WO₃·nH₂O Crystals with Controllable Morphology/Phase and Their Optical Absorption Properties
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ABSTRACT: In this work, a one-step hydrothermal route is developed to prepare WO₃·nH₂O crystals with various morphology/phases, for which any surfactants, templates, or structure-directing agents are not used. Five types of WO₃·nH₂O crystals, including orthorhombic WO₃·H₂O nanoplates, rectangular monoclinic WO₃ nanosheets, orthorhombic WO₃·0.33H₂O microspheres, hexagonal WO₃ nanorods, and bundle-like hexagonal WO₃ hierarchical structures, are successfully obtained by adjusting the amount of H₂SO₄ and reaction temperature. According to the experimental results, the formation mechanism for various WO₃·nH₂O species is proposed. In addition, the optical absorption properties of these WO₃·nH₂O crystals are also investigated by UV–vis absorption spectra.

1. INTRODUCTION
The controllable preparation of crystals is a challenging issue in the field of chemistry and materials. Particularly, the synthesis of transition-metal oxides (TMOs) with controllable morphology and crystal phase has gotten widespread international attention because of the strongly determined physical and chemical properties of TMOs. Among these TMOs, tungsten trioxide and its hydrates (WO₃·nH₂O) have been widely investigated owing to their distinct optical and electrical properties and the functional applications in photocatalytic degradation, gas sensors, water splitting, supercapacitors, lithium ion batteries, and electro/opto/gasochromic devices.

Over the past two decades, many approaches, such as spray pyrolysis, sol–gel, anodization, thermal decomposition, microemulsion technique, chemical vapor deposition, hydro/solvothermal reactions, etc., have been used to prepare WO₃·nH₂O crystals with various morphologies/phases. However, most of them have more or less shortcomings, such as expensive equipment/reagents, complicated operation, and time-consuming processes, which makes large-scale economic production difficult. In this situation, a one-step hydrothermal method may be a viable candidate for preparing WO₃·nH₂O crystals due to the simple operation, lower energy consumption, good repeatability, and mild environment. For example, Shi et al. produced orthorhombic WO₃·H₂O hierarchical structures via a hydrothermal route with Na₂SO₄ additive, and three types of crystals (cubic octahedron-shaped WO₃·0.5H₂O, hexagonal WO₃ nanorods, and orthorhombic WO₃·0.33H₂O nanoplates) can be produced. Zhang et al. prepared orthorhombic WO₃·H₂O hierarchical structures by a hydrothermal route with the assistance of cetrimonium bromide (CTAB) surfactant. Mohamed et al. employed the hydrothermal method to prepare hexagonal WO₃ with various morphologies by using metal salts as structure-directing agents. Although great progress has been made, there remains a huge challenge in the preparation of WO₃·nH₂O crystals with controllable morphology/phase, which usually require surfactants, templates, or structure-directing agents.

Herein, a one-step hydrothermal method was developed for preparing controllable WO₃·nH₂O crystals by using Na₂WO₄·2H₂O and H₂SO₄ as the starting materials. No surfactants, templates, or structure-directing agents were used in this hydrothermal system. Five types of WO₃·nH₂O crystals, including orthorhombic WO₃·H₂O (o-WO₃·H₂O) nanoplates, rectangular monoclinic WO₃ (m-WO₃) nanosheets, orthorhombic WO₃·0.33H₂O (o-WO₃·0.33H₂O) microspheres, hexagonal WO₃ (h-WO₃) nanorods, and bundle-like hexagonal WO₃ hierarchical structures, were successfully synthesized by adjusting the amount of H₂SO₄ and the reaction temperature. The formation mechanism of these WO₃·nH₂O crystals was
proposed. In addition, the optical absorption properties and band gaps of them were also evaluated.

2. EXPERIMENTAL PROCEDURE

All chemicals were used without further purification; they are of analytical grade. In a typical preparation, 4.6 g of Na2WO4·2H2O and a certain amount of H2SO4 solution (96–98 wt %) were added to 40 mL of ultrapure water under vigorous stirring. The obtained solution was transferred into a 50 mL stainless steel Teflon-lined autoclave, which was heated under different temperatures (100–200 °C) for 3 h. The different hydrothermal conditions are listed in Table 1. The final products were obtained by centrifugation. Each experiment was repeated three times. The WO3·nH2O crystals obtained by this hydrothermal method have high yield, good repeatability, and stability.

The phase was analyzed by X-ray diffraction (XRD, Bruker D8 Advance) with Cu Kα radiation at λ = 1.5418 Å. The microstructures were characterized by scanning electron microscope (SEM, Zeiss Sigma) and transmission electron microscope (TEM, FEI Tecnai G2 20). The optical adsorption spectra of the products were measured by a PerkinElmer Lambda 35 UV–vis spectrometer.

3. RESULTS AND DISCUSSION

The morphology/phase of the obtained products under different hydrothermal conditions was characterized by SEM and XRD, respectively. Figure 1a displays the as-prepared nanoplates (~150 nm in edge length, ~20 nm in thickness), which were prepared by adding 3 mL of H2SO4 at 100 °C.

Table 1. Summary of the As-Prepared Products under Different Hydrothermal Conditions

| mass of Na2WO4·2H2O | amount of H2SO4 solution | reaction temperature/time | morphology | crystal phase |
|----------------------|--------------------------|---------------------------|------------|--------------|
| 4.6 g                | 3 mL                     | 100 °C/3 h                | nanoplates | o-WO3·H2O    |
| 4.6 g                | 3 mL                     | 150 °C/3 h                | nanoplates | Much o-WO3·H2O little o-WO3·0.33H2O m-WO3 |
| 4.6 g                | 3 mL                     | 200 °C/3 h                | rectangular nanosheets | Much o-WO3·H2O, few o-WO3·0.33H2O |
| 4.6 g                | 2 mL                     | 100 °C/3 h                | nanoplates nanoparticles | o-WO3·H2O, o-WO3·0.33H2O |
| 4.6 g                | 2 mL                     | 150 °C/3 h                | nanoparticles microspheres | o-WO3·H2O, o-WO3·0.33H2O |
| 4.6 g                | 2 mL                     | 200 °C/3 h                | microspheres | o-WO3·H2O, o-WO3·0.33H2O |
| 4.6 g                | 1 mL                     | 100 °C/3 h                | nanorods | h-WO3 |
| 4.6 g                | 1 mL                     | 150 °C/3 h                | bundle-like hierarchical structures | h-WO3 |
| 4.6 g                | 1 mL                     | 200 °C/3 h                | nanorods | h-WO3 |

Figure 1. SEM images of the products prepared by adding 3 mL of H2SO4 at (a) 100, (b) 150, and (c) 200 °C, 2 mL of H2SO4 at (d) 100, (e) 150, and (f) 200 °C, and 1 mL of H2SO4 at (g) 100, (h) 150, and (i) 200 °C.
Nevertheless, the XRD pattern (Figure 2a at 150 °C) shows that some weak diffraction peaks appear and can be identified as the orthorhombic phase of WO$_3$·0.33H$_2$O (JCPDS No. 72-0199), suggesting a little amount of WO$_3$·H$_2$O has been dehydrated to form WO$_3$·0.33H$_2$O. At 200 °C, the rectangular sheet-like products (70 to 240 nm) were obtained (Figure 1c), which can be assigned to the monoclinic phase of WO$_3$·0.33H$_2$O (JCPDS No. 72-0199, a = 0.7306 nm, b = 0.7540 nm, and c = 0.7692 nm) (Figure 2a at 200 °C).

As shown in Figure 1d–f, the products were prepared by adding 2 mL of H$_2$SO$_4$ at different reaction temperatures. At 100 °C, a large number of nanoplates coexist with a few nanoparticles (Figure 1d). The XRD pattern confirms that a small amount of WO$_3$·H$_2$O has been dehydrated to form WO$_3$·0.33H$_2$O at this reaction temperature (Figure 2b at 100 °C). At 150 °C (Figure 1e), more WO$_3$·H$_2$O nanoparticles dissolved, and the species with a microsphere-like appearance began to form. The XRD pattern (Figure 2b at 150 °C) also confirms that WO$_3$·H$_2$O nanoplates were further converted into WO$_3$·0.33H$_2$O, for which the diffraction peaks of WO$_3$·0.33H$_2$O intensified, while those of WO$_3$·H$_2$O decreased. As the reaction temperature further increases to 200 °C, lots of microspheres (∼6 μm in diameter) can be obtained (Figure 1f), and these microspheres are a pure orthorhombic phase of WO$_3$·0.33H$_2$O (JCPDS No. 72-0199, a = 0.7359 nm, b = 1.2513 nm, and c = 0.7704 nm) (Figure 2b at 200 °C). From the magnified SEM image (inset in Figure 1f), it can be seen that the microsphere is made up of many primary WO$_3$·0.33H$_2$O nanorhomboids.

As shown in Figure 1g–i, the products were prepared by adding 1 mL of H$_2$SO$_4$ at different reaction temperatures. At 100 °C, the nanorods (∼12 nm in diameter, ∼60 nm in length) were obtained (Figure 1g). All the diffraction peaks (Figure 2c at 100 °C) of these nanorods match well with the hexagonal phase of WO$_3$ (JCPDS No. 75-2187, a = 0.7298 nm, c = 0.3899 nm). At 150 °C, the product shows a bundle-like hierarchical structure, which is composed of many primary nanorods with different sizes (Figure 1h). The XRD pattern confirms that these bundle-like hierarchical structures are the hexagonal phase of WO$_3$ (Figure 2c at 150 °C). As the reaction temperature further increased to 200 °C, the nanorods (∼20 nm in diameter, ∼130 nm in length) were obtained again (Figure 1i) with the hexagonal phase (Figure 2c at 200 °C). It is evident that the average size of nanorods obtained at 200 °C is larger than that of nanorods obtained at 100 °C.

The morphology/phase of as-prepared products under different hydrothermal conditions are listed in Table 1. It can be seen that five types of WO$_3$·nH$_2$O crystals, including o-WO$_3$·H$_2$O nanorods, rectangular m-WO$_3$ nanosheets, o-WO$_3$·0.33H$_2$O microspheres, h-WO$_3$ nanorods (with two different sizes obtained at 100 and 200 °C, respectively), and bundle-like h-WO$_3$ hierarchical structures, were successfully synthesized by adjusting the amount of H$_2$SO$_4$ and the reaction temperature in our experiments.

Furthermore, TEM characterizations were further performed to comprehend the growth rule of these WO$_3$·nH$_2$O crystals (Figure 3). The TEM image shows o-WO$_3$·H$_2$O nanorods in Figure 3a. The clear and ordered lattice fringes were observed in a high-resolution TEM (HRTEM) image taken along the [010] zone axis (Figure 3d), confirming that these nanorods are single crystals. The crystal interplanar distances of 0.261 and 0.256 nm correspond to the (200) and (002) facets of orthorhombic WO$_3$·H$_2$O. The single-crystalline nature was also demonstrated by the corresponding fast Fourier transform (FFT) diffractogram (inset in Figure 3d). Combining the HRTEM image and FFT diffractogram, it can be known that the top and bottom facets of the o-WO$_3$·H$_2$O nanoplate are (010) facets. Figure 3b shows a TEM image of rectangular m-WO$_3$ nanosheets. The HRTEM image (Figure 3e) taken along the [001] zone axis and the corresponding FFT diffractogram (inset in Figure 3e) reveal the single-crystalline nature of these nanosheets, and the surface of them consists of a major top (002) and minor lateral (020) and (200) facets. The TEM image of as-prepared o-WO$_3$·0.33H$_2$O microspheres was shown in Figure 3c, and the HRTEM image (Figure 3f) displays that the blocks (o-WO$_3$·0.33H$_2$O nanorhomboids) of these microspheres are single crystals.

Figure 3g shows a TEM image of h-WO$_3$ nanorhomboids obtained at 100 °C, and the HRTEM image (Figure 3j) of an individual nanorhomboid shows a crystal interplanar distance of 0.383 nm for the (001) facet, confirming its single-crystalline nature and preferential growth along the c-axis of a hexagonal structure. Figure 3h displays a TEM image of bundle-like h-WO$_3$ hierarchical structures. The HRTEM image (Figure 3k) indicates that the blocks of this hierarchical structure, that is,
the nanorods, are single crystals with the same growth direction (the c-axis of the hexagonal structure). The TEM results of h-WO₃ nanorods obtained at 200 °C are shown in Figure 3i,l, which are similar to the h-WO₃ nanorods obtained at 100 °C.

Generally, the external reaction conditions and intrinsic crystal structures determine the crystal growth behavior. The amount of H₂SO₄ and the reaction temperature play key roles in the preparation of various WO₃·nH₂O crystals. According to the above experimental results, the suggested reaction routes in this hydrothermal system could be described as follows.

\[ \text{Na}_2\text{WO}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{o-WO}_3\cdot\text{H}_2\text{O} + \text{Na}_2\text{SO}_4 \]  \hspace{1cm} (1)

\[ \text{o-WO}_3\cdot\text{H}_2\text{O} \rightarrow \text{o-WO}_3\cdot0.33\text{H}_2\text{O} + 0.67\text{H}_2\text{O} \]  \hspace{1cm} (2)

\[ \text{o-WO}_3\cdot0.33\text{H}_2\text{O} \rightarrow \text{h-WO}_3 + 0.33\text{H}_2\text{O} \]  \hspace{1cm} (3)

\[ \text{h-WO}_3 \rightarrow \text{m-WO}_3 \]  \hspace{1cm} (4)

The o-WO₃·H₂O was obtained by acidic precipitation according to eq 1, when the H₂SO₄ solution was added to the Na₂WO₄ solution during the hydrothermal process. This o-WO₃·H₂O has a layered perovskite-like ReO₃ structure, which in turn governs its growth and facilitates growth along the a-axis and c-axis to form a plate-like morphology. It is believed that a higher concentration of H⁺ ions can inhibit the dehydration of tungsten trioxide hydrates, while a higher reaction temperature can promote the dehydration of them during a hydrothermal process. When the hydrothermal reaction occurs at a high concentration of H⁺ ions (by adding
WO₃ crystals were identified as shown in Figure 3e. The exposed facets of the m-WO₃_H₂O has been dehydrated to form o-WO₃·0.33H₂O in eq 2. Further increasing the reaction temperature to 200 °C, o-WO₃·H₂O was completely dehydrated to obtain pure-phase o-WO₃·0.33H₂O. The morphology of these o-WO₃·0.33H₂O is microsphere, which is composed of many primary o-WO₃·0.33H₂O nanoflakes. Without the introduction of any surfactant during the hydrothermal process, the o-WO₃·0.33H₂O microsphere may be generated by the assembly of primary nanoflakes through a van der Waals interaction to decrease the system energy. This formation process of o-WO₃·0.33H₂O microsphere is similar to that of the o-WO₃·H₂O microsphere reported by Huang et al. 

When the concentration of H⁺ ions further decreased (by adding 1 mL of H₂SO₄), the dehydration trend of o-WO₃·H₂O was also further enhanced. The pure phase of h-WO₃ nanorods was obtained at the low reaction temperature (100 °C) by eqs 1−3. The h-WO₃ crystal can be regarded as a polar crystal with ±(001) polar facets, which tends to grow preferentially along its polar direction (the c-axis of hexagonal structure), favoring the formation of a one-dimensional structure. At 150 °C, the bundle-like h-WO₃ hierarchical structures were obtained through the assembly of primary nanorods in an oriented mode. The lateral capillary force provides the energy for the assembly of the nanorod to decrease the system surface energy. When the reaction temperature was further increased to 200 °C, the smaller h-WO₃ nanorods dissolved and the larger h-WO₃ nanorods formed due to the strongly Ostwald ripening process. Of course, the possible bundle-like hierarchical structures would be destroyed at this high reaction temperature (200 °C) during the hydrothermal process.

The optical absorption properties of WO₃·nH₂O crystals with various morphologies/phases were evaluated by UV−vis absorption spectra. The UV−vis absorption spectra of various WO₃·nH₂O crystals were shown in Figure 4a. The values of absorption edges of these WO₃·nH₂O crystals can be obtained from Figure 4a, as listed in Table 2. It can be seen that the absorption edges of these crystals are located at visible light region that is in the wavelength range from 438 to 592 nm. The band gap E₉ can be determined by the Tauc equation $(\alpha hν)^{n} = B(hν - E_{g})$ for a semiconductor, where $\alpha$ is the absorption coefficient, $hν$ is the photon energy, B is the edge width parameter, and n is a constant characterizing the nature of the band transition. Considering that WO₃·nH₂O crystals are indirect band gap semiconductors, the value of n can be taken as 0.5. As in the method described by Tauc, the band gap is evaluated simply by fitting a straight line to the linear portion of the absorption spectrum (Tauc linear fit). However, this method usually brings large errors to the value of band gap, and some researchers point out that an intersection of the Tauc linear fit and the baseline will give a more reasonable band gap estimation. Accordingly, the values of band gaps for WO₃·nH₂O crystals can be obtained from Figure 4b in light of this improved method, and these values are also listed in Table 2. The obtained values of band gaps for WO₃·nH₂O crystals range from 2.33 to 2.91 eV, which is in the visible light region, suggesting some possible

Table 2. Experimental Values of Absorption Edges and Band Gaps for the As-Prepared Products

| product                        | absorption edge (nm) | band gap (eV) |
|--------------------------------|----------------------|---------------|
| o-WO₃·H₂O nanorods             | 554                  | 2.33          |
| rectangular m-WO₃ nanosheets    | 488                  | 2.58          |
| o-WO₃·0.33H₂O microspheres     | 438                  | 2.76          |
| h-WO₃ nanorods (obtained at 100 °C) | 592              | 2.81          |
| bundle-like h-WO₃ hierarchical structures | 468              | 2.91          |
| h-WO₃ nanosheets (obtained at 200 °C) | 452              | 2.83          |

3 mL of H₂SO₄ and low reaction temperature (100 °C), the dehydration of o-WO₃·H₂O was obviously inhibited, so pure-phase o-WO₃·H₂O nanorods can be obtained. Under a higher reaction temperature (150 °C), the dehydration trend of o-WO₃·H₂O increases stronger, and a small amount of o-WO₃·H₂O has been dehydrated to form o-WO₃·0.33H₂O, as shown in eq 2. Further increasing the reaction temperature to 200 °C, o-WO₃·0.33H₂O can be dehydrated to obtain h-WO₃, as shown in eq 3. However, h-WO₃ belongs to a metastable phase, which can be transformed into more stable m-WO₃ under an appropriate hydrothermal condition, as shown in eq 4. From the TEM result of Figure 3e, the exposed facets of the m-WO₃ crystals were identified as (002), (020), and (200). Because the order of surface energy of these exposed facets is (002) > (020) > (200), this will result in the formation of rectangular m-WO₃ nanosheets with a larger area of (200) exposed facet and lower the system energy.

When the concentration of H⁺ ions decreased (by adding 2 mL of H₂SO₄), the dehydration trend of o-WO₃·H₂O was enhanced. Even at a low reaction temperature (100 °C), some o-WO₃·H₂O was dehydrated to form o-WO₃·0.33H₂O. As the reaction temperature became higher (150 or 200 °C), the dehydration trend of o-WO₃·H₂O became stronger, resulting in the increase of the proportion of o-WO₃·0.33H₂O. Under 200 °C, o-WO₃·H₂O was completely dehydrated to obtain pure-phase o-WO₃·0.33H₂O. The morphology of these o-WO₃·0.33H₂O is microsphere, which is composed of many primary o-WO₃·0.33H₂O nanoflakes. Without the introduction of any surfactant during the hydrothermal process, the o-WO₃·0.33H₂O microsphere may be generated by the assembly of primary nanoflakes through a van der Waals interaction to decrease the system energy. This formation process of o-WO₃·0.33H₂O microsphere is similar to that of the o-WO₃·H₂O microsphere reported by Huang et al. 

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applications of them, such as visible light photocatalysts, etc. Obviously, the different values of absorption edges and band gaps depend on the different morphologies and crystal phases of \( \text{WO}_3 \cdot n\text{H}_2\text{O} \) crystals.

4. CONCLUSIONS

In summary, \( \text{WO}_3 \cdot n\text{H}_2\text{O} \) crystals with controllable morphology/phase have been prepared by a one-step hydrothermal method without employing any surfactants, templates, or structure-directing agents. It was found that five types of \( \text{WO}_3 \cdot n\text{H}_2\text{O} \) crystals, including \( \alpha\text{-WO}_3 \cdot \text{H}_2\text{O} \) nanorods, \( \alpha\text{-WO}_3 \cdot 0.33\text{H}_2\text{O} \) microspheres, \( \alpha\text{-WO}_3 \) nanorods, and bundle-like \( \alpha\text{-WO}_3 \) hierarchical structures, can be obtained by adjusting the amount of \( \text{H}_2\text{SO}_4 \) and reaction temperature. The formation mechanism of these \( \text{WO}_3 \cdot n\text{H}_2\text{O} \) crystals was proposed. Moreover, the absorption edges and band gaps of as-prepared \( \text{WO}_3 \cdot n\text{H}_2\text{O} \) crystals were measured to be in the ranges of 438–592 nm and 2.33–2.91 eV, respectively. The current study puts forward a promising method for preparing \( \text{WO}_3 \cdot n\text{H}_2\text{O} \) crystals, which may fulfill the requirements of potential applications and industrial production.

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Notes

The authors declare no competing financial interest.

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