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Fabrication of lead tungstate microcrystals on a lead surface at room temperature

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ABSTRACT

A new strategy has been successfully designed to synthesize lead tungstate ($PbWO_4$) microcrystals on a lead surface by employing a novel solution-phase approach at room temperature. This method consists of a liquid–solid reaction between Na_2WO_4 solution and lead substrate itself in the assistance of glycine, L-glutamic acid, sodium citrate, or sodium adipic acid, respectively. The existence of these organic molecules plays an important role in the current synthetic process (serves as a growth promoter and organic structure-directing agent). This approach provides a facile strategy to produce $PbWO_4$ microcrystals on a lead substrate, which may be applicable to the synthesis of other inorganic materials on other metal substrates with various potential applications.

1. Introduction

In recent years, the chemical synthesis of inorganic materials with different morphologies has attracted considerable attention. Since the morphology of materials and their properties are closely related, different morphologies often have different properties [1–5]. The solution-phase chemical synthesis has been considered as one of the most promising methods, due to its low cost and potential advantage for large-scale production. In particular, low-temperature (typically <100 °C) aqueous-phase approaches are attractive because of their low energy requirements, and environmentally friendly processing [6,7]. In the aqueous-phase synthesis, oriented crystalline films are deposited on a substrate in aqueous media by a heterogeneous nucleation and subsequent growth. The resultant film structure is controlled by a complicated set of interactive processes in both solution and solid phases [8–10].

Lead tungstate ($PbWO_4$) has been attracting increasing attention because of its technological importance as an inorganic scintillating crystal (now widely used in particle and nuclear physics). As compared to other well-known scintillators, $PbWO_4$ is most attractive for high-energy physics applications because of its high density ($8.3\,g/cm^3$), short decay time (less than 10 ns for a large part of light output), high-irradiation damage resistance (10^7 rad for undoped and 10^8 rad for La-doped $PbWO_4$), interesting excitonic luminescence, thermoluminescence, and stimulated Raman scattering behavior [11,12]. $PbWO_4$ single crystals have usually been grown from the melt using the Czochralski and Bridgeman methods [13,14]. Several references reported the synthesis of $PbWO_4$ nano- and microcrystals with various morphologies by wet chemical methods [15–19]. However, it is still very important to develop some other, more convenient methods for the preparation of $PbWO_4$ in mild reaction conditions.

Herein, a new strategy has been successfully designed by employing a liquid–solid reaction between an aqueous solution of Na_2WO_4 and a lead substrate at room temperature. The lead substrates are used not only as a source of lead, but also as a support for $PbWO_4$ crystals. The controlled reactions allow the large scale, template-free, cost-effective synthesis of $PbWO_4$ with an ordered, uniform, and stable structure. Especially, $PbWO_4$ crystals, they grow directly on the conducting lead substrate with good electrical contact, which is of crucial importance for the development of a device with high performance.

2. Experimental

The starting solutions of analytical grade glycine (NH_2CH_2COOH) and sodium tungstate (Na_2WO_4) were freshly prepared. Lead foils (99.9%) were freshly cut from the lead rod (the diameter is about 8.0 mm). In a typical procedure, a piece of lead foil was first laid on the bottom of a 20-mL glass vial containing glycine and sodium tungstate aqueous solution. The mixed reaction solution was left undisturbed at room temperature (~20 °C) under atmospheric environment for 4–7 days. The lead foil was then removed from the glass vial, washed with deionized water and anhydrous ethanol (respectively) several times, and dried in the air for subsequent characterizations. In parallel experiments, glycine (NH_2CH_2COOH) was replaced by L-glutamic acid ($HOOCCH_2CH_2CH(NH_2)COOH$), sodium citrate, or sodium adipic acid ($NaOOC(CH_2)_4COONa$), respectively.

The phase and crystallographic structure of the as-prepared samples were determined by powder X-ray diffraction (XRD, Rigaku mini diffractometer equipped with the graphite monochromatized *Cu Kα* radiation) in the 2θ angles ranging from 10° to 70°. The morphology and size of these microcrys-

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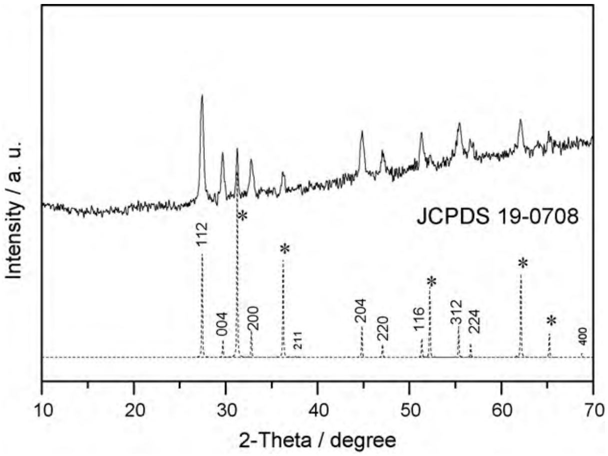

Fig. 1. XRD patterns of $PbWO_4$ microcrystals on the lead substrate with a high surface coverage. The solid curve is the experimental XRD pattern; the dashed curve is the simulated one, which is taken from the data in JCPDS No. 19-0708, the reflection peaks generated by the lead substrate are marked with an asterisk.

tals were characterized by a Hitachi S-3000N scanning electron microscope (SEM).

3. Results and discussion

Lead tungstate ($PbWO_4$) occurs in nature as tetragonal stolzite, space group $I4_1/a$ and monoclinic raspite, space group $P2_1/a$. A high-pressure form, with space group $P2_1/n$ has also been reported [20]. Fig. 1 shows the XRD patterns of the as-prepared products via the mild solution route. These diffraction peaks can be clearly indexed as a pure tetragonal stolzite structure (space group $I4_1/a$) and matched well with the reported data (JCPDS Card No. 19–0708), except those marked with asterisks from the lead substrate. No diffraction peaks for other materials or phases are observed in XRD patterns, within the resolution limit of XRD, the lead tungstate crystals appear pure.

Lead is a soft, heavy, toxic and malleable poor metal. Lead is bluish white when freshly cut, but tarnishes to a dull gray when exposed to air [21]. The surfaces of all these lead substrates were tarnished (when viewed by the naked eye) after they had been treated in the mixed solution at room temperature. Further examination under an electron microscope indicated that the formation of $PbWO_4$ microcrystals is over the entire surfaces of these substrates, which covered a large area of the lead substrate uniformly and compactly. Fig. 2a and b clearly shows a large-area microcrystals of $PbWO_4$ grown on a lead foil substrate, which was successfully covered with well-defined sheaves of $PbWO_4$ microcrystals. As shown in Fig. 2c and d, dumbbell-shaped $PbWO_4$ aggregates were obtained. These $PbWO_4$ dumbbells consist of two dandelion-like heads that are composed of radially aligned, needle-like crystals.

In the presence of aqueous solution of glycine, lead can form Pb^{2+} and react easily with $WO_4{}^{2-}$ to form $PbWO_4$ crystals on the surface of lead substrates. The formation processes of the arrays prepared at different reaction stages are, respectively studied by SEM measurements, as shown in Fig. 3. The growth procedure can be described as follows: at the beginning of reaction, the lead surface was first oxidized into a large quantity of $PbWO_4$ nanoclusters, which served as the nuclei for the crystal growth. The growth of $PbWO_4$ stemmed from these clusters and continued. During this period a typical dissolution-crystallization state was established under the current

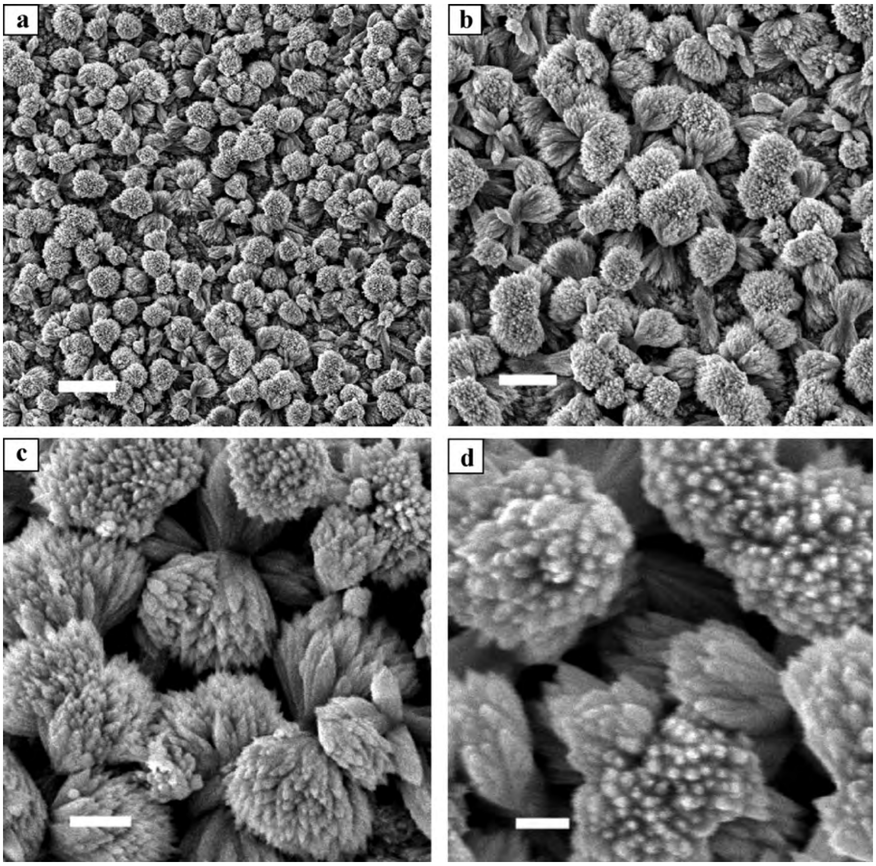

Fig. 2. SEM images of $PbWO_4$ microcrystals on a lead substrate (experimental conditions: 1.0 mL Na_2WO_4 (1.0 M) + 1.0 mL glycine (1.0 M) + 8.0 mL H_2O, at room temperature for 4 days). (a and b) Panoramic morphologies, scale bar = 10 and 5 μm, respectively. (c and d) Detailed views in high magnification, scale bar = 2 and 1 μm, respectively.

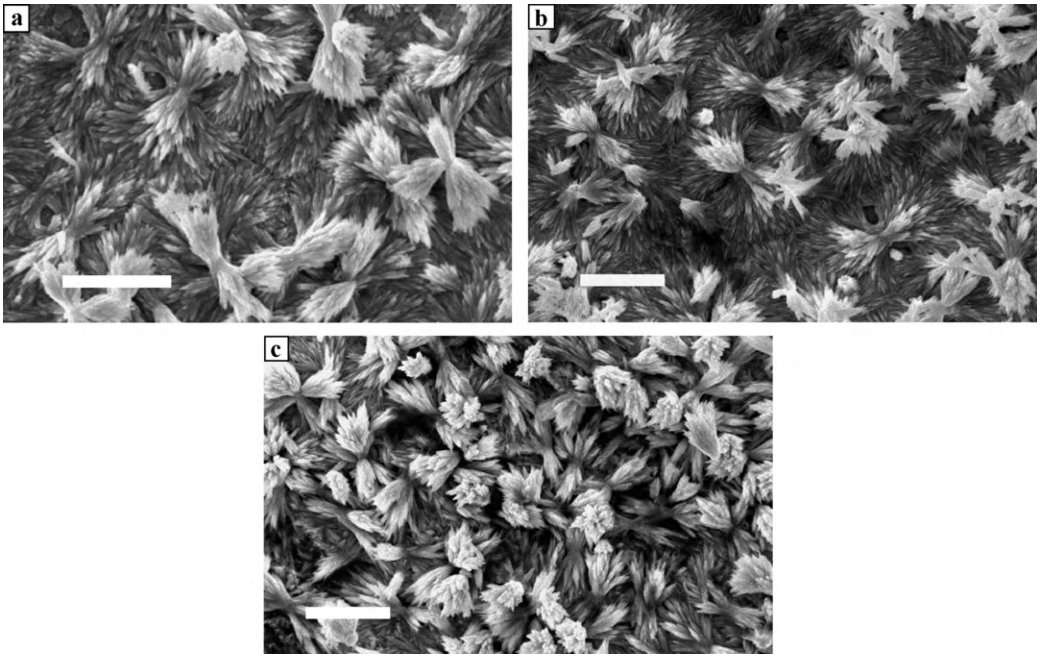

Fig. 3. Shape-evolution of $PbWO_4$ microcrystals on a lead substrate at different growth stages (experimental conditions: 1.0 mL Na_2WO_4 (1.0 M) + 1.0 mL glycine (1.0 M) + 8.0 mL H_2O, at room temperature). (a) 1 day; (b) 2 days; (c) 3 days, respectively. Scale bar = 5 μm.

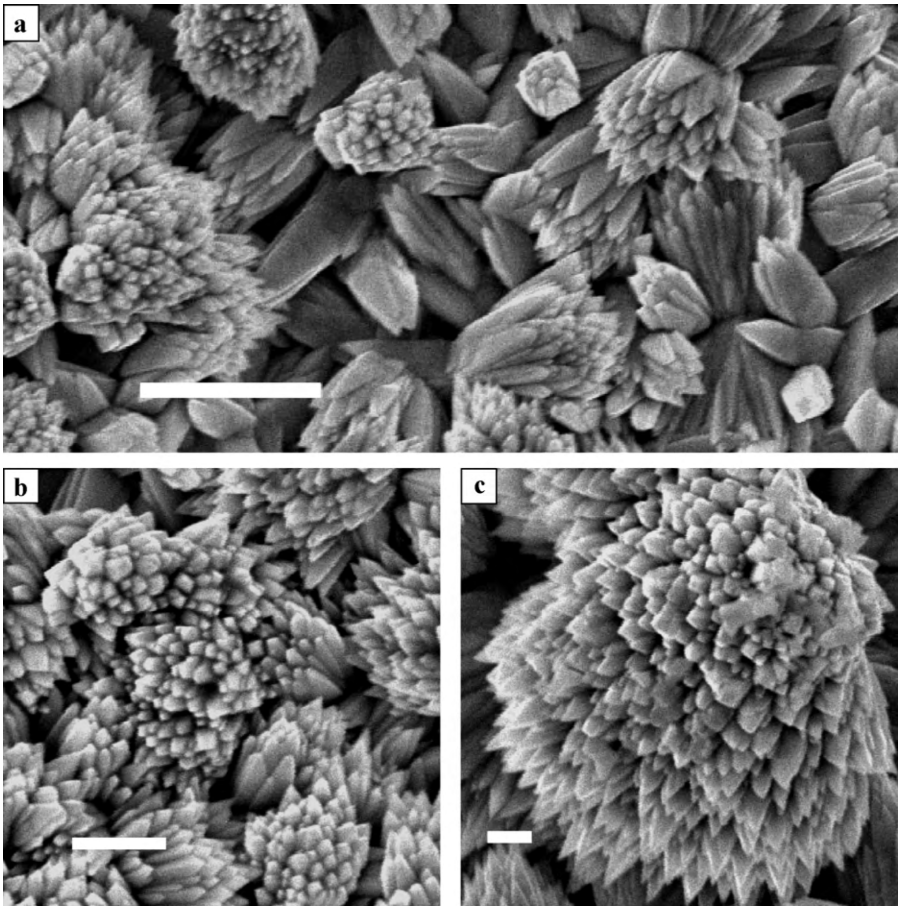

Fig. 4. SEM images of $PbWO_4$ microcrystals on a lead substrate (experimental conditions: 1.0 mL Na_2WO_4 (0.2 M) + 9.0 mL L-glutamic acid (0.01 M), at room temperature for 7 days). (a) Panoramic morphologies, scale bar = 5 μm. (b and c) Detailed views in high magnification, scale bar = 2 and 1 μm, respectively.

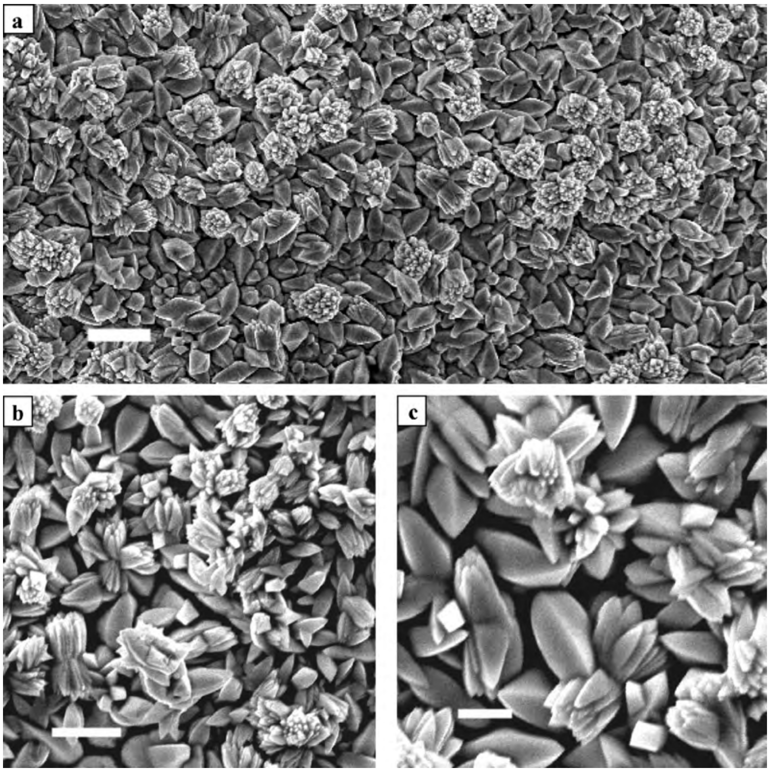

Fig. 5. SEM images of $PbWO_4$ microcrystals on a lead substrate (experimental conditions: 1.0 mL Na_2WO_4 (0.2 M) + 1.0 mL sodium citrate (1.0 M) + 8.0 mL H_2O, at room temperature for 7 days). (a) Panoramic morphologies, scale bar = 10 μm. (b and c) Detailed views in high magnification, scale bar = 5 and 2 μm, respectively.

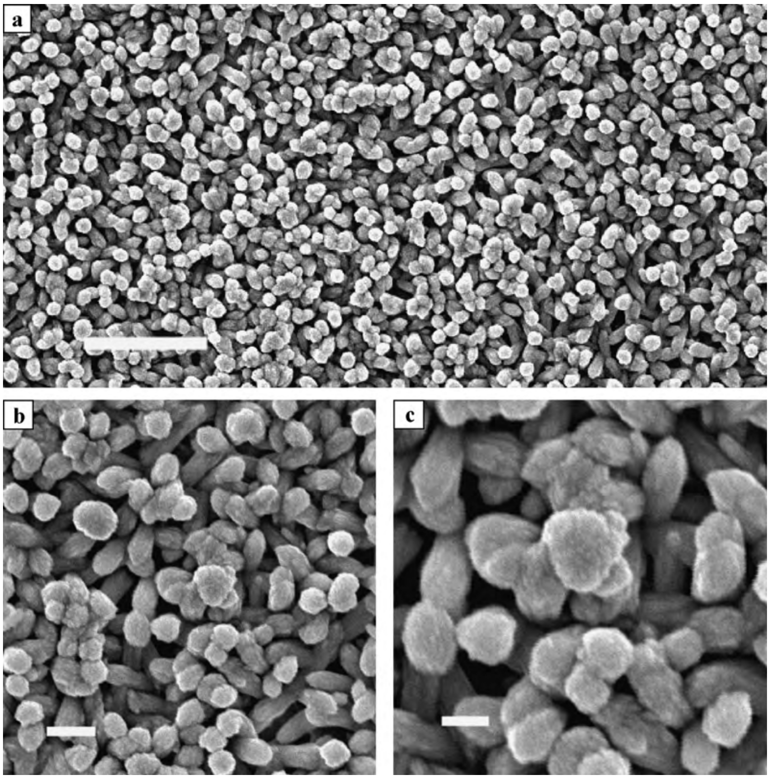

Fig. 6. SEM images of $PbWO_4$ microcrystals on a lead substrate (experimental conditions: 1.0 mL Na_2WO_4 (0.2 M) + 1.0 mL sodium adipic acid (1.0 M) + 8.0 mL H_2O, at room temperature for 7 days). (a) Panoramic morphologies, scale bar = 10 μm. (b and c) Detailed views in high magnification, scale bar = 2 and 1 μm, respectively.

experimental conditions. The formation of $PbWO_4$ microcrystals on a lead substrate includes a simple oxidation-crystallization process, and the involved chemical process is as follows:

$$Pb + 2NH_2CH_2COOH \rightarrow Pb(NH_2CH_2COO)_2 + H_2 \quad (1)$$

$$Pb(NH_2CH_2COO)_2 + Na_2WO_4 \rightarrow PbWO_4 + 2Na(NH_2CH_2COO) \quad (2)$$

In the presence of Na_2WO_4 aqueous solution, $Pb(NH_2CH_2COO)_2$ can react with $WO_4{}^{2-}$ to form $PbWO_4$ crystals on the lead surface, as shown in Formulae (1) and (2). During the whole process, Pb^{2+} ions were released slowly and gradually from the lead substrate, which is essential to form the well-defined morphology. As we known, well-defined morphologies are usually difficult to be produced by directly mixing two incompatible solutions of metal salts because of a rapid decrease in supersaturation and further depletion of reaction nutrients in a short period of time. For example, when equimolar Na_2WO_4 was mixed with a $Pb(CH_3COO)_2$ in a reaction solution, immediate fast precipitation of $PbWO_4$ with a highly reduced growth rate, results in a rapid formation of poorly controlled morphology. In the present synthetic approach, pure lead ions can be supplied statically to retain sustained supersaturation via the natural oxidation of metal lead during a long period of time. As opposed to the previous solution-based synthesis, the high rate of crystallization and continuous environmental disturbance can be avoided for the slow and progressive growth of $PbWO_4$ microcrystals.

Understanding the nucleation and growth kinetics in solution synthesis is significant in fundamental crystal science. The use of organic species for controlling the inorganic crystal growth has been extensively studied [22]. COOH-terminated organic molecules (such as L-glutamic acid, sodium citrate, and sodium adipic acid) are also suitable for growing $PbWO_4$ microcrystals in the current synthetic system. These organic molecules (also call as ligands) have the similar function with glycine. All of these organic molecules facilitate the oxidation of metal lead into Pb^{2+} ions in the mixture solution at room temperature (as shown in Formulae (1) and (2)). The corresponding SEM images of the as-prepared samples are shown in Figs. 4–6, respectively.

As compared with glycine (NH_2CH_2COOH), L-glutamic acid molecules with two functional groups ($HOOCCH_2CH_2CH(NH_2)COOH$) have higher binding affinity to lead atoms, leading to the formation of $PbWO_4$ microcrystals. Fig. 4 shows SEM images of the as-prepared samples, which are similar to the results of Fig. 2. Citrate is an important biological ligand for metal ions. It can form strong complexes with Ca^{2+}, Mg^{2+}, Fe^{3+}, Zn^{2+}, and Ag^{+} ions. In previous works, citrate has been most widely used as a shape controller and stabilizer in the synthesis of inorganic functional materials [23]. On the basis of our experiment results, we believe citrate has similar effects with glycine on the growth of the $PbWO_4$ crystals (compared Fig. 5 with Fig. 2). Sodium adipic acid ($NaOOC(CH_2)_4COONa$) is a linear molecule with two COOH functional groups at the heads of the molecule. As shown in Formulae (1) and (2), sodium adipic acid can also accelerate oxidation of metal lead and combine with Pb^{2+} ions, resulting in the formation of $PbWO_4$ crystals at room temperature (Fig. 6 shows $PbWO_4$ crystals with the rod-like morphology).

It is well-known that the crystal growth and morphology are determined by the degree of supersaturation, diffusion of the reaction, surface energy and crystal structure. That is the extrinsic and intrinsic factors (both crystal growth environments and crystal structure) have significant effects on the final morphology [24–26]. During the crystallization process (as shown in Formula (1)), lead ions (Pb^{2+}) with different ligands (organic molecules) have significant effect on the formation of $PbWO_4$ crystals (as shown in Formula (2)) in the real growth environments. It should be noted that selective adsorption of organic molecules (including glycine, L-glutamic acid, sodium citrate, or sodium adipic acid) on different crystallographic planes of $PbWO_4$ crystals may play an important role in the anisotropic growth. The default experiments (in the absence of any organic molecules) have been employed for evaluating the role of organic molecules in crystal growth. Only some irregular particles are formed on the surface of the lead substrate. Therefore, the existence of organic molecules play multiple roles during the whole crystallization process.

4. Conclusions

A useful strategy has been successfully designed to synthesize $PbWO_4$ microcrystals on lead substrate at room temperature. This synthesis involves a template-less and surfactant-less aqueous method, which enables us to generate, at large scale, low cost, and moderate temperature, advanced $PbWO_4$ films with a selectable complexity. This innovative, soft-solution approach provides a general route to the synthesis of $PbWO_4$ microcrystals on the lead substrate. Furthermore, this new strategy may be applicable for making other interesting structures or changing the substrate to another metal, alloy, and any substrate coated with lead.

Acknowledgments

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References

[1] R.D. Robinson, B. Sadtler, D.O. Demchenko, C.K. Erdonmez, L. Wang, A.P. Alivisatos, Science 317 (2007) 355.
[2] J.V. Barth, G. Costantini, K. Kern, Nature 437 (2005) 671.
[3] D.P. Wang., H.C. Zeng, J. Phys. Chem. C 113 (2009) 8097.
[4] G. Shen, Y. Bando, C. Ye, X. Yuan, T. Sekiguchi, D. Golberg, Angew. Chem. Int. Ed. 45 (2006) 7568.
[5] Y. Hou, H. Kondoh, T. Ohta, Cryst. Growth Des. 9 (2009) 3119.
[6] J. Xu, D. Xue, J. Phys. Chem. B 110 (2006) 11232.
[7] J. Xu, D. Xue, Y. Zhu, J. Phys. Chem. B 110 (2006) 17400.
[8] B.C. Bunker, P.C. Rieke, B.J. Tarasevich, A.A. Campbell, G.E. Fryxell, G.L. Graff, L. Song, J. Liu, J.W. Virden, Science 264 (1994) 48.
[9] T.L. Sounart, J. Liu, J.A. Voigt, J.W.P. Hsu, E.D. Spoerke, Z. Tian, Y. Jiang, Adv. Funct. Mater. 16 (2006) 335.
[10] L. Vayssieres, Adv. Mater. 15 (2003) 464.
[11] M. Kobayashi, M. Ishii, Y. Usuki, Nucl. Instrum. Methods Phys. Res., Sect. A 406 (1998) 442.
[12] K. Hara, M. Ishii, M. Kobayashi, M. Nikl, H. Takano, M. Tanaka, K. Tanji, Y. Usuki, Nucl. Instrum. Methods Phys. Res., Sect. A 414 (1998) 325.
[13] K. Nitsch, M. Nikl, S. Ganschow, P. Reiche, R. Uecker, J. Cryst. Growth 165 (1996) 163.
[14] K. Tanji, M. Ishii, Y. Usuki, M. Kobayashi, K. Hara, H. Takano, J. Cryst. Growth 204 (1999) 505.
[15] B. Liu, S. Yu, L. Li, Q. Zhang, F. Zhang, K. Jiang, Angew. Chem. Int. Ed. 43 (2004) 4745.
[16] J. Geng, J. Zhu, D. Lu, H. Chen, Inorg. Chem. 45 (2006) 8403.
[17] J. Yu, X. Zhao, S. Liu, M. Li, S. Mann, D. Ng, Appl. Phys. A 87 (2007) 113.
[18] J. Geng, J. Zhu, H. Chen, Cryst. Growth Des. 6 (2006) 321.
[19] D. Chen, G. Shen, K. Tang, Z. Liang, H. Zheng, J. Phys. Chem. B 108 (2004) 11280.
[20] R. Chipaux, G. Andre, A. Cousson, J. Alloys Compd. 325 (2001) 91.
[21] K. Thurmer, E. Williams, J. Reutt-Robey, Science 297 (2002) 2033.
[22] T. Zhang, W. Dong, M. Keeter-Brewer, S. Konar, R.N. Njabon, Z.R. Tian, J. Am. Chem. Soc. 128 (2006) 10960.
[23] J. Liang, J. Liu, Q. Xie, S. Bai, W. Yu, Y. Qian, J. Phys. Chem. B 109 (2005) 9463.
[24] J. Xu, D. Xue, J. Phys. Chem. B 110 (2006) 7750.
[25] H. Bai, X. Liu, Y. Zhang, Mater. Lett. 63 (2009) 100.
[26] X. Liu, K. Zhou, L. Wang, B. Wang, Y. Li, J. Am. Chem. Soc. 131 (2009) 3140.