Hydrothermal synthesis and characterization of WO₃ nanostructures: Effect of reaction time

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Abstract
1-D and 2-D WO₃ nanostructures were successfully prepared by hydrothermal technique as a low temperature, low cost, compatible with the environment, and powerful method with controllability of particle size, shape, and stoichiometry. The effect of hydrothermal duration time was studied to investigate morphological, structural and optical properties and to propose the possible growth mechanisms of WO₃ nanostructures. X-ray diffraction (XRD), Field emission scanning electron microscopy (FESEM), Fourier transform infrared spectroscopy (FTIR), and Diffuse reflectance spectroscopy (DRS) analyses were done on the samples synthesized at different hydrothermal duration times of 6, 12, 24, and 36 h. The results indicated that the morphology evolutions of nanostructures strongly depend on hydrothermal duration time and concentration of capping agents. Two crystal phase transitions in accordance with the morphology evolution were also observed. The absorption edge of the samples exhibited a blue- and then red-shift by increasing the reaction time. The bandgaps of the samples were almost independent of the reaction time and the samples were transparent in a wide range of the visible light region. So, they can be regarded as excellent candidates for optoelectronic devices.

1. Introduction
Tungsten oxide (WO₃) as a metal oxide semiconductor with n-type conductivity, indirect and adaptable wide-bandgap has attracted great interests due to the particular applications in supercapacitors [1], binder-free lithium-ion batteries [2], electrochromic [3], photocatalysis [4], photoelectocatalyses (PEC) [5], and the environmental devices like a high performance humidity and temperature sensors [6]. Today, cancer is one of the major problems in the world which theoretical and experimental studies are proceeding to solve it [7, 8]. Recently, the success of cancer treatment using tungsten oxide and ICG has been confirmed in mice [9]. Therefore, the synthesis of tungsten oxide is an interesting domain. So far, different well-defined morphologies [10–17] have been reported using several techniques such as sol-gel [18], hydrothermal [6], and so on.

The morphology, crystallinity, and optical properties of WO₃ nanostructures can be controlled by varying hydrothermal temperature, duration or reaction time, capping agents, and precursor material. Using a variety of inorganic capping agents (such as sodium sulfate, potassium sulfate, sodium chloride, sodium nitrate [19–22]), organic acids (such as tartaric, oxalic, and citric acid [4, 20, 21, 25, 24]), and precursor material (such as Ammonium meta-tungstate (AMT), sodium tungstate, and tungsten oxide powder [4, 21, 25]) have been reported. Recently, we considered the effects of capping agent and pH on the morphology and optical properties of tungsten oxide nanostructures. The results confirmed that capping agents and pH significantly affect the morphology of nanostructures. Also, nanostructures with smaller bandgaps and blue-shifted absorption edges have been formed with decreasing the pH [26]. Hydrothermal synthesis of WO₃ nanorods has been reported at a hydrothermal temperature of 100 °C and calcination temperatures of 200 °C–800 °C. According to the results, gas sensing parameters are truly controlled by calcination temperatures and 200 °C has been an appropriate calcination temperature for gas sensing applications [27]. Also, the effect of duration time 1–9h was considered...
on tungsten oxide nanostructures synthesized by hydrothermal method. The results revealed that a short reaction time caused directionally uniform and short nanorods. Indeed, increasing the duration time or reaction time led to form separate nanorods with longer length [28]. Also, another research on the effect of hydrothermal reaction times of tungsten oxide nanostructures revealed that the morphology has not been changed by increasing the reaction time [29]. Furthermore, h-WO3 nanotube bundles with oxygen have been produced through a mixed solvent of ethylene glycol and water. It has been confirmed that the reaction time dramatically affects the morphology of the product and evolution of the morphology from nanosheets to nanotubes and from nanotubes to nanotube bundles has been observed during increasing the reaction time in the range of 2–24 h [29]. Obviously, the growth mechanism of tungsten oxide nanostructures and the effect of reaction time on the morphology, physical and chemical properties of WO3 nanostructures is not completely clear yet.

In this paper, we successfully produced 1-D and 2-D WO3 nanostructures using hydrothermal method and a wide range of duration times 6–36 h was considered as a critical parameter. This study provides an excellent opportunity to explore the effect of hydrothermal duration time on the growth mechanism, morphology evolution, structural and optical properties. Possible growth mechanism was proposed according to our experimental results.

2. Materials and methods

Tungsten oxide nanostructures were produced by using the hydrothermal method. Typically 0.005 mol Sodium tungstate (Na2WO4·2H2O, Merck Company, 99.9%), 0.025 mol sodium sulfate (Na2SO4, Merck Company, 99.2%), and 0.006 mol citric acid (C6H8O7·H2O, Merck Company 99.9%) were used to synthesize the nanostructures. For this purpose, sodium tungstate, citric acid, and sodium sulfate were dissolved in 50 ml deionized water. Hydrochloric acid 2M was gradually added to an aqueous solution when a transparent solution was formed. In this way, pH was set to 2. The solution was kept stirred for 10 min and then transferred to a 100 ml Teflon-lined autoclave. The hydrothermal synthesis was done for different times of 6, 12, 24, and 36 h at a fixed temperature of 180 °C. The obtained precipitate was then filtered and washed thoroughly by deionized water and ethanol. The final product was put in an oven for 10 h at 60 °C.

The crystalline structure of the synthesized samples was studied by x-ray powder diffraction (XRD) technique using a Brucke model D8-Advance x-ray diffractometer with Cu-Kα (λ = 0.154 nm) radiation in the range of 2θ = 10–90°. Field-emission scanning electron microscopy (FESEM, TESCAN model MIRA3) was used to investigate the morphological properties. The chemical bonding configuration of the products was analyzed by Fourier transform infrared spectroscopy (FTIR, Shimadzu, model 8400S) from 400 to 4000 cm⁻¹. Diffuse reflectance spectroscopy (DRS, AvaSpec-2048-TEC) was employed to study the optical properties of the samples and to determine their bandgap by the Kubelka-Munk relation.

3. Results and discussion

The XRD patterns of the samples synthesized at different hydrothermal times of 6, 12, 24, and 36 h were shown in figure 1. The samples were labeled according to their hydrothermal duration times. The sample 6h showed a crystalline structure which is related to the cubic hemihydrate tungsten oxide (WO3·0.5H2O) with the lattice parameters of a = b = c = 10.30 Å as confirmed by the standard card (JCPDS 84–1851). Increasing the reaction time from 6h to 12h led to a crystal phase transition to hexagonal WO3 (JCPDS 33–1387) with (200) preferred orientation and lattice constants of a = b = 7.298 Å, c = 3.889 Å. The XRD pattern of the sample 24 h was similar to 12h, but the presence of sharp and strong peaks shows that the crystallinity of the product was significantly enhanced. However, further increase in reaction time up to 36 h led to another phase transition from hexagonal WO3 to cubic hemihydrate tungsten oxide. The normalized intensities of the most intense diffraction peaks for each sample and the corresponding standard JCPDS references were shown in Table 1 for comparison.

The crystallite size of the samples can be estimated from XRD data by using Scherrer’s method (equation (1)) and its modified form namely Williamson-Hall method (equation (2)) as follows:

\[ D = \frac{K\lambda}{\beta \cos \theta} \]  
\[ \beta \cos \theta = \frac{K\lambda}{D} + 4\varepsilon \sin \theta \]

where \( \beta \) is the full width at half maximum (FWHM) of diffraction peaks, \( K \) is the shape factor (~0.9), \( \lambda \) is the wavelength of X-ray radiation, \( \theta \) is the Bragg angle, \( D \) is the mean crystallite size, and \( \varepsilon \) is the lattice strain. The calculated values of crystallite size determined by using both Scherrer’s equation (\( D_{\text{Scherrer}} \)) and Williamson-Hall
method ($D_{\text{W}_{0.5}H_{0.5}}$) were listed in Table 2. It is seen that the crystallite size has been increased as hydrothermal time increased from 6 to 24 h; however, crystal growth has been suppressed with further increase in the reaction time. The lattice strains of the samples were also calculated from XRD data analysis and shown in Table 2. The sample 24 h exhibited the lowest lattice strain which shows this is the most relaxed nanostructure.

Figures 2(a)–(d) show the morphology of WO$_3$ samples prepared at different reaction times. The FESEM image of the sample 6h shows irregular and agglomerated plate-like nanostructures with different shapes and sizes. However, a different morphology, partly regular nanorods, was observed for the sample 12 h. The average length and diameter of the nanorods were 219 nm and 35 nm, respectively. Therefore their aspect ratio was 6.25. The sample 24 h also exhibited the same morphology, in which the more growth of nanorods was observed due to having enough growing time. These nanorods were in the range of 200–800 nm in length and 25 nm in diameter, and hence, the aspect ratio of ~12 was recorded which has been doubled compared to the sample 12 h. Surprisingly, further increase in reaction time to 36 h did not lead to longer nanorods, but a two-dimensional sheet-like structure was obtained. These observations can be correlated to the XRD results as well.

From the above results, it is concluded that the hydrothermal time importantly controls the morphology of WO$_3$ nanostructure and various one- or two-dimensional structures can be formed with changing
hydrothermal duration time. Short hydrothermal duration only gives non-regular nanoparticles, but extending the reaction time provides a desirable condition for the growth of one-dimensional nanorods. This can be due to the effect of citric acid and sodium sulfate as the structure-directing agents [4, 21, 24]. It might be expected that applying more reaction time leads to the longer nanorods, but the morphology evolution of the nanostructures occurred under excess reaction time. This change in morphology can be attributed to the inadequate remaining concentration of capping agents in the solution for growth of nanorods. Therefore, the growth can be continued in additional directions. Since the concentration of sodium sulfate in this work was much higher than citric acid, it can be regarded as a dominant capping agent controlling the growth. Therefore, the two-dimensional structure was formed under a longer hydrothermal time of 36 h. It should be noticed that we previously verified the formation of the 2D structure of WO₃ using only sodium sulfate as a capping agent [26]. It means that the hydrothermal time plays a significant role for the effective action of capping agents and the morphology of nanostructures.

Chemical bonding configuration of tungsten oxide nanostructures was investigated by FTIR spectroscopy. Figure 3 shows the FTIR spectra of the samples. These spectra include a broad absorption band in the wavenumber range of 420–1000 cm⁻¹ attributed to the vibration modes of W–O bond that verifies the formation of tungsten oxide. Presence of this characteristic band in all samples FTIR spectra indicates that they have reasonably similar chemical structure. The bonding assignments of the component peaks of this band were summarized in table 3. Other absorption peaks located at 1623 cm⁻¹ and 3000–3550 cm⁻¹ are due to H–O–H bending mode and O–H stretching mode which are usually induced by water molecules in the samples.

The optical properties of WO₃ nanostructures were studied by DRS measurement. Figure 4 shows the diffuse reflectance spectra and F(R) functions, so-called Kubelka-Munk relation, for the samples as defined by:

\[ F(R) = \frac{(1 - R)^2}{2R} \]

where R is diffuse reflectance. Since this function is directly proportional to the absorption coefficient (α), the optical behavior of the samples can be directly derived from it.

![Figure 2. FESEM images of tungsten oxide powder synthesized under various hydrothermal times of 6, 12, 24, and 36 h.](image)
Figure 3. FTIR spectra of tungsten oxide powders synthesized under various hydrothermal times of 6, 12, 24, and 36 h.

Table 3. FTIR absorption peaks and their corresponding chemical bonds and vibration modes of WO₃ samples synthesized under various hydrothermal times of 6, 12, 24, and 36 h.

| Chemical bond | Vibration mode | Wavenumber (cm⁻¹) | Reference |
|---------------|----------------|-------------------|-----------|
| W=O           | Stretching     | 975               | [30]      |
| W–O           | Stretching     | 827               | [31, 32]  |
| W–O–W         | Stretching     | 657               | [31, 32]  |
| W–O           | Bending        | 603,599           | [32]      |

Figure 4. Kubelka-Munk functions of synthesized WO₃ nanostructures. The diffuse reflectance spectra of the samples are shown in the inset.
The absorption edge has blue-shifted with increasing the reaction time from 6 to 24 h, and then it notably experienced a red-shift with further increase in the reaction time up to 36 h. Therefore, a turning point is observed for the sample 24 h which showed the shortest absorption edge wavelength.

The (indirect) bandgap of the samples was calculated from $F(R)$ function by using Tauc method:

$$\alpha E^{0.5} = B(E - E_g)$$

where $\alpha$ is absorption coefficient, $E$ is photon energy, $B$ is constant, and $E_g$ is the material bandgap that can be determined from the intercept of $(\alpha E)^{0.5}$ versus $E$. Figure 5 shows the Tauc’s plots of the samples synthesized at different reaction time. The calculated bandgaps have been listed in the inset of Figure 5. The results revealed that the bandgap of the samples were not very different. However, the nanostructures with similar morphology and crystalline structure had approximately the same bandgap. This means that the optical properties of the nanostructures can be controlled by their morphologies and crystalline structures. From our results, sheet-like nanostructures exhibited slightly wider bandgap than the rod-like nanostructures. However, the sizes of bandgaps were more than previously reported values for WO$_3$ nanostructures. Thus, our products are transparent in a wide range of the visible light region. So, they can be excellent candidates for optoelectronic devices.

4. Conclusion

WO$_3$ nanostructures were successfully synthesized by the hydrothermal method at different reaction times of 6–36 h to study the effect of hydrothermal reaction time on the morphology, growth mechanism, structural and optical properties of the samples. FTIR spectra of the samples synthesized at different hydrothermal reaction time verified the formation of tungsten oxide in all investigated conditions. According to the XRD patterns of the samples, two crystal phase transitions from the cubic to hexagonal phase and vice versa were observed by increasing the reaction time from 6 h to 36 h. Also, two morphological evolutions from agglomerated plate-like (2-D) WO$_3$ nanostructures to nanorods (1-D) and vice versa happened. They were in accordance with their XRD patterns. These morphology evolutions can be attributed to the insufficient reaction time for capping agents’ contribution in the case of first evolution and the inadequate remaining concentration of capping agents for the growth of nanorods in the case of the second one. The crystallite size/strain of the samples first increased/decreased with increasing the reaction time and then decreased/increased. The maximum value of crystallite size (73 nm) and the minimum strain (0.0016) was achieved for the sample prepared at reaction time of 24 h. The absorption edge of the samples exhibited a blue- and then red-shift with increasing the reaction time. However, the bandgap of the samples were almost independent of the reaction time. The samples synthesized at different hydrothermal reaction times were transparent in a wide range of the visible light region. So, they can be regarded...
as excellent candidates for applications in optoelectronic devices. Finally, the best WO3 nanorods with high aspect ratio and low micro-strain were synthesized at a hydrothermal reaction time of 24 h.

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