

## Hydrothermal synthesis of one-dimensional tungsten oxide nanostructures using cobalt ammonium sulfate as a structure-directing agent

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**Abstract**—Hydrothermal synthesis of one-dimensional tungsten oxide nanostructures was performed using cobalt ammonium sulfate as a structure-directing agent, and the effect of the concentration of cobalt ammonium sulfate on the characteristics of the tungsten oxide nanostructures was investigated. XRD measurements showed that hexagonal tungsten oxide (h-WO<sub>3</sub>) structures were obtained at a higher concentration of cobalt ammonium sulfate (0.2 M), while cubic tungsten oxide (c-WO<sub>3</sub>) structures were obtained at a lower concentration of cobalt ammonium sulfate (0.01 M). Mixed structures of h-WO<sub>3</sub> and c-WO<sub>3</sub> were observed at an intermediate concentration of cobalt ammonium sulfate. Morphological studies revealed that h-WO<sub>3</sub> appeared as nanowires with a diameter of about 40 nm and an average length of 1 μm. c-WO<sub>3</sub> was shaped in pillar-like nanorods with a diameter of about 30 nm. A red-shift in the UV/Vis absorption peak was observed with different phases of tungsten oxide nanostructures.

Key words: Hydrothermal, Tungsten Oxide, Nanostructures, Structure-directing Agent

### INTRODUCTION

Metal oxides with one-dimensional nanostructures have drawn much attention because of their unique optical and electronic properties [1]. Among them, tungsten oxides have been used in a variety of applications such as field emission, photocatalysts, electrochromic devices, and gas sensors [2-8]. Various preparation methods were used to synthesize the nanostructures of tungsten oxides including laser pyrolysis [9], thermal evaporation [10], hydrothermal methods [2-4], and so on. Among these, a hydrothermal method has advantages in that this technique is easy to operate, cost effective, and environmentally friendly [2-4].

Recently, it was reported that, during a hydrothermal process, the addition of alkali salts such as Li<sub>2</sub>SO<sub>4</sub>, NaCl, Na<sub>2</sub>S, Na<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub>, and Rb<sub>2</sub>SO<sub>4</sub> into the reaction mixtures caused the growth of tungsten oxides and the resultant products were hierarchical nanostructures [2,11-15]. The above-mentioned additives are called structure-directing agents and most of the structure-directing agents are in the form of salts of group I cations. The exact reason for this controlled growth is still under investigation. But, other studies suggest that the controlled growth may result from the presence of sulfate ions in the reaction [11-13].

In the present study, we report on a hydrothermal method for the fabrication of one-dimensional tungsten oxide nanostructures using cobalt ammonium sulfate as a structure-directing agent. Cobalt ammonium sulfate (group IX metal complex) was chosen in order to offer a new structure-directing agent as an alternative to the group I compounds. The structural, morphological, and optical properties of the tungsten oxide nanostructures were investigated by varying the

concentration of cobalt ammonium sulfate. The use of a transition metal salt as a structure-directing agent is a new approach for the synthesis of metal oxide nanostructures.

### EXPERIMENTAL

Sodium tungstate (Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O) was the source material for the synthesis of tungsten oxide nanowires. Oxalic acid (C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O) and cobalt ammonium sulfate [(NH<sub>4</sub>)<sub>2</sub>Co(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O] were used as surfactant and structure-directing agent, respectively.

Sodium tungstate and cobalt ammonium sulfate were dissolved separately in double distilled water, and these two solutions were mixed under vigorous stirring. A light violet slurry mixture was obtained, and was dissolved by adding oxalic acid of 0.2 M. The resultant solution was transparent and pink. This solution was transferred into a Teflon-lined stainless steel autoclave and maintained at 180 °C for 12 hours to get the final product. The as-obtained products were washed several times both in water and ethanol, and finally dried at 100 °C for two hours. Throughout this study, the concentrations of both sodium tungstate and oxalic acid were fixed at 0.2 M. The concentration of cobalt ammonium sulfate was varied from zero to 0.2 M.

The surface morphology of the tungsten nanostructures was examined using scanning electron microscopy (SEM, 5600 JEOL JSM). The crystalline nature of the nanostructures was analyzed through an x-ray diffractometer (PANalytical XPERT PRO). Optical measurements were carried out using a UV-Vis spectrophotometer (SHIMADZU 3600).

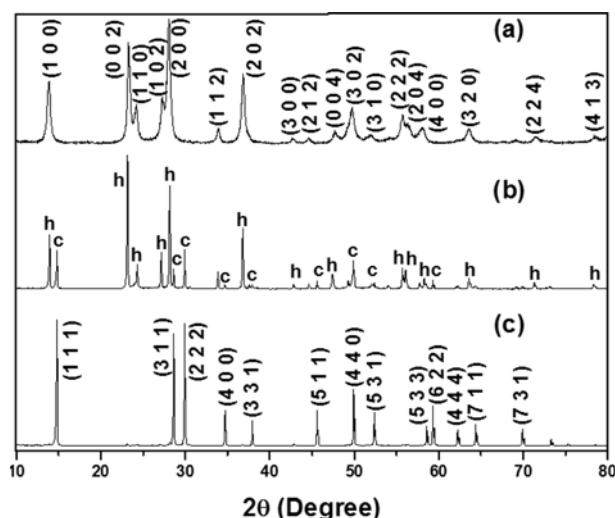
### RESULTS AND DISCUSSION

Fig. 1 shows X-ray diffraction (XRD) patterns of tungsten oxides obtained at various concentrations of cobalt ammonium sulfate. The XRD pattern of the tungsten oxide sample prepared at 0.2 M cobalt

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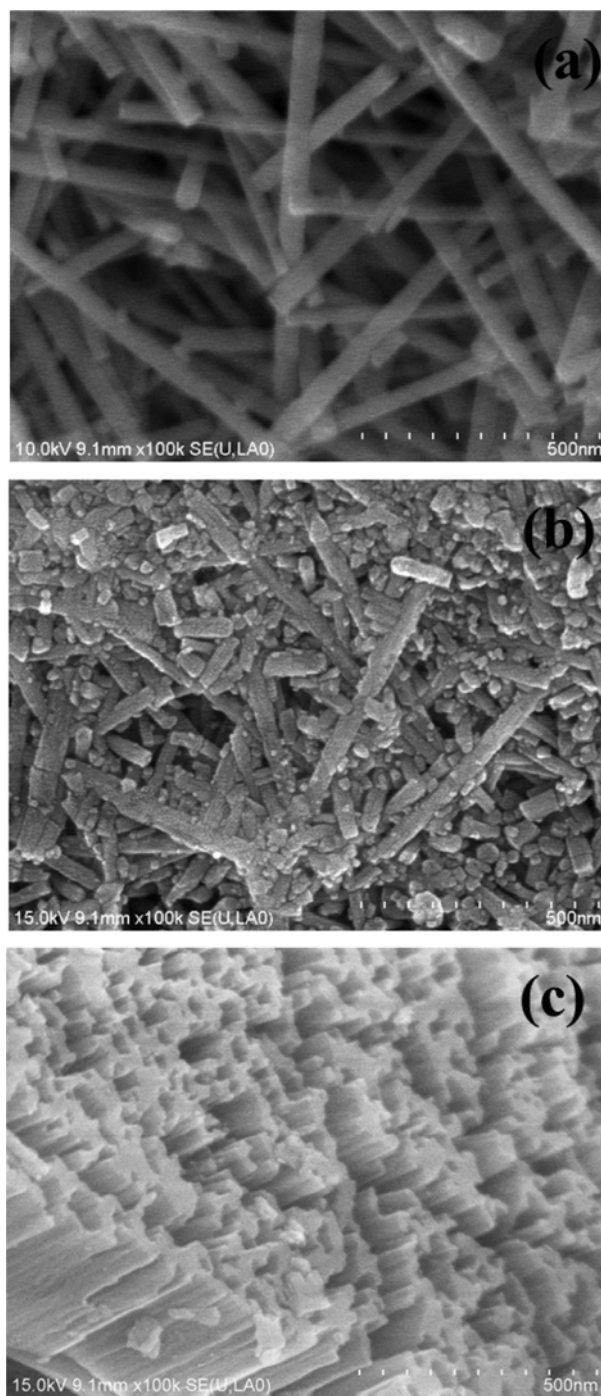


**Fig. 1.** XRD spectra of tungsten oxides prepared at cobalt ammonium sulfate concentrations of (a) 0.2 M, (b) 0.1 M, and (c) 0.01 M. In (b), h and c represent hexagonal and cubic structures of tungsten oxide, respectively.

ammonium sulfate (Fig. 1(a)) follows the hexagonal tungsten oxide ( $h\text{-WO}_3$ ) crystal structure. The lattice parameters of  $h\text{-WO}_3$  are  $a=7.324 \text{ \AA}$  and  $c=7.668 \text{ \AA}$  (JCPDS card No: 85-2460) [16]. Fig. 1(b) shows the XRD pattern of the sample prepared at 0.1 M cobalt ammonium sulfate, which represents a mixed structure of hexagonal and cubic tungsten oxide. Further reducing the concentration of cobalt ammonium sulfate to 0.01 M (Fig. 1(c)), we observed cubic  $\text{WO}_3$  ( $c\text{-WO}_3$ ) crystal structure whose lattice parameter is  $a=10.27 \text{ \AA}$  (JCPDS card No: 44-0363) [17]. From this observation, it can be said that cobalt ammonium sulfate worked as a structure-directing agent and pure tungsten oxide could be obtained under the current synthetic route.

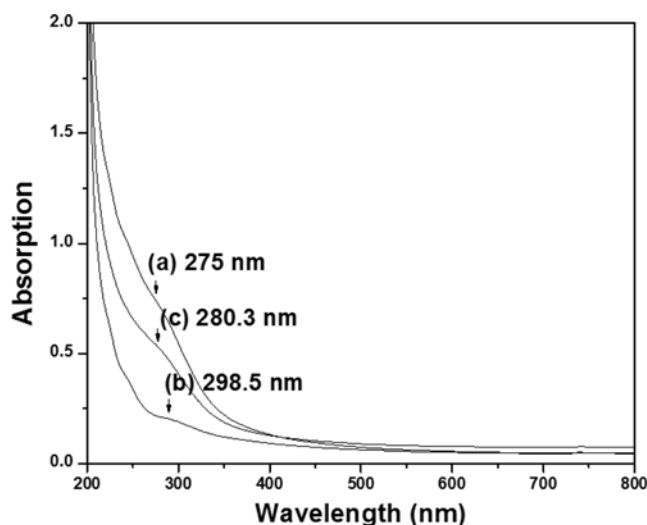
In the absence of cobalt ammonium sulfate, the hydrothermal reaction of the mixture of sodium tungstate and oxalic acid produced a transparent solution of tungsten oxalate which was easily dissolved in water.

The introduction of cobalt ammonium sulfate as a structure-directing agent into the reaction mixture induced the formation of tungsten oxide nucleation, even at very low concentration, such as 0.01 M. Therefore, apart from acting as structure-directing agent, cobalt ammonium sulfate initiates the nucleation of tungsten oxide. In addition, the sulfate ions from cobalt ammonium sulfate are selectively adsorbed on the surface of the seed nucleus of tungsten oxide, and correspondingly the surface energy of the nucleus of tungsten oxide decreases in all directions, except for the specific direction, leading to one-dimensional growth [18]. Tungsten oxide continues to grow in this specific unperturbed direction through agglomeration with other seed nuclei. From the XRD results, it is clear that concentration-dependent structures of tungsten oxide are possible by changing the lattice parameter 'a' from  $10.27 \text{ \AA}$  of cubic structure to  $7.324 \text{ \AA}$  of hexagonal structure. The chemical composition of the tungsten oxides was not measured in the present work, but a molar ratio of tungsten with respect to oxygen is expected to be close to 1 : 3 based on other reports on the hydrothermal synthesis of tungsten oxide using sodium tungstate as a source material [18,19].



**Fig. 2.** SEM images of tungsten oxides prepared at cobalt ammonium sulfate concentrations of (a) 0.2 M, (b) 0.1 M, and (c) 0.01 M.

Fig. 2 shows SEM images of tungsten oxides at various concentrations of cobalt ammonium sulfate.  $h\text{-WO}_3$ , which was prepared at 0.2 M cobalt ammonium sulfate, appears as a cluster of nanowires with a diameter of about 40 nm and an average length of  $1 \mu\text{m}$  (Fig. 2(a)). A mixed structure of tungsten oxide, which was obtained at 0.1 M cobalt ammonium sulfate, appears as broken nanorods with a uniform diameter of about 30 nm (Fig. 2(b)). Further reduction of the cobalt ammonium sulfate concentration to 0.01 M resulted



**Fig. 3.** UV/Vis absorption spectra of different crystalline structures of tungsten oxides. (a) hexagonal, (b) mixed structures of hexagonal and cubic, and (c) cubic tungsten oxides obtained at cobalt ammonium sulfate concentrations of (a) 0.2 M, (b) 0.1 M, and (c) 0.01 M, respectively.

in vertically oriented pillar-like nanorods of c-WO<sub>3</sub> (Fig. 2(c)). In Fig. 2(c), the bottom of the WO<sub>3</sub> nanorods was mostly agglomerated with each other. Therefore, they were grown as pillar-like nanorods of WO<sub>3</sub>. This vertically oriented structure was obtained without using any templates or substrates.

UV/Vis absorption spectra were taken for the hexagonal, cubic, and mixed structures of tungsten oxide, and are shown in Fig. 3. An absorption peak at 275 nm was obtained for the h-WO<sub>3</sub> nanowire cluster structure (pattern a), whereas a red-shifted absorption was seen for the c-WO<sub>3</sub> pillar-like nanorod structure (pattern c). The optical band gap values of h-WO<sub>3</sub> and c-WO<sub>3</sub> structures were evaluated to be 3.36 eV and 3.13 eV, respectively. Other studies also reported that the band gap was dependent on the crystallinity of the tungsten oxide films [20]. Further red-shift with reduced intensity was observed due to the nature of the mixed crystalline structures (pattern b). From this observation, it can be said that the tungsten oxide with mixed structures exhibits poor optical properties, whereas the single phase tungsten oxide, either hexagonal or cubic, exhibits noticeable absorption results.

## CONCLUSIONS

One-dimensional tungsten oxide nanostructures were synthesized by a facile hydrothermal reaction, with the help of cobalt ammonium sulfate as a structure-directing agent. The concentration-dependent reactions exhibited different structures of tungsten oxide products. At higher cobalt ammonium sulfate concentration (0.2 M), high aspect-ratio hexagonal tungsten oxide (h-WO<sub>3</sub>) nanowires were obtained, whereas cubic tungsten oxide (c-WO<sub>3</sub>) shaped in pillar-like nanorods was observed at lower concentration (0.01 M). Mixed structures of hexagonal and cubic tungsten oxides were observed at an

intermediate concentration of cobalt ammonium sulfate. From optical absorption maxima, a red-shift was realized for the different phases of tungsten oxide nanostructures.

This work revealed the feasibility of fabricating one-dimensional tungsten oxide nanostructures and controlling their phases by a hydrothermal method.

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