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Controllable synthesis of $CdWO_4$ nanorods and nanowires via a surfactant-free hydrothermal method

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Single-crystalline $CdWO_4$ nanorods and nanowires have been controllably synthesized via a simple surfactant-free hydrothermal route. The obtained samples were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and electron diffraction (ED). The results showed that the starting material played a crucial role in the controllable preparation of $CdWO_4$ nanorods and nanowires. The synthesis mechanism was also discussed.

Key-words : Controllable synthesis, Hydrothermal, Surfactant-free, $CdWO_4$ nanorods, Nanowires

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1. Introduction

One-dimensional nanomaterials, such as nanorods, nanowires, and nanotubes, have attracted intensive interest owing to their potential applications in optoelectronic devices.[1)–3)] Therefore, the preparation of nanowires has been subjected to intense research in order to understand the role of dimensionality and size in optical and magnetic properties. Cadmium tungstate ($CdWO_4$) is deemed to be an important material due to its chemical and optical properties.[4),5)] Various techniques have been developed to synthesize $CdWO_4$ crystals, such as solid-state metathetic reaction for $CdWO_4$ particles,[6)] co-precipitation method for nanoparticles,[7)] and molten salt route for nanorods.[8)] Hydrothermal method is considered as an effective and convenient synthetic process. Up to now, $CdWO_4$ nanorods and nanowires have been successfully synthesized by the hydrothermal method assisted by copolymers, CTAB and citric acid.[9)–11)] However, the controllable synthesis of $CdWO_4$ nanorods and nanowire by a simple and surfactant-free method is still a significant challenge.

In the present paper, we report the controllable synthesis of $CdWO_4$ nanorods and nanowires via a simple and surfactant-free hydrothermal method. Furthermore, the aspect ratio and size of the resultant one-dimensional $CdWO_4$ nanostructures can be simply controlled.

2. Experimental

Analytical grade sodium tungstate ($Na_2WO_4 2H_2O$), cadmium chloride ($CdCl_2 2.5H_2O$), and potassium carbonate (K_2CO_3) were used as the starting materials. Appropriate amounts of Na_2WO_4 and $CdCl_2$ were dissolved in distilled water to form aqueous solutions, separately; and then mixed together with strongly magnetic stirring at room temperature. The suspension solution was transferred into the stainless-steel autoclave for hydrothermal treatment. The autoclave was sealed, heated, held for some time, and then cooled to room temperature naturally. After the above hydrothermal treatment, the products were filtered, washed with distilled water and absolute ethanol for several times, and then dried at 70°C for 4 h for characterization.

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The effect of starting material on the formation of $CdWO_4$ was investigated. In the contrast experiment, the $CdCl_2$ solution was first mixed with K_2CO_3 solution under strongly magnetic stirring, and then the obtained $CdCO_3$ solution was mixed with Na_2WO_4 solution. Finally, the mixed solution was transferred into the stainless-steel autoclave for the same hydrothermal treatment.

X-ray diffraction was performed on an X-ray diffractometer (D8 Focus, Germany) using Cu Kα radiation. Transmission electron microscope (TEM) images were taken with a JEOL, 200CX TEM by using an acceleration voltage of 160 kV.

3. Results and discussion

Figures 1(a)–1(c) shows the XRD patterns of the as-prepared $CdWO_4$ powders synthesized by the hydrothermal method at different temperatures using Na_2WO_4 and $CdCl_2$ as starting material. All XRD patterns can be indexed to the JCPDS card NO. 14-676 and no impurity peaks were detected in the experimental range. Furthermore, the diffraction peaks became

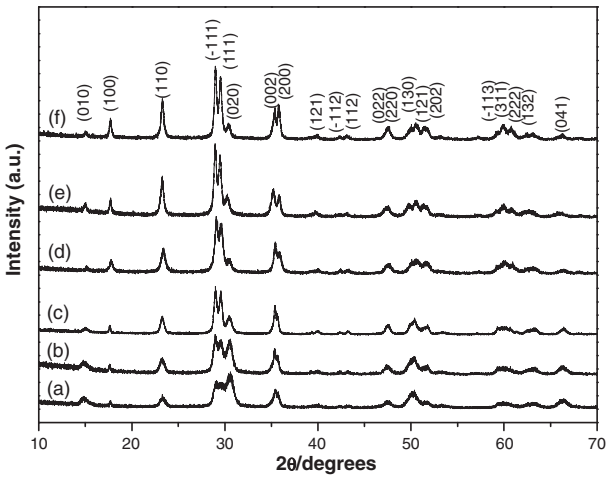

Fig. 1. XRD patterns of the as-prepared $CdWO_4$ samples synthesized by the hydrothermal process using Na_2WO_4 and $CdCl_2$ as starting material at (a) 120°C, (b) 160°C, (c) 200°C, and using Na_2WO_4 and $CdCO_3$ as starting material at (d) 120°C, (e) 160°C, (f) 200°C, respectively.

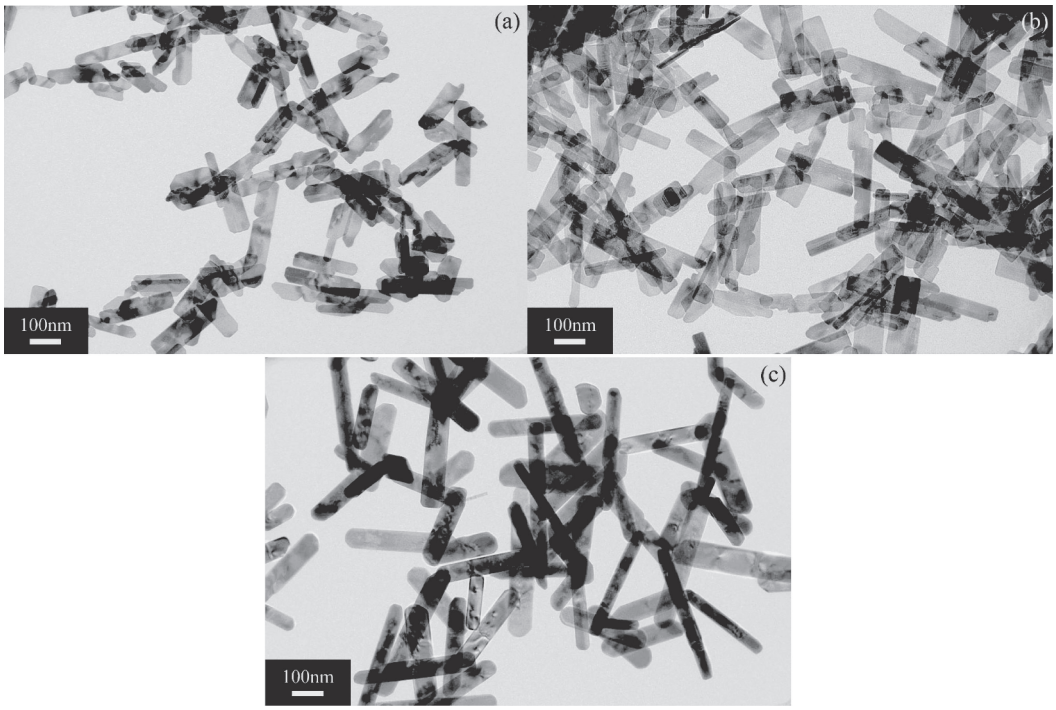

Fig. 2. TEM image of the as-prepared $CdWO_4$ samples synthesized by the hydrothermal process using Na_2WO_4 and $CdCl_2$ as starting material at different temperatures, (a) 120°C, (b) 160°C, and (c) 200°C, respectively.

stronger and sharper when the reaction temperature was increased from 120 to 200°C, indicating that higher temperature would be beneficial to the crystallization and evolution of $CdWO_4$ crystallites. In addition, as illustrated in Figs. 1(d)–1(f), pure $CdWO_4$ were obtained by the same hydrothermal route using Na_2WO_4 and $CdCO_3$ as starting material instead of Na_2WO_4 and $CdCl_2$. Based on the above results, it can be concluded that well-crystallized $CdWO_4$ crystals can be successfully obtained under the current synthetic conditions by using deferent starting materials.

Figure 2 displays the TEM images of the $CdWO_4$ samples synthesized by the hydrothermal method at different temperatures using Na_2WO_4 and $CdCl_2$ as starting material. As shown in Fig. 2(a), it is clear that the products obtained at 120°C consist of nanorods with average diameters of 20–40 nm and lengths of about 150–200 nm. Furthermore, when the reaction temperature was increased from 120 to 160, and 200°C, $CdWO_4$ nanorods with more uniform diameter and larger length were formed. The aspect ratio of the resultant nanorods is about 4–6, as depicted in Figs. 2(b) and 2(c). However, when Na_2WO_4 and $CdCO_3$ were used as starting material instead of Na_2WO_4 and $CdCl_2$, it is interesting to find that the obtained powders are homogeneous nanowires with diameters of 40–50 nm and lengths of about 0.5–1 μm, as illustrated in **Fig. 3**(a). Furthermore, as displayed in Figs. 3(b) and 3(c), obvious growth of nanowires can be observed in the case of further increasing the reaction temperature. The aspect ratio of the resultant nanowires is larger than 40. The TEM image [Fig. 3(d)] of a single separate nanowire clearly shows that the obtained nanowire is straight and uniform in diameter. The corresponding electron diffraction pattern taken from the chosen single nanowire is displayed in Fig. 3(d). The ED patterns indicate that the nanowires are single-crystal and grow along the [100] direction, which was also consistent with the above XRD results and the reports.[9),10),12)]

The formation process of $CdWO_4$ nanorods and nanowires in the hydrothermal system was based on the two following reactions, respectively.

$$CdCl_2 + Na_2WO_4 \rightarrow CdWO_4 + 2NaCl \text{ (nanorods)}$$

$$CdCO_3 + Na_2WO_4 \rightarrow Na_2CO_3 + CdWO_4 \text{ (nanowires)}$$

We conjecture that the $CdWO_4$ crystals possess the characteristic of oriented growth. Therefore, $CdWO_4$ nanorods were easily formed in the case of using Na_2WO_4 and $CdCl_2$ as starting material. The role of starting material $CdCO_3$ on the formation of $CdWO_4$ nanowires was investigated. **Figure 4** shows the TEM image of $CdCO_3$ obtained by the reaction $CdCl_2$ solution with K_2CO_3. It is clear that the morphology of $CdCO_3$ crystals was cube-like, which was greatly different from that of the obtained $CdWO_4$ nanowires [as displayed in Fig. 3(c)]. Therefore, we think that $CdCO_3$ can not act as a role of template in the present process. But, compared with the free Cd^{2+}, the presence of $CdCO_3$ may result in a lower nucleation rate which would benefit to the orientation growth. According to the analysis, many compounds containing cadmium could be favorable for the formation of nanowires. To verify the speculation, many experiments using different starting materials [such as $Cd(OH)_2$, CdC_2O_4, and $Cd(CH_3COO)_2$] have been carried out, and all the obtained $CdWO_4$ powders were composed with nanowires with large aspect ratio, which is consistent with the above analysis. As the reaction mechanism and hydrothermal conditions are complicated, the exact mechanism for the controllable synthesis of $CdWO_4$ nanorods and nanowires still needs to be further investigated.

4. Conclusions

$CdWO_4$ nanorods and $CdWO_4$ nanowires have been controllably synthesized by a surfactant-free hydrothermal method. The diameter and length of nanorods were about 20–40 nm and

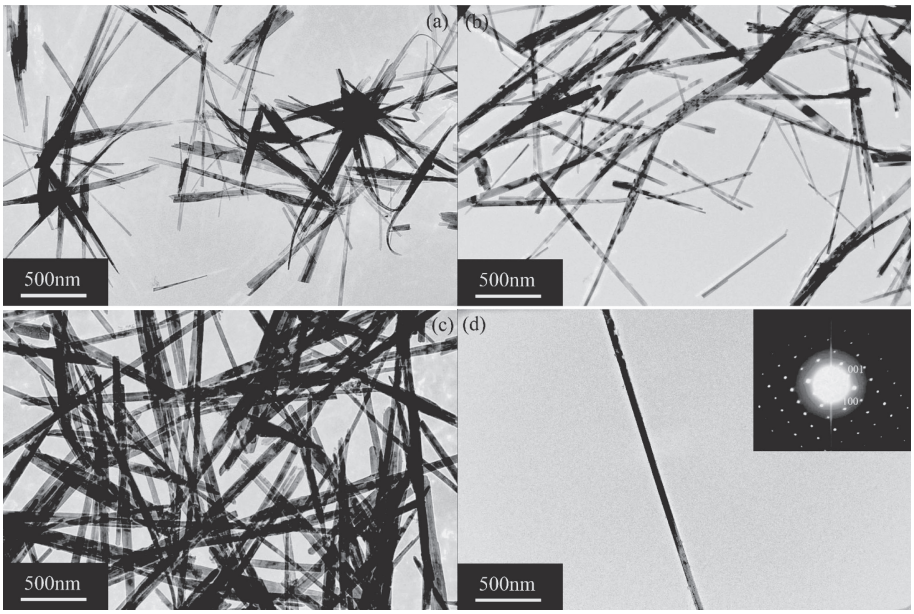

Fig. 3. TEM image of the as-prepared $CdWO_4$ samples synthesized by the hydrothermal process using Na_2WO_4 and $CdCO_3$ as starting material at different temperatures, (a) 120°C, (b) 160°C, and (c) 200°C, respectively, (d) one nanowire randomly chosen from Fig. 3(c) and corresponding electron diffraction pattern (inset).

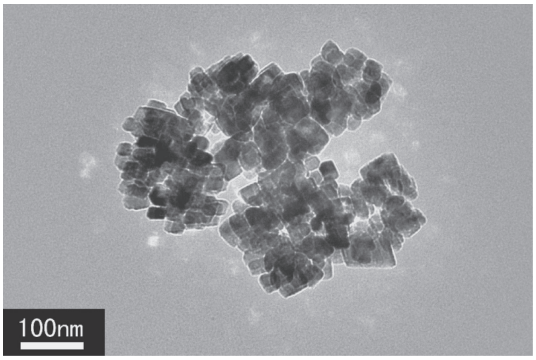

Fig. 4. (a) TEM image of starting material $CdCO_3$.

150–300 nm, respectively. The diameter of the obtained nanowires were about 30–50 nm and the length was up to several micrometers. It was found that the starting material played a key role in the controllable synthesis of $CdWO_4$ nanorods and nanowires. Our study may provide a new route for the control growth of one-dimensional $CdWO_4$ crystals, and the investigations of the morphology-dependent properties of $CdWO_4$ crystals are underway, which will be reported elsewhere in the near future.

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