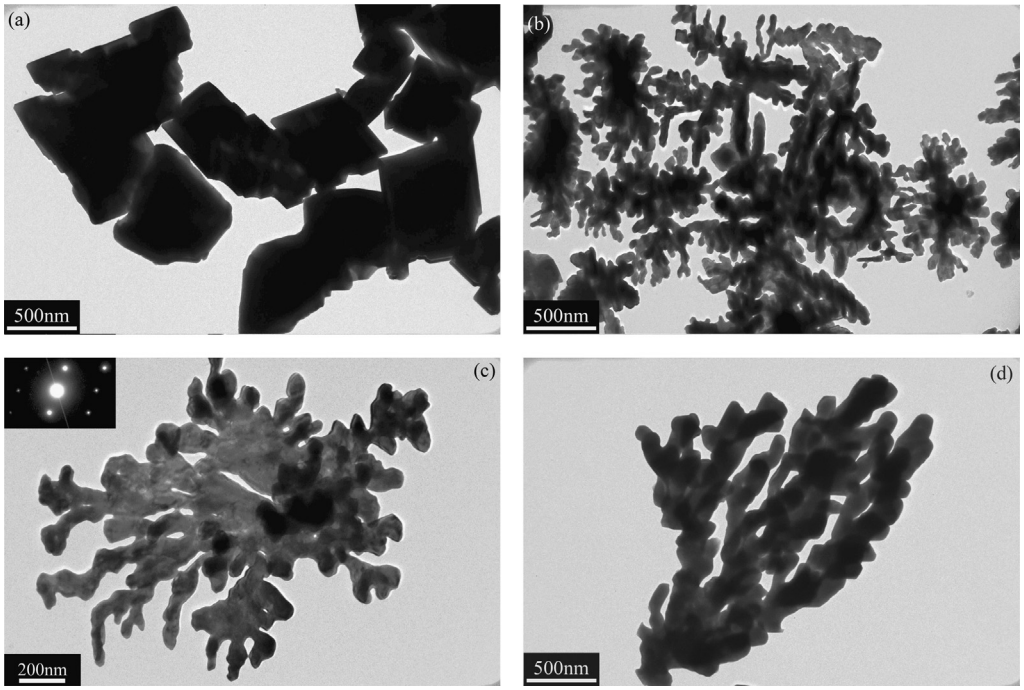

Fig. 2. TEM images of the as-prepared $PbWO_4$ samples synthesized by the sonochemical process for the ultrasonic time 1 h at pH 7 with different $[WO_4^{2-}]/[Pb^{2+}]$ molar ratios: (a) 1:1, (b) 5:1, (c) one dendrite randomly chosen from Fig. 2b and inset is the corresponding electron diffraction pattern recorded from the entire dendritic structure. (d) TEM image of the as-prepared $PbWO_4$ samples synthesized by the sonochemical process at pH 14 with $[WO_4^{2-}]/[Pb^{2+}]$ of 5:1.

magnification TEM image of a single dendrite is presented in Fig. 2c, which clearly reveals the dendritic structure. The diameter of the branches of the $PbWO_4$ dendrites was about 40 nm. Inset of Fig. 2c is the corresponding ED pattern recorded from the entire dendritic structure, which confirms that the $PbWO_4$ dendrites synthesized by the present procedure were single-crystalline in structure. The effect of the pH value on the formation of $PbWO_4$ crystallites was also investigated. When the pH value was increased from 7 to 14, as displayed in Fig. 2d, $PbWO_4$ dendrites with a larger size were obtained.

The effect of the initial solution concentration on the formation of $PbWO_4$ was studied in detail. Fig. 3a–d shows TEM photographs of the $PbWO_4$ samples obtained by the sonochemical process under different solution concentrations. When the solution concentration varied from 0.0125 M, 0.025 M, 0.05 M to 0.1 M, all the obtained $PbWO_4$ crystals appeared dendrite-like shaped. Specifically, Fig. 3e shows the HRTEM image of adjacent branches in a dendrite. It is observed that the adjacent branches shared a common crystallographic orientation and the grain boundary was not found. A typical single $PbWO_4$ dendrite is presented in Fig. 4a. Inset of Fig. 4a is the corresponding ED pattern recorded from the entire dendrite, which confirms that the $PbWO_4$ dendrites obtained by the present method were single-crystalline in structure. Further structural characterization is carried out by HRTEM. Fig. 4b–e displays the HRTEM images recorded from different areas in a single dendrite labeled b–e (the black box area in Fig. 4a). It is worth pointing out that the crystalline plane orientations in all the HRTEM images are the same, which further demonstrates the single-crystalline nature of the obtained $PbWO_4$ dendrites [10,11]. Furthermore, as displayed in Fig. 4e, it can be clearly observed that the growth units landed on the facet of $PbWO_4$ crystals, which resulted in the formation of single-crystal $PbWO_4$ dendrites. This growth process may be explained by the dissolution–precipitation mechanism.

Fig. 5 shows the XRD patterns of the as-prepared $PbWO_4$ samples prepared by the sonochemical process at

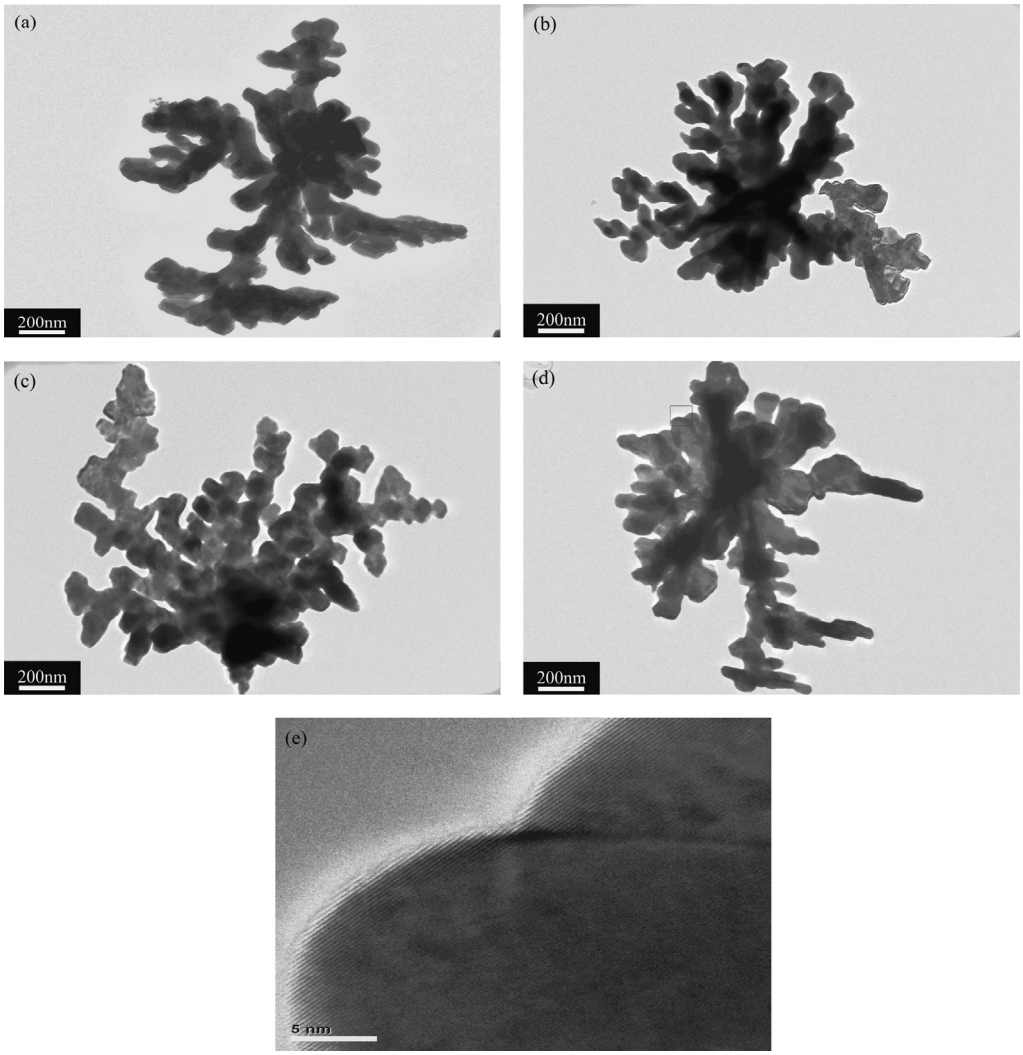

Fig. 3. TEM images of the as-prepared $PbWO_4$ samples synthesized by the sonochemical process under different solution concentrations: (a) 0.0125 M, (b) 0.025 M, (c) 0.05 M and (d) 0.1 M. All products were obtained at $[WO_4^{2-}]/[Pb^{2+}]=5:1$. (e) Higher resolution TEM images recorded in the part labeled by the black box in (d).

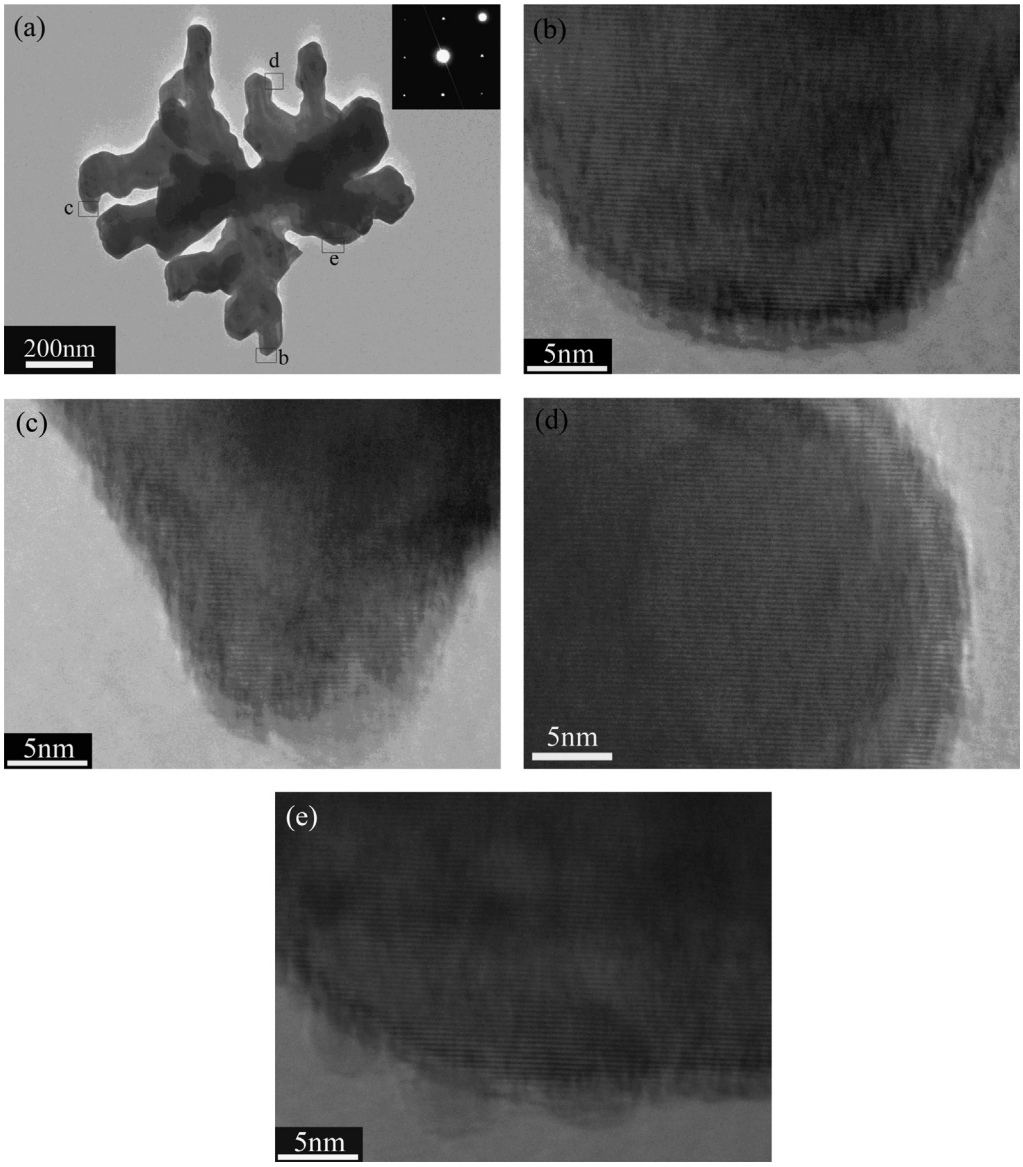

Fig. 4. (a) A typical TEM image of a single dendrite, inset is the corresponding electron diffraction pattern recorded from the entire dendritic structure. (b)–(e) Higher resolution TEM images recorded in different parts labeled by the black box in (a).

pH 7 with $[WO_4^{2-}]/[Pb^{2+}]$ of 5:1 for different ultrasonic times. When the ultrasonic time was increased from 2 min to 60 min, all the diffraction peaks can be indexed to a tetragonal phase $PbWO_4$ with a scheelite structure, matching well the reported data (JCPDS no. 85-1857).

A detailed time course study is expected to provide direct evidence of the detailed $PbWO_4$ dendrite formation process. Fig. 6a–d displays TEM photographs of the as-prepared $PbWO_4$ samples synthesized by the sonochemical process at pH 7 with $[WO_4^{2-}]/[Pb^{2+}]$ of 5:1 for different ultrasonic times. As illustrated in Fig. 6a, it is interesting to observe that the as-prepared $PbWO_4$ powders consisted of branches in the case of ultrasonic time 2 min. When the ultrasonic time was increased from 2 min to 10 min, the obtained branches have more leaves, as depicted in Fig. 6b. As shown in Fig. 6c and d, when the ultrasonic time was further increased to 30 min and 60 min, it is interesting to find that $PbWO_4$ dendrites were formed.

The surface morphology of crystals depends on the deviation degree of formation condition from equilibrium [12,13]. When the system is near equilibrium, crystals grown under these conditions generally have simple shapes with a minimum surface energy. However, as the system is driven farther from equilibrium, dendritic growth can be promoted because the growth rate of crystals greatly exceeds the mass transport rate of ions that feed the growing crystals [14,15]. In supersaturation-based crystallization, both the growth rate and the mass transport rate are governed by the concentration of the reactant [16]. We consider that the system was driven farther from equilibrium, and the growth rate of crystals was greatly increased when molar ratio of $[WO_4^{2-}]/[Pb^{2+}]$ was 5:1.

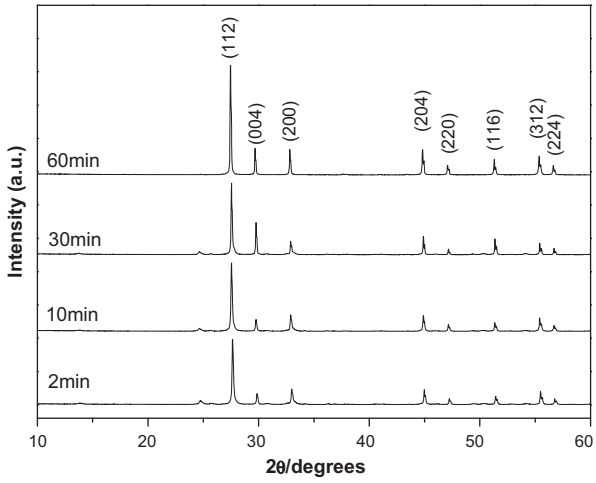

Fig. 5. Powder X-ray diffraction patterns of the as-prepared $PbWO_4$ samples synthesized by the sonochemical process at pH 14 for different ultrasonic times: (a) 2 min, (b) 10 min, (c) 30 min, and (d) 60 min.

Therefore, $PbWO_4$ dendrites were formed. Based on the morphology evolution (Fig. 6a–d), the growth process of $PbWO_4$ dendrites by the sonochemical process is simply described in Fig. 7. As the growth process is very complicated, the exact mechanism for the control synthesis of $PbWO_4$ dendrites is worthy of further study.

4. Conclusions

In summary, we have developed a new route for the controlled synthesis of $PbWO_4$ dendrites. It is found that the molar ratio of $[WO_4^{2-}]/[Pb^{2+}]$ was crucial for the sonochemical synthesis of $PbWO_4$ dendrites. $PbWO_4$ dendrites can be obtained in the case of molar ratio 5:1. This novel route is proved to be environment-friendly, and may be extended to the controllable synthesis of other tungstates.

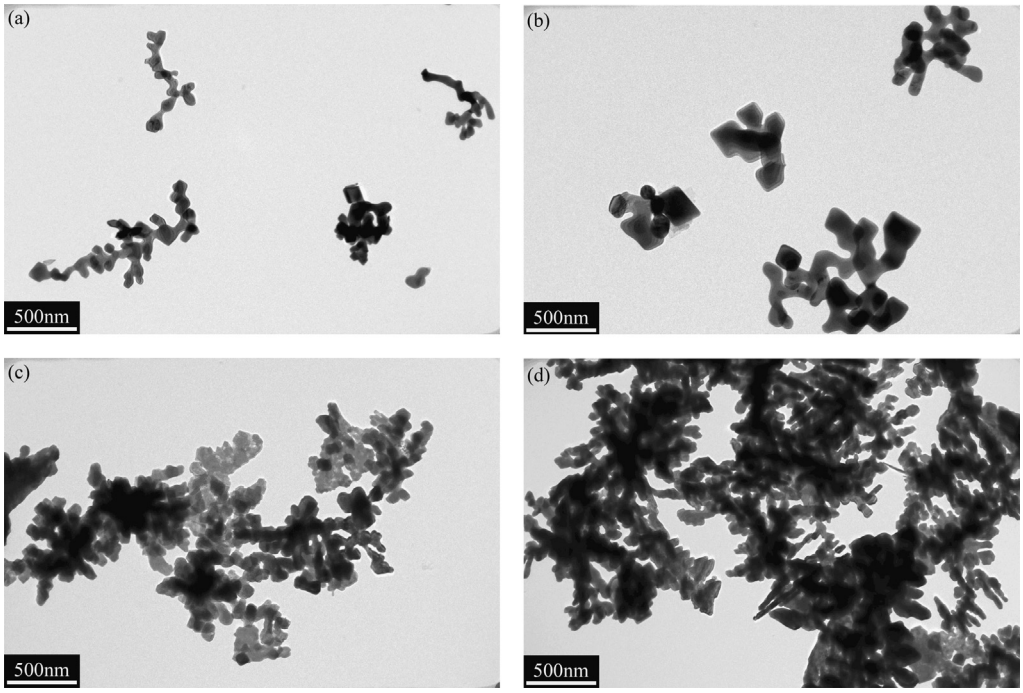

Fig. 6. TEM images of the as-prepared $PbWO_4$ samples synthesized by the sonochemical process with $[WO_4^{2-}]/[Pb^{2+}]$ of 5:1 for different ultrasonic times: (a) 2 min, (b) 10 min, (c) 30 min, and (d) 60 min.

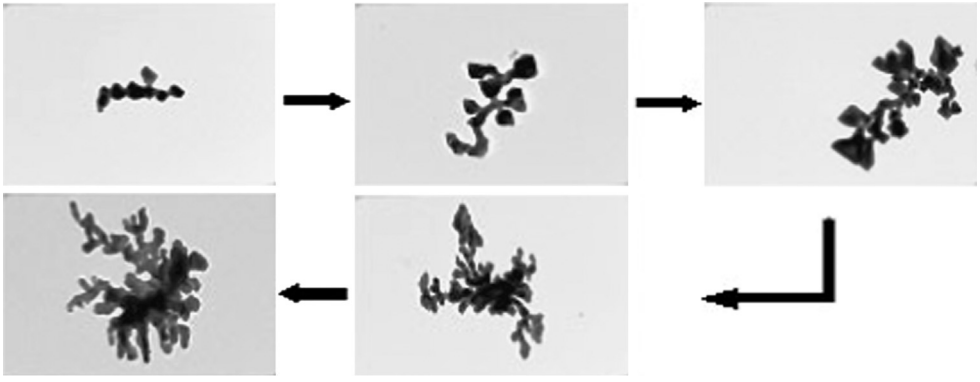

Fig. 7. Schematic representation of the growing process of $PbWO_4$ dendritic structures.

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References

[1] A. Sukhanova, A.V. Baranov, T.S. Perova, J.H.M. Cohen, I. Nabiev, Controlled self-assembly of nanocrystals into polycrystalline fluorescent dendrites with energy-transfer properties, Angewandte Chemie International Edition 45 (2006) 2048–2052.

[2] S.O. Cho, E.J. Lee, H.M. Lee, J.G. Kim, Y.J. Kim, Controlled synthesis of abundantly branched, hierarchical nanotrees by electron irradiation of polymers, Advanced Materials 18 (2006) 60–65.

[3] M. Kobayashim, M. Ishii, Y. Usuki, Comparison of radiation damage in different $PbWO_4$ scintillating crystals, Nuclear Instruments and Methods in Physics Research Section A 406 (1998) 442–450.

[4] K. Hara, M. Ishii, M. Kobayashi, M. Nikl, H. Takano, M. Tanaka, et al., La-doped $PbWO_4$ scintillating crystals grown in large ingots, Nuclear Instruments and Methods in Physics Research Section A 414 (1998) 325–331.

[5] L. Huo, Y. Chu, Controlled synthesis of $PbWO_4$ crystals via microemulsion-based solvothermal method, Materials Letters 60 (2006) 2675–2681.

[6] F. Lei, B. Yan, H.H. Chen, Q. Zhang, J.T. Zhao, Surfactant-assisted hydrothermal synthesis, physical characterization, and photoluminescence of $PbWO_4$, Crystal Growth Design 9 (2009) 3730–3736.

[7] G.J. Zhou, S.F. Wang, M.K. Li, Z.L. Xiu, H.P. Zhang, Surfactant-assisted synthesis and characterization of $PbWO_4$ dendritic nanostructure, Materials Chemistry and Physics 93 (2005) 138–141.

[8] A. Gedanken, Using sonochemistry for the fabrication of nanomaterials, Ultrasonics Sonochemistry 11 (2004) 47–55.

[9] K. Okitsu, A. Yue, S. Tanabe, H. Matsumoto, Y. Yobiko, Y.B. Yoo, Sonolytic control of rate of gold(iii) reduction and size of formed gold nanoparticles: relation between reduction rates and sizes of formed nanoparticles, Bulletin of the Chemical Society of Japan 75 (2002) 2289–2295.

[10] H.Q. Yan, R.R. He, J. Johnson, M. Law, R.J. Saykally, P.D. Yang, Dendritic nanowire ultraviolet laser array, Journal of the American Chemical Society 125 (2003) 4728–4729.

[11] Z.W. Pan, S.M. Mahurin, S. Dai, D.H. Lowndes, Nanowire array gratings with ZnO combs, Nano Letters 5 (2005) 723–727.

[12] Y. Oaki, H. Imai, Experimental demonstration for the morphological evolution of crystals grown in gel media, Crystal Growth and Design 3 (2003) 711–716.

[13] T. Kuroda, T. Irisawa, A. Ookawa, Growth of a polyhedral crystal from solution and its morphological stability, Journal of Crystal Growth 42 (1977) 41–46.

[14] C.M. Lopez, K.S. Choi, Electrochemical synthesis of dendritic zinc films composed of systematically varying motif crystals, Langmuir 22 (2006) 10625–10639.

[15] A.A. Chernov, Stability of faceted shapes, Journal of Crystal Growth 24 (1974) 11–31.

[16] R. Devon, F.J. Rose, D. Douthat, J. Maselko, Complex morphology in a simple chemical system, Chemical Communications 13 (2005) 1678–1680.