

# Effect of different anions upon the WO<sub>3</sub> morphology and structure

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In this study the effects of various anions (SO<sub>4</sub><sup>2-</sup>, ClO<sub>4</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup>) were investigated on the hydrothermal treatment of WO<sub>3</sub> from Na<sub>2</sub>WO<sub>4</sub> and HCl at 180 and 200 °C. The products were analyzed by XRD and SEM. With the usage of SO<sub>4</sub><sup>2-</sup> the obtained product was hexagonal (h-) WO<sub>3</sub> in the form of nanorods at both temperatures. Applying ClO<sub>4</sub><sup>-</sup> resulted in a mixture of WO<sub>3</sub>·0.33 H<sub>2</sub>O and small amount of m-WO<sub>3</sub> at 180 °C and pure WO<sub>3</sub>·0.33 H<sub>2</sub>O 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 PO<sub>4</sub><sup>3-</sup> no product formed at either temperature. Using the combination of SO<sub>4</sub><sup>2-</sup>, and ClO<sub>4</sub><sup>-</sup> the product was h-WO<sub>3</sub> at both 180 and 200 °C with rod-like crystals; thus, the effect of ClO<sub>4</sub><sup>-</sup> was overdominated by the SO<sub>4</sub><sup>2-</sup> ions. Utilization of PO<sub>4</sub><sup>3-</sup> together with SO<sub>4</sub><sup>2-</sup>, and/or ClO<sub>4</sub><sup>-</sup> resulted again in no product, meaning that adding PO<sub>4</sub><sup>3-</sup> 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, SO<sub>4</sub><sup>2-</sup>, ClO<sub>4</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>

## 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 (WO<sub>3</sub>) is prepared by the reaction of sodium tungstate (Na<sub>2</sub>WO<sub>4</sub>) 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 SO<sub>4</sub><sup>2-</sup> as a capping agent to favor the formation of h-WO<sub>3</sub> 1D nanostructures probably the most studied. E.g. Gu et al. used alkali metal sulfates to influence the morphology of the

obtained h-WO<sub>3</sub>. [16] Urchinlike nanostructures were prepared by the usage of Rb<sub>2</sub>SO<sub>4</sub>, ribbons with K<sub>2</sub>SO<sub>4</sub> and cylindrical nanowires bundles through the addition of Na<sub>2</sub>SO<sub>4</sub> or Li<sub>2</sub>SO<sub>4</sub>. Furthermore, when they used (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> 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 Na<sub>2</sub>WO<sub>4</sub> and HCl were also reported. When PEG-1000 is used as structure directing agent, flowerlike WO<sub>3</sub> 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 SO<sub>4</sub><sup>2-</sup>, other inorganic anions (e.g. ClO<sub>4</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup>) 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, Na<sub>2</sub>WO<sub>4</sub> and HCl. In particular, we investigated the influence of ClO<sub>4</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, and as reference SO<sub>4</sub><sup>2-</sup>. In order to eliminate the possible cation effect, all anions had the same cation, i.e. Na<sup>+</sup>; thus, the used materials were NaClO<sub>4</sub>, Na<sub>3</sub>PO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub>. 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

Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O (≥99 %), (COOH)<sub>2</sub>·2H<sub>2</sub>O (≥99 %), Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O (≥99 %), NaClO<sub>4</sub>·H<sub>2</sub>O (99.99 %), Na<sub>3</sub>PO<sub>4</sub> (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 Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O 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)<sub>2</sub> 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 Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O (**1-2**), NaClO<sub>4</sub>·H<sub>2</sub>O (**3-4**) and Na<sub>3</sub>PO<sub>4</sub> (**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 Na<sub>2</sub>SO<sub>4</sub> and NaClO<sub>4</sub> at 180 and 200 °C (**7-8**), while Na<sub>2</sub>SO<sub>4</sub> and Na<sub>3</sub>PO<sub>4</sub> (**9**) or NaClO<sub>4</sub> and Na<sub>3</sub>PO<sub>4</sub> (**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 $\alpha$  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 Na<sub>2</sub>SO<sub>4</sub> as an additive resulted pure hexagonal h-WO<sub>3</sub> (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 Na<sub>2</sub>SO<sub>4</sub>, NaClO<sub>4</sub> was used alone in the reaction solution, the product was composed of WO<sub>3</sub>·0.33 H<sub>2</sub>O (ICDD 04-016-3582) and of a small amount of monoclinic (m-)WO<sub>3</sub> (13 %) (ICDD 01-075-207) at 180 °C (**3**), while it consisted of only WO<sub>3</sub>·0.33 H<sub>2</sub>O at 200 °C (**4**). In the case of using only Na<sub>3</sub>PO<sub>4</sub> as an additive, no product was obtained at either temperatures.

Applying together Na<sub>2</sub>SO<sub>4</sub> and NaClO<sub>4</sub> resulted pure h-WO<sub>3</sub> at both temperatures (**7-8**). In every other experiment, when we added Na<sub>3</sub>PO<sub>4</sub> 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  $\mu$ m long and less than 1  $\mu$ 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 Na<sub>2</sub>SO<sub>4</sub> and NaClO<sub>4</sub> at the same time (**7-8**) resulted nanorods, which were similar to those prepared with only Na<sub>2</sub>SO<sub>4</sub>. 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  $\mu$ 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  $\text{SO}_4^{2-}$  acts as a structure directing capping agent, favoring the growth of 1D h- $\text{WO}_3$  nanostructures. We suggest that  $\text{ClO}_4^-$  ions do not lead to h- $\text{WO}_3$  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  $\text{SO}_4^{2-}$  ions are used together with  $\text{ClO}_4^-$  ions, the nanorod morphology remains unvaried, meaning that the effect of  $\text{ClO}_4^-$  is overdominated by the  $\text{SO}_4^{2-}$  ions. Utilization of  $\text{PO}_4^{3-}$  alone or together with  $\text{SO}_4^{2-}$  and/or  $\text{ClO}_4^-$  results in no solid product, meaning that adding  $\text{PO}_4^{3-}$  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  $\text{ClO}_4^-$  and  $\text{PO}_4^{3-}$  anions in the hydrothermal reactions of  $\text{Na}_2\text{WO}_4$  and HCl. As reference, the influence of  $\text{SO}_4^{2-}$  was also investigated. To eliminate the cation affect, we used sodium containing salts, i.e.  $\text{Na}_2\text{SO}_4$ ,  $\text{NaClO}_4$  and  $\text{Na}_3\text{PO}_4$ . The products were studied by XRD and SEM.

The addition of  $\text{Na}_2\text{SO}_4$  alone resulted pure h- $\text{WO}_3$  at both temperatures which appeared as nanorods with 5-10  $\mu\text{m}$  length and had 50 to 300 nm and 150-500 nm thickness at 180 °C and at 200 °C, respectively. Applying only  $\text{NaClO}_4$  resulted  $\text{WO}_3 \cdot 0.33 \text{H}_2\text{O}$  and small amount of m- $\text{WO}_3$  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  $\text{Na}_3\text{PO}_4$  is not beneficial to the reaction since nothing formed at either temperatures.

With adding both  $\text{Na}_2\text{SO}_4$  and  $\text{NaClO}_4$  we prepared h- $\text{WO}_3$  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  $\text{ClO}_4^-$  ions did not have critical role in influencing the morphology, when the  $\text{SO}_4^{2-}$  ions were also present, as the nanorod morphology and the h- $\text{WO}_3$  structure formed again which is characteristic of the  $\text{SO}_4^{2-}$  additive. The combination of  $\text{Na}_3\text{PO}_4$  with  $\text{Na}_2\text{SO}_4$  and/or  $\text{NaClO}_4$  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 <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O	180	h-WO <sub>3</sub>
2	2 g (0.0062 mol) Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O	200	h-WO <sub>3</sub>
3	2 g (0.0143 mol) NaClO <sub>4</sub> ·H <sub>2</sub> O	180	WO <sub>3</sub> ·0.33 H <sub>2</sub> O, m-WO <sub>3</sub>
4	2 g (0.0143 mol) NaClO <sub>4</sub> ·H <sub>2</sub> O	200	WO <sub>3</sub> ·0.33 H <sub>2</sub> O
5	2 g (0.0122 mol) Na <sub>3</sub> PO <sub>4</sub>	180	-
6	2 g (0.0122 mol) Na <sub>3</sub> PO <sub>4</sub>	200	-
7	1 g (0.0031 mol) Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O + 1 g (0.0072 mol) NaClO <sub>4</sub> ·H <sub>2</sub> O	180	h-WO <sub>3</sub>
8	1 g (0.0031 mol) Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O + 1 g (0.0072 mol) NaClO <sub>4</sub> ·H <sub>2</sub> O	200	h-WO <sub>3</sub>
9	1 g (0.0031 mol) Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O + 1 g (0.0061 mol) Na <sub>3</sub> PO <sub>4</sub>	200	-
10	1 g (0.0072 mol) NaClO <sub>4</sub> ·H <sub>2</sub> O + 1 g (0.0061 mol) Na <sub>3</sub> PO <sub>4</sub>	200	-
11	0.66 g (0.0020 mol) Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O + 0.66 g (0.0047 mol) NaClO <sub>4</sub> ·H <sub>2</sub> O + 0.66 g (0.0040 mol) Na <sub>3</sub> PO <sub>4</sub>	200	-

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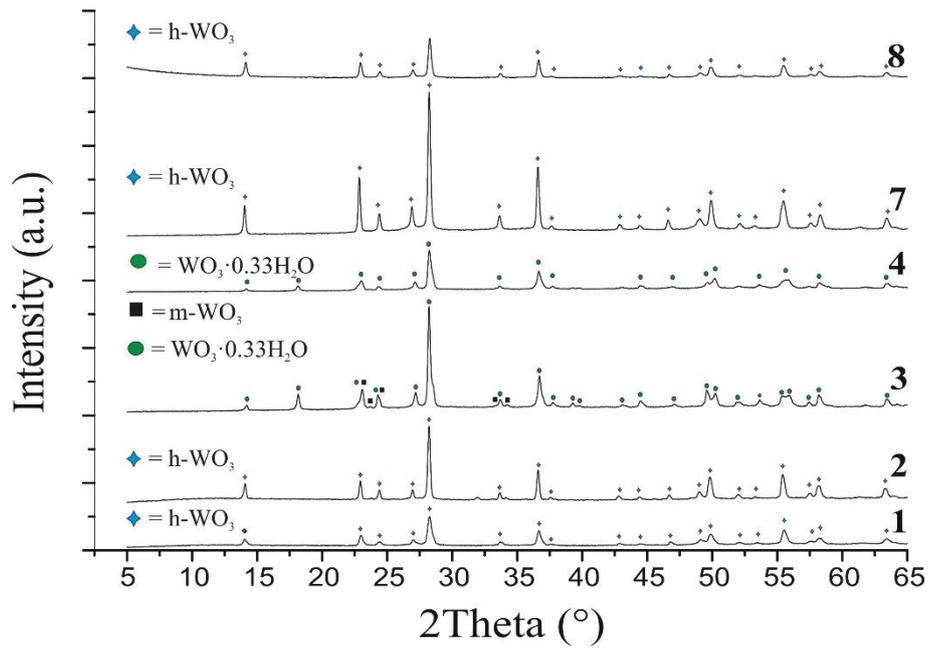


Figure 1. T. Nagyné-Kovács et al.

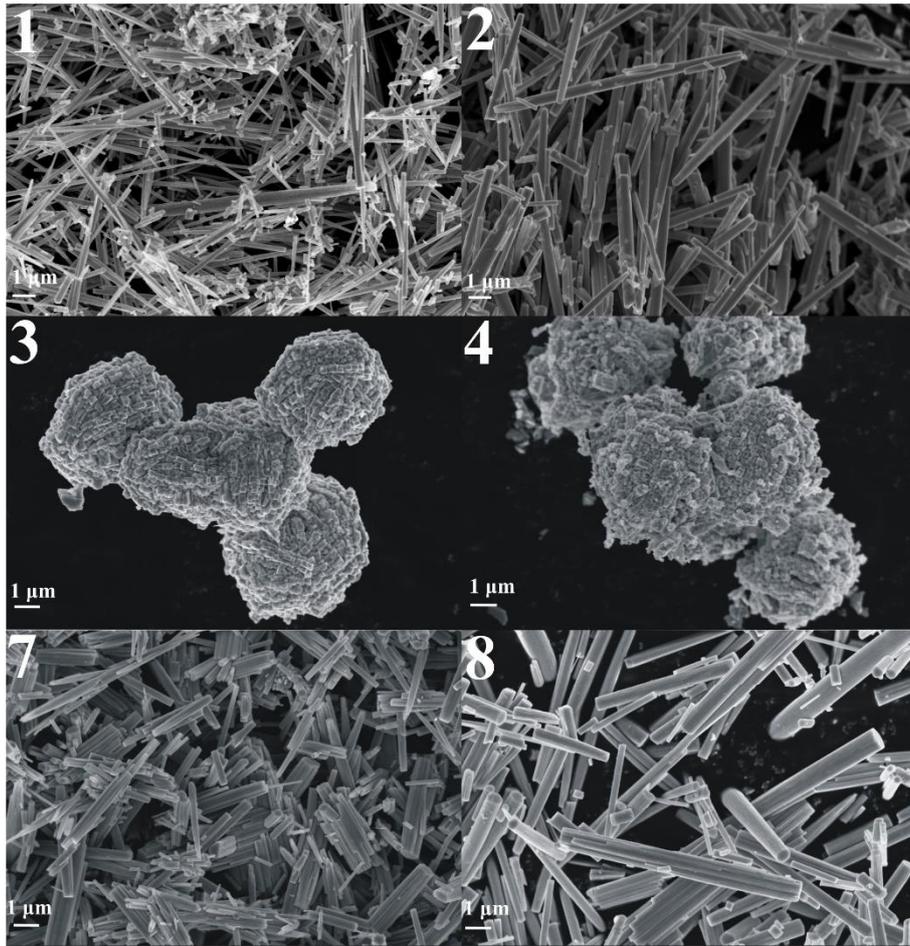


Figure 2. T. Nagyné-Kovács et al.

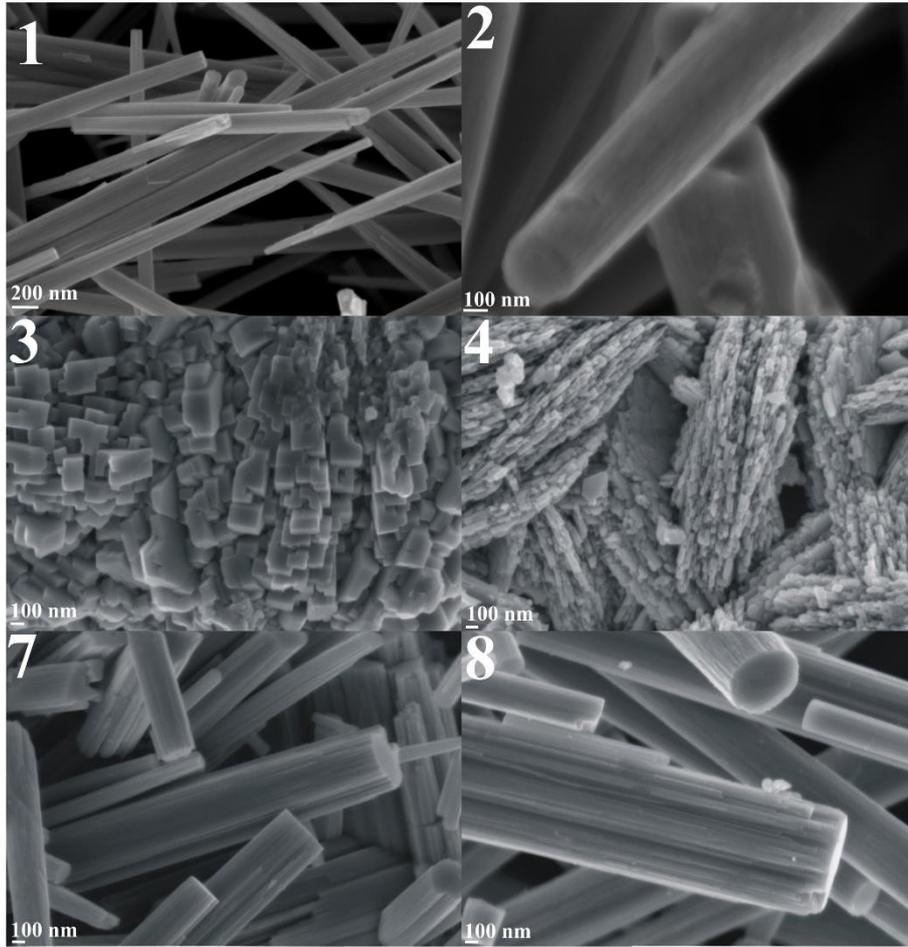


Figure 3. T. Nagyné-Kovács et al.