TAILORING THE STRUCTURE AND MORPHOLOGY OF WO$_3$ NANOSTRUCTURES BY HYDROTHERMAL METHOD

Luu Thi Lan Anh, Pham Tuan Phong, Han Viet Phuong, Duong Vu Truong, Le Xuan Vung, Pham Trung Son, Do Duc Tho, Dang Duc Vuong, Nguyen Huu Lam, Nguyen Cong Tu*

School of Engineering Physics, Hanoi University of Science and Technology, No 1, Dai Co Viet street, Ha Noi

*Email: tu.nguyencong@hust.edu.vn

Received: 15 August 2017; Accepted for publication: 30 March 2018

ABSTRACT

Tungsten oxide nanostructures were synthesized by hydrothermal and acid precipitation (hydrothermal at room temperature) methods without using any supporting agent or structure-directing reactant. The morphology and crystalline structure of nanostructures strongly depended on pH of the precursor solution and synthesis method. With pH = -1.0, using acid precipitation method, orthorhombic nanoplate was observed. Using hydrothermal method, with the pH = -1.0, we obtained directly stable monoclinic nanoparticle WO$_3$. With pH = 1.1, the mixing of nanoparticle and nanorod with the hexagonal frame was acquired. When pH reaches to 1.7, only bundle of hexagonal nanorods was observed. To characterize the morphology and structure of tungsten nanostructures, we used Field Emission Scanning Electron Microscopy, X-ray diffraction, and micro Raman spectroscopy. The micro Raman spectroscopy was used to support the X-ray diffraction analysis. These results imply that adjusting pH is an efficient and promising method to manipulate both morphology and crystal structure of WO$_3$ nanostructure for selective applications.

Keywords: tungsten oxide, nanoparticle, nanoplate, nanorod, hydrothermal.

1. INTRODUCTION

Tungsten oxide (WO$_3$) is a metal oxide semiconductor with the band gap in the range of visible region [1]. Many groups have studied tungsten oxide for different applications such as photocatalyst [2], smart window [3] etc. In recent years, WO$_3$ appeared to be attractive materials for electrochemistry - electrode for lithium ion battery [4, 5], photocatalysis of water [1, 6, 7] and gas sensor [8-10]. For different applications, various nanostructures of WO$_3$ having different crystal structures or morphologies were designed. Poongodi et al. purposely synthesized WO$_3$ nanoplate for smart window [3], Marques et al. used WO$_3$ nanoparticles for the colorimetric detection of electrochemically active bacteria [11] etc.
The common methods to grow WO₃ nanostructure are acid precipitation [1], electrodeposition [3], solution combustion [5], and hydrothermal method [4, 7-10]. Because of the simplicity and flexibility, acid precipitation and hydrothermal methods are the most widely used methods. Using these methods, many efforts have been dedicated to finding the way to engineer or manipulate morphology [1, 11, 12], crystalline structure [11, 13, 14] and crystal facet [6, 15] of WO₃ nanostructures. In these works, both supporting agents, structure-directing reactant, and pH value are used as control parameters. Also using the hydrothermal and acid precipitation methods, in this study, our purpose is to synthesize and engineer WO₃ nanostructures without using any supporting agents. Especially, a simple method to directly grow stable monoclinic structure of WO₃ is also presented. We used only two precursors: sodium tungsten dehydrate (Na₃WO₄·2H₂O) and hydrochloric acid (HCl). To manipulate the morphology and crystal properties of WO₃ nanostructure, we tuned the pH value and temperature.

WO₃ has various crystal patterns such as monoclinic, triclinic, orthorhombic, tetragonal, cubic and hexagonal [2]. In addition, the natural appearance of phase WO₃(x<3) having complex X-ray diffraction (XRD) patterns in WO₃ nanostructures makes crystal analyzing more difficult. To investigate the crystal structure of WO₃ nanostructures, the researcher used the combination of analysis techniques such as the combination of XRD and micro Raman spectroscopy [1, 12, 18]. Raman spectroscopy was also used to investigate the photocatalytic and electrochromic of WO₃ nanostructures [2, 3]. In this work, Micro Raman spectroscopy was used as a supplement for XRD analysis in investigating structure and morphology of WO₃ nanostructures.

2. MATERIALS AND METHODS

2.1. Sample preparation

In this paper, WO₃ nanostructures were synthesized by hydrothermal method or acid precipitation method (hydrothermal method at room temperature – RT) with two reactants: sodium tungsten dehydrate (Na₃WO₄·2H₂O), and hydrochloric acid (HCl) in analytical reagent level without any further purification. 8.25 g of Na₃WO₄·2H₂O was dissolved in 25 mL of bi-distilled water under constant stirring at room temperature to get a transparent Na₃WO₄ solution. The buffer solution of HCl, then, was dropped gradually into the transparent solution to create H₂WO₄ as the following equation:

\[
\text{Na}_3\text{WO}_4 + 2\text{HCl} \rightarrow \text{H}_2\text{WO}_4 + 2\text{NaCl}
\]

The appearance of H₂WO₄ causes coloring of solution which changes from transparent to milk-like color and finally yellow. pH of solution was controlled with HCl buffer solution. After stirring for 4 hours, the obtained solution was put into Teflon-lined stainless-steel autoclave. In this work, we grew four WO₃ nanostructures: one sample synthesized by acid precipitation method with pH = -1.0 (labeled o-WO₃) and three samples synthesized by hydrothermal method in three different acidic environments (pH = -1.0, 1.1, 1.7 labeled m-WO₃, h-WO₃, hn-WO₃ respectively). The hydrothermal process was carried out at 180 °C or 120 °C for 48 hours. When hydrothermal process finished, the autoclave was let to cool down gradually to room temperature (RT) in the oven. The acid precipitation process is similar to the hydrothermal process, but the autoclave was kept at room temperature for 48 hours (technically we could count this method as a hydrothermal method at RT). The products of hydrothermal process or acid precipitation – aggregated slurry which was a suspension at the bottom of Teflon-shell -
was cleaned and filtrated three times with bi-distilled water and filter paper. The obtained products were then dried in ambient at 80 °C during 2 hours. The dried product was ground by agate mortar and pestled to get WO₃ powder.

2.2. Analytical methods

The pH of solution was measured by Hanna instruments (model HI2020-02) with the pH range from -2.000 to 16.000, and working temperature from -20 °C to 120 °C. The Field-Emission Scanning Electron Microscopy (FESEM) HITACHI S4800 was used to investigate the morphology of obtained samples. The crystalline properties of samples were obtained by using X’pert Pro (PANalytical) MPD with a CuKα radiation (λ = 1.54065 Å) at a scanning rate of 0.03º/s in the 2θ range from 10º to 70º. The micro Raman spectroscopy was observed by Renishaw Invia Raman Microscope using 633-nm laser and Leica N PLAN L50x/0.50 BD Microscope objective.

3. RESULTS AND DISCUSSION

3.1. The morphology of samples

Figure 1 shows the FESEM images of four samples. In all four cases, WO₃ nanostructures with different morphologies were observed. Sample o-WO₃ had big nanoplate morphology (Figure 1a) with smooth surfaces and corners. Nanoplates are uniform with the various distribution of size. In similar conditions but temperature increased to 180°C (sample m-WO₃) WO₃ nanoparticles are observed (Figure 1b). These nanoparticles have the smooth surface with sharp corners. The size of NPs diverse from 50x50 nm to 150x150 nm, but they all have a rectangular shape with the biggest dimension was about 150 nm.

When pH increased to 1.1, at 180°C (sample h-WO₃) the mixture of nanorod with bundle of very small nanoparticles were observed (Figure 1c). The dimension of nanoparticles is about 40 nm which is in the same size with the diameter of nanorod. At 120°C, with pH=1.7, these nanoparticles disappeared and only bundles of nanorods were observed (Figure 1.d). The diameter of nanorod is also approximate to the dimension of nanoparticle acquired at pH = 1.1. From FESEM images, it is clear that pH of precursor solution strongly affects the morphology of WO₃ nanostructures. The high acid concentration environment drives WO₃ molecules to make big structures. When pH value increased, WO₃ nanostructures tended to form structures with smaller dimension. But there is a critical value of pH, at which WO₃ nanostructures - nanoparticles get its minimum dimension. Above this value, nanoparticles tend to aggregate into nanorods (pH = 1.1 to 1.7). When acid environment got dilute, there was no aggregation obtained after the hydrothermal process (pH>2.5).

3.2. The XRD pattern of samples

To characterize the effect of synthesis parameters on crystallization of samples, XRD patterns of four samples were measured. Figure 2 exhibits the XRD patterns of four samples. All peaks in XRD pattern of o-WO₃ (Figure 2.a) are identified to orthorhombic structure WO₃·H₂O (noted by star sign *) with space group Pmnb and lattice constant a = 0.5249 nm, b = 1.711 nm, c = 0.5133 nm, α = β = γ = 90º (ICDD: 01-084-0886). But XRD analyses show that o-WO₃ was composed of two phases having the same orthorhombic structure, tungsten oxide hydrate WO₃·H₂O and tungsten oxide WO₂.625 (ICDD: 01-081-1172). This result is reinforced by
scattering Raman spectra. The content of WO$_3$.H$_2$O and WO$_{2.625}$ in o-WO$_3$ sample are 82% and 18%, respectively.

![Figure 1. FESEM images of samples (a) large nanoplate o-WO$_3$, (b) nanoparticle m-WO$_3$, (c) mixture of nanorod with very small nanoparticle h-WO$_3$, and (d) the bundle of nanorod h-WO$_3$.](image)

In the XRD pattern of sample m-WO$_3$ (Figure 2.b), the peaks of two phases with the same monoclinic structure were recognized: WO$_3$ (60% of content – marked with closed circles) and W$_{17}$O$_{47}$ (40% of content and marked with hash sign #). Monoclinic WO$_3$ has space group P21/n and lattice constants $a = 0.73013$ nm, $b = 0.75389$ nm, $c = 7.6893$ nm, $\alpha = \gamma = 90^\circ$ and $\beta = 90.893^\circ$ (ICDD: 01-083-0951). W$_{17}$O$_{47}$ has monoclinic structure with P2/m space group and lattice structure $a = 1.884$ nm, $b = 0.3787$ nm, $c = 1.233$ nm, $\alpha = \gamma = 90^\circ$ and $\beta = 102.67^\circ$ (ICDD: 01-079-0171). Up to our knowledge, this is the first-time as-grown monoclinic nanostructure was observed. In other works, to get monoclinic structure, as-grown hexagonal WO$_3$ nanostructures were annealed up to 500°C [8,9,16] but here monoclinic nanostructures could be obtained directly by hydrothermal method.

Figure 2.c shows the XRD pattern of h-WO$_3$ sample. In this pattern, all peaks were indexed to hexagonal structure tungsten oxide WO$_3$ (closed gray rectangular) with lattice constant $a = 0.7298$ nm; $b = 0.7298$ nm; $c = 0.3899$ nm, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$ (ICDD: 01-075-2187). No evidence of other phase or impurities was obtained in analyzing XRD pattern. It means that the nanoparticles and nanorods have the same crystal structure. Moreover, nanoparticles had the same dimension as the diameter of nanorod (Figure 1.c). These results imply that nanoparticles are seeds of nanorods. To explain this phenomenon, we use the widely accepted theory which states that at the beginning of the hydrothermal process, nanoparticles were created, then
nanoparticles assembled in preference direction to form nanorod [7,17]. The strong acidic environment (pH < 1.0) prevented this assembly, when pH got to the higher value 1.67 – 1.8, nanoparticles mostly aggregated into nanorod and we obtained only bundle of nanorods as observed in Figure 1.d. The similarity between the XRD pattern of hn-WO₃ (Figure 2.d) and that of h-WO₃ (Figure 2.c) also supports this theory. Compared to the hn-WO₃ pattern, the XRD pattern of h-WO₃ is sharper, it implies that h-WO₃ has higher crystallization. This result is also supported by Raman spectra.

![Figure 2. Normalized XRD patterns of samples (a) o-WO₃, (b) m-WO₃, (c) h-WO₃, and (d) hn-WO₃.](image)

These XRD results exhibit the possibility to manipulate the crystalline structure of WO₃ from orthorhombic, to monoclinic and hexagonal by hydrothermal method and acid precipitation method. By changing the pH value from -1.0 to 1.1, the crystal structure of WO₃ nanostructures transforms from monoclinic to hexagonal. With pH = -1.0, by changing the temperature from RT to 180 °C, the morphology changes from nanoplate to nanoparticle in company with transformation of structure from metastable orthorhombic to the stable monoclinic pattern. It means that pH and temperature of hydrothermal process strongly affect the crystallization of WO₃ structures. Table 1 shows the evolution of morphology and structure of WO₃ nanostructures with the pH value and temperature.

<table>
<thead>
<tr>
<th>Name</th>
<th>pH*</th>
<th>Temperature</th>
<th>Morphology</th>
<th>Chemical formula</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-WO₃</td>
<td>-1.0</td>
<td>Room temperature</td>
<td>Nanoplate</td>
<td>WO₃·H₂O and WO₂₆.₂₅</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>m-WO₃</td>
<td>-1.0</td>
<td>180 °C</td>
<td>Nanoparticle</td>
<td>WO₃ and W₁₇O₄₇</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>h-WO₃</td>
<td>1.1</td>
<td>180 °C</td>
<td>Nanorod and Nanoparticle</td>
<td>WO₃</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>hn-WO₃</td>
<td>1.7</td>
<td>120 °C</td>
<td>Nanorod</td>
<td>WO₃</td>
<td>Hexagonal</td>
</tr>
</tbody>
</table>

(*: The value measured by Hanna HI2020-02 instrument.)
3.3. Raman spectroscopy of samples

In Figure 3, the normalized micro Raman spectra of samples are presented. In Raman spectra of o-WO$_3$ (Figure 3.a), there is a sharp and strong peak at wavenumber 945 cm$^{-1}$ corresponding to W$^{6+}$-O bond, which relates to the appearance of water molecular between layers of WO$_6$ octahedron [1, 18]. The water molecular causes the distortion of WO$_6$ octahedron and then causes an appearance of broadening the peak at 636 cm$^{-1}$ which is assigned to be the stretching vibration of W$^{6+}$-O bond. Two peaks at 636 cm$^{-1}$ and 945 cm$^{-1}$ identify the appearance of water molecular in WO$_3$ structure [1, 18]. The weak peak at wavenumber 812 cm$^{-1}$ is specified for the stretching mode of O-W$^{6+}$-O bond which supports the result of XRD analysis about the appearance of WO$_{2.625}$ phase in o-WO$_3$ sample.

The Raman spectrum of sample m-WO$_3$ (Figure 3.b) is the typical Raman spectrum of monoclinic WO$_3$ [18-21]. Two strong and sharp peaks at wavenumbers of 806 cm$^{-1}$ and 717 cm$^{-1}$ correspond to the stretching vibration of O-W$^{6+}$-O in octahedral WO$_6$. Three weaker peaks at 326 cm$^{-1}$, 273 cm$^{-1}$, and 241 cm$^{-1}$ are assigned to the bending vibration of W$^{6+}$-O-W$^{6+}$ bond of corner oxygen. The peaks at lower region (180 and 132 cm$^{-1}$) are attributed to the lattice vibration [18-21]. The presence of W$_{17}$O$_{47}$ phase is confirmed by the appearance of peak at 935 cm$^{-1}$ corresponding to the lacking of oxygen in WO$_6$ octahedron.

Figure 3. Normalized micro Raman spectra of WO$_3$ nanostructures: (a) o-WO$_3$, (b) m-WO$_3$, (c) h-WO$_3$, and (d) hn-WO$_3$.

Figure 3.c and 3.d show the Raman spectra of samples h-WO$_3$ and hn-WO$_3$, respectively. These patterns of spectra are similar, the reason is the sameness of crystal structure – hexagonal. The regions below 400 cm$^{-1}$ wavenumber of two samples are alike corresponding to the same deformation and lattice vibration in the same crystal structure. The wide range spectra from 600 to 1000 cm$^{-1}$ stands for the stretching mode of a typical hexagonal structure. The difference between two spectra is clearly shown in this region. In spectrum of h-WO$_3$, the peaks at 665, 753, 960 cm$^{-1}$ are clearly showed but in hn-WO$_3$ these peaks almost disappear and become the shoulders of peaks at 806 and 928 cm$^{-1}$. The clearer peaks responses to the higher crystallization of sample h-WO$_3$ in higher acid concentration compare to sample hn-WO$_3$ synthesized in lower acid concentration. These results strengthen the role of pH on crystallization process of WO$_3$ nanostructures.
4. CONCLUSIONS

We have successfully synthesized WO\textsubscript{3} nanostructures with three different morphologies: nanoplate, nanoparticle and nanorod by hydrothermal and acid precipitation methods without using any structure-directing agent. The crystal of WO\textsubscript{3} nanostructures transformed from orthorhombic, monoclinic to hexagonal corresponding with the change of morphologies from nanoplate, nanoparticle to nanorod. With pH = -1.0, at room temperature, WO\textsubscript{3} had plate-like morphology with orthorhombic structure. Using the same condition, but higher temperature, WO\textsubscript{3} nanostructure obtained is nanoparticle type and has monoclinic crystal with less hydration. With pH = 1.1 at 180 °C, the nanorod appeared with bundle of very small nanoparticles which all had hexagonal structure. When pH gets to 1.7, only bundle of hexagonal nanorods was observed. These results imply a promising process to tailor the morphology and structure of WO\textsubscript{3} nanostructures without using any supporting agent, they also mean that it is possible to manipulate the optical, photocatalytic, electrochromic properties and surface state of WO\textsubscript{3} nanostructures for different applications. Up to our knowledge, this the first time monoclinic WO\textsubscript{3} nanoparticles were directly synthesized by hydrothermal method without using any supporting reactant. The mechanism of transforming from orthorhombic to monoclinic pattern in company with the dehydration process in WO\textsubscript{3} nanostructures at low pH value (pH = -1.0) is still unclear and needs more research.

Acknowledgments. This research was supported by Hanoi University of Science and Technology (HUST) under project number T2017-PC-134.

REFERENCES

5. Zhiwei L., Ping L., Yuan D., Qi W., Fuqiang Z., Alex A. Volinsky, Xuanhui Q. - Facile preparation of hexagonal WO\textsubscript{3}.0.33H\textsubscript{2}O/C nanostructures and its electrochemical properties for lithium-ion batteries, Applied Surface Science 394 (2017) 70–77.
7. Tianyou P., Dingning K., Jianguang X., Li W., Jun H., Ling Z. - Hexagonal phase WO\textsubscript{3} nanorods: hydrothermal preparation, formation mechanism and its photocatalytic O\textsubscript{2}...


