

Effect of different anions upon the WO₃ morphology and structure

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In this study the effects of various anions (SO₄²⁻, ClO₄⁻ and PO₄³⁻) were investigated on the hydrothermal treatment of WO₃ from Na₂WO₄ and HCl at 180 and 200 °C. The products were analyzed by XRD and SEM. With the usage of SO₄²⁻ the obtained product was hexagonal (h-) WO₃ in the form of nanorods at both temperatures. Applying ClO₄⁻ resulted in a mixture of WO₃·0.33 H₂O and small amount of m-WO₃ at 180 °C and pure WO₃·0.33 H₂O at 200 °C. The morphology was consisted of cuboid shapes arranged into spherical structures at 180 °C and longitudinal ones at 200 °C. By the application of PO₄³⁻ no product formed at either temperature. Using the combination of SO₄²⁻ and ClO₄⁻ the product was h-WO₃ at both 180 and 200 °C with rod-like crystals; thus, the effect of ClO₄⁻ was overdominated by the SO₄²⁻ ions. Utilization of PO₄³⁻ together with SO₄²⁻ and/or ClO₄⁻ resulted again in no product, meaning that adding PO₄³⁻ to the reaction mixture completely blocks the hydrothermal formation of solid products by forming water soluble phosphotungstic acids.

Keywords Tungsten oxides, Hydrothermal treatment, Structure, Morphology, SO₄²⁻, ClO₄⁻, PO₄³⁻

1. Introduction

Tungsten oxides are one of the most intensively investigated metal oxides due to their promising properties in the field of catalysis[1, 2], photocatalysis[3–6], electrochromism[7–9], photochromism[10] or gas sensing[3, 11–14]. Tungsten oxides can be prepared in many ways, such as wet chemical processes [10], hydro- or solvothermal[6, 15–17] or chemical solution routes[5], electrospinning[18], spray pyrolysis[19] or annealing[20].

Hydrothermal treatment is a widespread preparation route due to its easy implementation, low cost and energy consumption. In a typical synthesis, tungsten trioxide (WO₃) is prepared by the reaction of sodium tungstate (Na₂WO₄) and hydrochloric acid, i.e. the precursor solution is transferred into an autoclave and maintained at 150–250 °C for several hours. [4, 6, 16, 21–23] Using certain additive materials the structure and the morphology of the product can be modified. The role of SO₄²⁻ as a capping agent to favor the formation of h-WO₃ 1D nanostructures probably the most studied. E.g. Gu et al. used alkali metal sulfates to influence the morphology of the

obtained h-WO₃. [16] Urchinlike nanostructures were prepared by the usage of Rb₂SO₄, ribbons with K₂SO₄ and cylindrical nanowires bundles through the addition of Na₂SO₄ or Li₂SO₄. Furthermore, when they used (NH₄)₂SO₄ only nanorods were generated. They found that sulfates and oxalic acid played a key role in controlling the morphology and enhancing the crystal growth, respectively. They suggested the difference is caused by the cation radius. The influence of polymers and organic molecules on the reaction of Na₂WO₄ and HCl were also reported. When PEG-1000 is used as structure directing agent, flowerlike WO₃ structures can be synthesized.[24] The length of the alkyl chain of an organic additive also affects the morphology since sodium decyl, dodecyl and tetradecyl sulfate resulted nanofibers, bundles of nanoneedles and individual ones.[25] Despite these efforts, there is still much room for research. Beside SO₄²⁻, other inorganic anions (e.g. ClO₄⁻ and PO₄³⁻) might also influence the reaction; however, to the best of our knowledge, their effect has not been reported yet.

Hence, in this study, our goal was to investigate the effect of different anions on the morphology and structure of the products in the hydrothermal reaction of the two raw materials, Na₂WO₄ and HCl. In particular, we investigated the influence of ClO₄⁻, PO₄³⁻, and as reference SO₄²⁻. In order to eliminate the possible cation effect, all anions had the same cation, i.e. Na⁺; thus, the used materials were NaClO₄, Na₃PO₄ and Na₂SO₄. They were used under the same conditions adding them alone to the solution or more of them at same time. We applied oxalic acid as an additive material as well beside the above listed chemicals since it improved the crystallinity of the obtained product[26]. We carried out the reactions at 180 and 200 °C to analyze the role of the temperature. The reaction products were studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

2. Experimental

2.1. Materials

Na₂WO₄·2H₂O (≥99 %), (COOH)₂·2H₂O (≥99 %), Na₂SO₄·10H₂O (≥99 %), NaClO₄·H₂O (99.99 %), Na₃PO₄ (96 %) were purchased from Sigma Aldrich as used as received. 3M HCl was diluted from 37 % HCl solution (Merck). Distilled water was used throughout the experiments.

2.2. Hydrothermal synthesis

During the hydrothermal reactions 4.1 g Na₂WO₄·2H₂O was dissolved in 100 ml water and stirred for 15 minutes at room temperature. The pH was set to 1-1.2 by 3 M HCl and a light greenish precipitate was obtained. 3.2 g (COOH)₂ was added to the mixture, after that the solution became translucent. Then it was diluted to 250 ml and stirred for 10 minutes again. Finally, 30 mL of the solution was transferred into a 45 mL Parr acid digest autoclave together with the certain additive materials. The autoclave was hydrothermally treated at 180 or 200 °C for 24 h. The products were filtered, washed first with distilled water and then with ethyl alcohol (96 V/V%) and dried at 60 °C for 2 h.

All performed hydrothermal treatments and conditions are summarized in Table 1. At first, we examined the influence of the Na₂SO₄·10H₂O (1-2), NaClO₄·H₂O (3-4) and Na₃PO₄ (5-6) at

180 and 200 °C on the morphology and crystal structure of the products. Then, we combined them and studied their joint effect. We used together Na₂SO₄ and NaClO₄ at 180 and 200 °C (**7-8**), while Na₂SO₄ and Na₃PO₄ (**9**) or NaClO₄ and Na₃PO₄ (**10**) only at 200 °C. Finally, we put all the three additives at once in the autoclave at 200 °C (**11**).

2.3. Structural and morphological characterization

X-ray powder diffraction analyses were carried out using a PANalytical X'Pert Pro MPD diffractometer with Cu K α radiation ($\lambda=0.15418$ nm). For observing the morphology, the size and shape of the obtained nanostructure a LEO 1540 XB scanning electron microscope was applied with accelerating voltage of 5 kV.

3. Results and Discussion

3.1. XRD

XRD measurements show that the usage of Na₂SO₄ as an additive resulted pure hexagonal h- WO₃ (ICDD 033-1387, Fig. 1) both at 180 (**1**) and 200 °C (**2**). The temperature difference did not have an effect on the crystal phase, but improved the crystallinity of **2**. It had narrower and sharper peaks referring to higher crystallinity. When instead of Na₂SO₄, NaClO₄ was used alone in the reaction solution, the product was composed of WO₃·0.33 H₂O (ICDD 04-016-3582) and of a small amount of monoclinic (m-)WO₃ (13 %) (ICDD 01-075-207) at 180 °C (**3**), while it consisted of only WO₃·0.33 H₂O at 200 °C (**4**). In the case of using only Na₃PO₄ as an additive, no product was obtained at either temperatures.

Applying together Na₂SO₄ and NaClO₄ resulted pure h-WO₃ at both temperatures (**7-8**). In every other experiment, when we added Na₃PO₄ as well to the autoclave (**9-11**), no solid products were formed.

3.2. SEM

The morphology of **1** and **2** was homogenous, they consisted of nanorods which were 5-10 μ m long and less than 1 μ m thick (Fig. 2). In contrast, **3** and **4** were composed of mostly cuboid shapes. They are some hundred nm long and wide and form spherical agglomerates in the scale of micrometers (Fig. 2).

Adding Na₂SO₄ and NaClO₄ at the same time (**7-8**) resulted nanorods, which were similar to those prepared with only Na₂SO₄. These rods were however a bit thicker, they were 300-600 nm wide at 180 °C and 300-800 nm at 200 °C. In addition, their length was not uniform. They contained more than 1 μ m long rods, similar to **1-2**; however, much shorter ones with only some hundred nm length also appeared in samples **7-8**. (Fig. 2).

In SEM images at higher magnification, it can be seen that the nanorods of **1** and **2** were composed of thin, only several ten nm thick needles stuck to each other during the hydrothermal treatment. Their thickness ranged from 50 to 300 nm at 180 °C (**1**, Fig. 3), while it increased up to 150-500 nm at 200 °C (**2**, Fig. 3). **3** and **4** were composed of cuboid shapes and sheets. These nanocubes have some hundreds of nm thickness and are greatly agglomerated. They are oriented

longitudinally to each other at 200 °C (**4**). **7** and **8** had very similar morphology to **1** and **2** as rodlike shapes formed at each temperature.

Based on these experiments, it is confirmed that SO_4^{2-} acts as a structure directing capping agent, favoring the growth of 1D h- WO_3 nanostructures. We suggest that ClO_4^- ions do not lead to h- WO_3 but to $\text{WO}_3 \cdot 0.33 \text{ H}_2\text{O}$. The preferred morphology in this case is built up by 200-300 nm large cuboid nanocrystals aligned to each other. When SO_4^{2-} ions are used together with ClO_4^- ions, the nanorod morphology remains unvaried, meaning that the effect of ClO_4^- is overdominated by the SO_4^{2-} ions. Utilization of PO_4^{3-} alone or together with SO_4^{2-} and/or ClO_4^- results in no solid product, meaning that adding PO_4^{3-} to the reaction mixture completely blocks the hydrothermal formation of products most probably by forming water soluble phosphotungstic acids[1].

4. Conclusion

In summary, we investigated the effect of ClO_4^- and PO_4^{3-} anions in the hydrothermal reactions of Na_2WO_4 and HCl. As reference, the influence of SO_4^{2-} was also investigated. To eliminate the cation affect, we used sodium containing salts, i.e. Na_2SO_4 , NaClO_4 and Na_3PO_4 . The products were studied by XRD and SEM.

The addition of Na_2SO_4 alone resulted pure h- WO_3 at both temperatures which appeared as nanorods with 5-10 μm length and had 50 to 300 nm and 150-500 nm thickness at 180 °C and at 200 °C, respectively. Applying only NaClO_4 resulted $\text{WO}_3 \cdot 0.33 \text{ H}_2\text{O}$ and small amount of m- WO_3 at 180 °C and pure $\text{WO}_3 \cdot 0.33 \text{ H}_2\text{O}$ at 200 °C. The products were homogenous in morphology containing some hundreds of nm thick cuboid shapes arranged into spheres at 180 °C and aligned longitudinally at 200 °C. The usage of Na_3PO_4 is not beneficial to the reaction since nothing formed at either temperatures.

With adding both Na_2SO_4 and NaClO_4 we prepared h- WO_3 at both temperatures. The products had a bit more robust nanorod feature with thickness ranging from 300 to 600 nm at 180 °C and 300-800 nm at 200 °C, respectively. In addition, beside longer nanorods, shorter ones also appeared. We found that ClO_4^- ions did not have critical role in influencing the morphology, when the SO_4^{2-} ions were also present, as the nanorod morphology and the h- WO_3 structure formed again which is characteristic of the SO_4^{2-} additive. The combination of Na_3PO_4 with Na_2SO_4 and/or NaClO_4 yielded no products due to that water soluble phosphotungstic acids could form.

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Figure captions

Table 1. Experimental conditions (additives, temperature) and products of hydrothermal reactions 1-11

Figure 1. XRD patterns of the products **1-4** and **7-8**

Figure 2. SEM images of the products **1-4** and **7-8** at lower magnification

Figure 3. SEM images of the products **1-4** and **7-8** at higher magnification

Product Nr.	Additive material	T (°C)	Crystalline phases of the product
1	2 g (0.0062 mol) Na ₂ SO ₄ ·10H ₂ O	180	h-WO ₃
2	2 g (0.0062 mol) Na ₂ SO ₄ ·10H ₂ O	200	h-WO ₃
3	2 g (0.0143 mol) NaClO ₄ ·H ₂ O	180	WO ₃ ·0.33 H ₂ O, m-WO ₃
4	2 g (0.0143 mol) NaClO ₄ ·H ₂ O	200	WO ₃ ·0.33 H ₂ O
5	2 g (0.0122 mol) Na ₃ PO ₄	180	-
6	2 g (0.0122 mol) Na ₃ PO ₄	200	-
7	1 g (0.0031 mol) Na ₂ SO ₄ ·10H ₂ O + 1 g (0.0072 mol) NaClO ₄ ·H ₂ O	180	h-WO ₃
8	1 g (0.0031 mol) Na ₂ SO ₄ ·10H ₂ O + 1 g (0.0072 mol) NaClO ₄ ·H ₂ O	200	h-WO ₃
9	1 g (0.0031 mol) Na ₂ SO ₄ ·10H ₂ O + 1 g (0.0061 mol) Na ₃ PO ₄	200	-
10	1 g (0.0072 mol) NaClO ₄ ·H ₂ O + 1 g (0.0061 mol) Na ₃ PO ₄	200	-
11	0.66 g (0.0020 mol) Na ₂ SO ₄ ·10H ₂ O + 0.66 g (0.0047 mol) NaClO ₄ ·H ₂ O + 0.66 g (0.0040 mol) Na ₃ PO ₄	200	-

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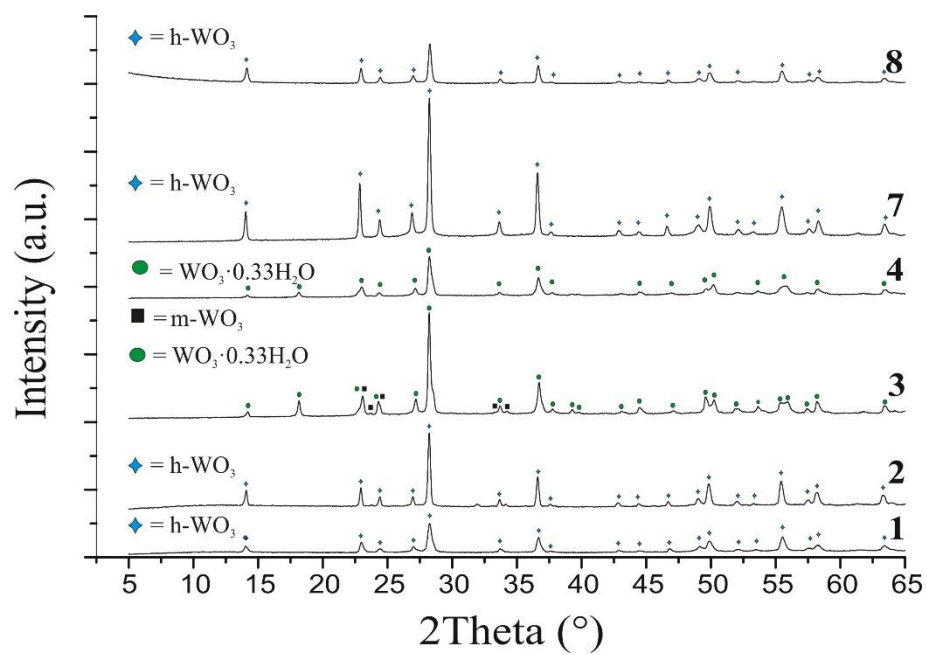


Figure 1. T. Nagyné-Kovács et al.

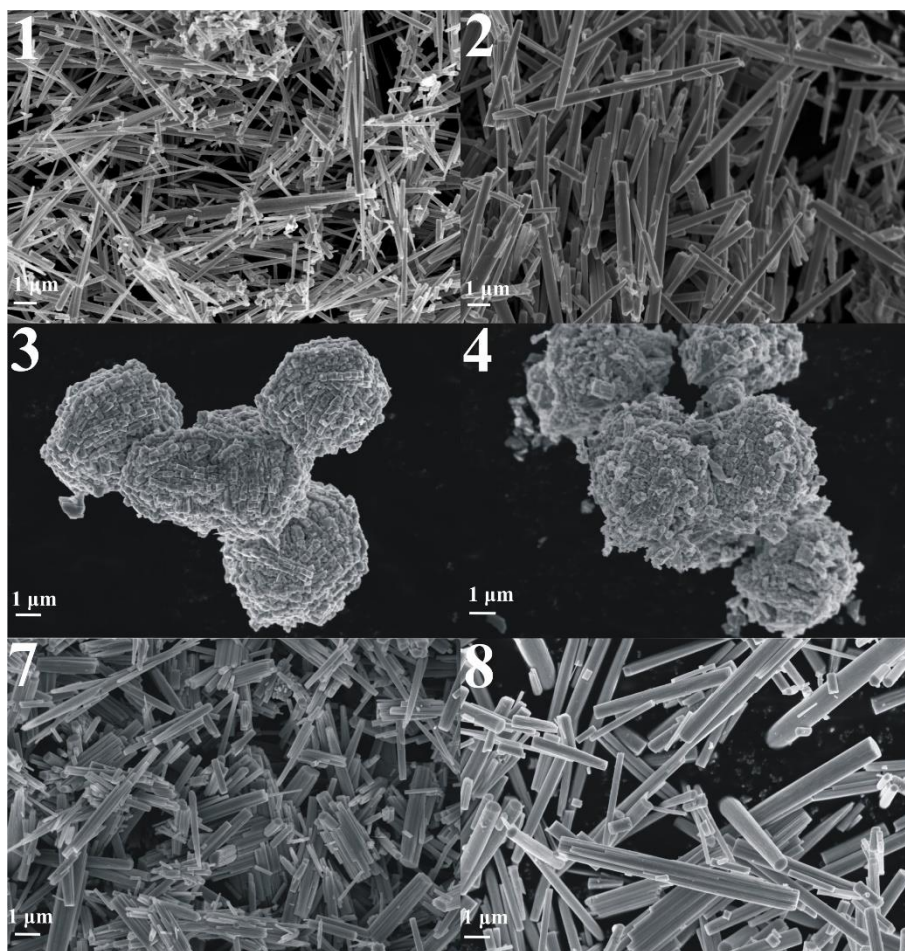


Figure 2. T. Nagyné-Kovács et al.

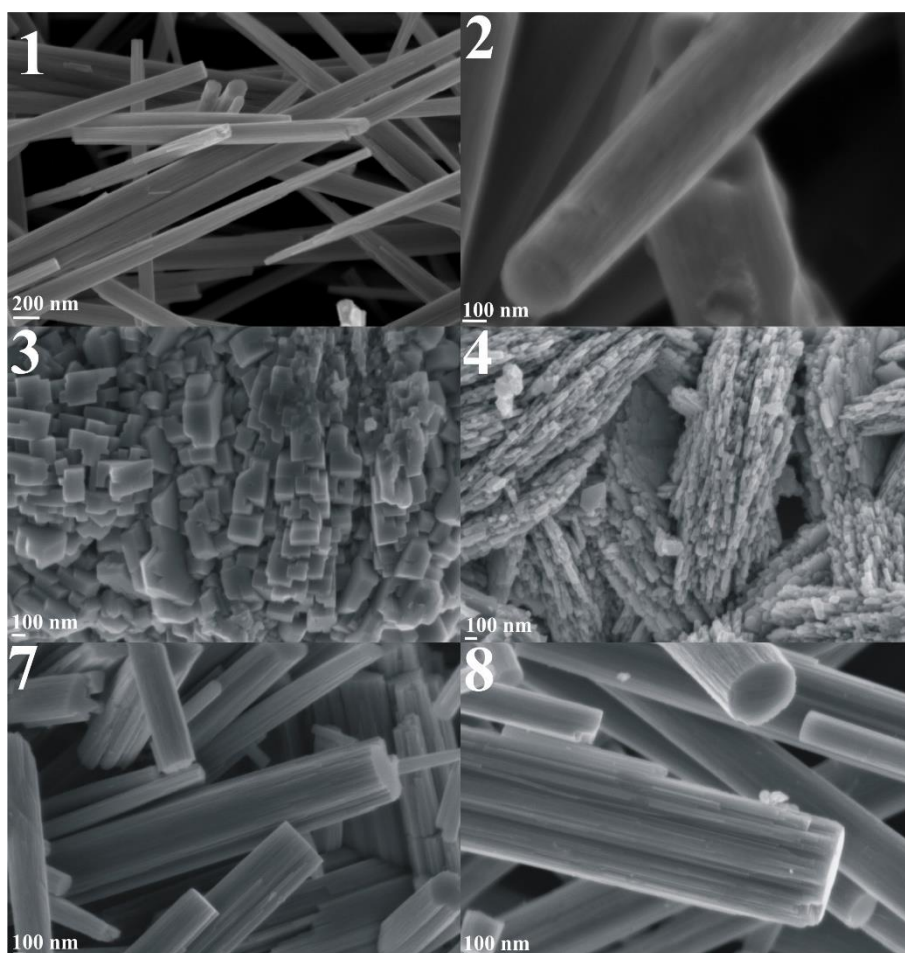


Figure 3. T. Nagyné-Kovács et al.