Impact of stirring time and the corresponding growth mechanism in the solvothermal synthesis of WO₃ nanostructures

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1. Introduction

The fabrication of semiconducting metal oxide (SMO) nanostructures by chemical reactions depends on several process parameters such as temperature [1,2], pressure [3,4], chemical properties [5,6], and the type and amount of catalyst [7,8]. In contrast, the growth of SMO nanostructures after nucleus formation is based on growth factors such as adsorbed species [9,10], incident species [11,12], growth rate [13,14], and supersaturation [15,16]. This enables the use of different growth factors even under the same process variable conditions; thus, the features related to the morphology [17], elemental composition [18], crystallinity [19], energy band structure [20], and surface-interaction interactions [21] of SMO nanostructures can be controlled. Moreover, it is possible for the crystallographic characteristics of SMO nanostructures to transition between the amorphous [22], polycrystalline [23], and monocristalline [24] states before, during, and after the process. As a result, the energy band state of the entire system must be changed because of the variation in the stable phases according to the process conditions. The number of variables to be considered increases exponentially; however, many parameters can be excluded because morphological characteristics provide information on growth.

Changes in morphology of SMO can be frequently observed in many nanomaterial synthesis methods with metals [25], oxides [26], and metallic salts [27] as precursors. Various nanostructures can be obtained by acidification [28], thermal oxidation [29], magnetron sputtering [30], sol-gel [31], and the soft-chemistry route [32], as well as the case of WO₃ which is a widely used functional material in gas sensors [33], photocatalysts [34], displays [35], information storage media [36], smart windows [37], and electrochromic processes [38]. A simple and efficient synthesis route for WO₃ nanostructures with desired morphological and crystallographic characteristics is always favorable for cost-effective production. Therefore, many researchers have employed the most accessible hydrothermal and solvothermal methods [39–47]. For example, Song et al. [41] reported the effect of alkali salts such as K₂SO₄, KNO₃, NaNO₃, and Na₂SO₄ on the morphology of WO₃ nanocrystals under hydrothermal conditions. Therese et al. [42] proposed a large-scale method to synthesize WO₃ nanorods, through which they can be reduced to multi-walled WS₂ nanorods. Zhou et al. [43]
also demonstrated the simple preparation of disk-shaped WO$_3$-0.33H$_2$O nanostructures by the hydrothermal treatment of an aqueous peroxopolytungstic acid solution. In the present study, a distinct method has been developed. We fabricated WO$_3$ nanostructures through a solvothermal synthesis method, which is one of the simplest routes for producing metal oxides and focused on the clarification of the reaction behavior in each step of the protocol that allows the identification of elusive process conditions related to the formation of WO$_3$ nanostructures. We noted that controlling the stirring time (1–120 min) was an essential factor in changing the growth mechanism of WO$_3$. Four cases were observed for the WO$_3$ nanostructures, which were classified according to the color of the solution and their corresponding variations in the morphology. With increasing stirring time, the morphology of WO$_3$ changed from nanoparticles (NPs) to three-dimensionally clustered jointed-nanosheets (NSs), suggesting a change in the growth mechanism from radial to unidirectional. The NO$_2$ gas sensing properties of WO$_3$ nanostructures were also measured to evaluate their surface reactivity. Although there have been reports on the NO$_2$ gas sensing of WO$_3$ nanostructures with the same microstructure, most of them, such as structures with nanorods [48] or microspheres [49], have a limited scope to change in terms of the morphology. Particularly, there are only a few reports on the relationship between the dimensional change of WO$_3$ from zero to three dimensions and the corresponding gas sensor performance. Hence, this approach of adjusting the process parameters of solvothermal synthesis to control crystal nucleation and growth provides a simple and efficient route for fabricating nanostructures of various metal oxides with targeted shapes and dimensions.

2. Experimental section

Tungsten hexachloride (WC$_6$, 99.9%, Sigma Aldrich) and ethanol (95%, Duksan Reagents) were used as the precursor and solvent, respectively. First, 3 g of WC$_6$ was added to 150 mL of ethanol and the solution was mixed using a magnetic stirrer at 200 rpm. The difference in stirring conditions has a significant impact on the solvothermal synthesis reaction, leading to variations in the crystal nucleation, growth direction, and growth rate. The color of the solution changed according to the stirring time: green (1 min), yellow (5 min), white (10 min), blue (10 min 10s), and blue-black (40, 60, and 120 min). The solutions were placed in an oven preheated to 80°C in a closed state and the temperature was increased to 200°C and maintained for 24 h. The old solvent was removed and filled with fresh ethanol when the solution was cooled after 24 h. The resulting suspension was sufficiently dispersed by sonication and subsequently centrifuged at 9000 rpm for 10 min for three repeated cycles. The precipitates were then redispersed by sonication with DI water, poured into a Petri dish, and dried in the oven at 80°C for 12 h. The dried powders were further calcined in a box furnace at 500°C for 2 h. Most WO$_3$ samples were yellowish in color, but with a change in the stirring condition, there was a slight difference in the brightness and chroma (Figure S1).

To characterize the WO$_3$ nanostructures, we carried out various analyses, including (1) scanning electron microscopy (SEM) for morphological characterization, (2) X-ray diffraction (XRD) for crystallographic characterization, and (3) X-ray photoelectron spectroscopy (XPS) for the determination of surface composition. In addition, gas sensing properties were measured using an in-house system to evaluate the adsorption and desorption between the gas and the WO$_3$ nanostructures. We used NO$_2$, H$_2$S, C$_2$H$_5$OH, C$_2$H$_2$O, H$_2$, and NH$_3$ as target gases, and the responses of the nanostructures were expressed as the ratio of their reactivities to air ($R_a$) and to the target gas ($R_g$). The response and recovery times were taken as reference points until 90% saturation occurred after target gas adsorption or desorption.

3. Results and discussions

3.1. Change in color of precursor solution with stirring time

The solutions (mixture of ethanol and the WCl$_6$ precursor) used for the solvothermal synthesis exhibited a clear difference in color with varying stirring times, as shown in Figure 1(a) and Video S1. A dark green color appeared approximately 1 min after the start of stirring. When the mixing time was increased to approximately 5 and 10 min, the color of the solution turned yellow and white, respectively. It is noted that the color of the solution suddenly turned blue within 10s. The solution finally turned blue-black after stirring for approximately 10 min 20s, and no further color change was observed, even after stirring for 120 min. This color change in solution was due to the conversion of the kinetic energy from stirring into thermal energy, thereby resulting in physicochemical changes in the bonding characteristics between the solvent and the solute. The duration of the retention of a particular color depended on the stability of different chemical bonds in the solution. In fact, the color of the solution can be easily changed even by a few minutes of stirring when the activation energy is low. In other words, the rapid color change indicates that the chemical conditions for maintaining the original chemical state were unstable. Based on a previous report [44], the morphology of WO$_3$ can be changed depending on the concentration of the precursor solution, reaction temperature, and reaction time. Zheng et al. [44]
reported that small WO₃ nuclei can spontaneously aggregate into larger spheres at high concentrations of H⁺, while at the same time, the high concentration of Cl⁻ can cause it to preferentially adhere to the side face as a capping agent. In addition, the color of the solution can be changed depending on the amounts of the precursor and solvent that participate in the reaction. Choi et al. [39] suggested that the color of the solvent could be changed to dark blue (0 vol% water), light blue (10 vol% water), and yellow (100 vol% water) depending on the ratio of ethanol and water, and that the color of tungsten oxide could be changed to brown (WO₃), blue (W), and yellow (WO₂) depending on the ratio of W and O. As a result, the color change in the system depending on the stirring time is inevitably closely related to the morphologies and crystalline phases of the final WO₃ samples. Changes in the morphology and crystallinity of the WO₃ nanostructures prepared from solutions of different colors are described in the following sections.

3.2. Change in morphology and crystallographic character of the WO₃ nanostructures with stirring time

Figure 1(b) shows the changes in the morphology and dimensions of the acquired WO₃ nanostructures as a function of the stirring time. WO₃ NPs (30–120 nm) were obtained from a solution prepared by short-time stirring for 1 (dark green) and 5 min (yellow). In contrast, formation of thin and elongated NSs of WO₃ [50–52] was initiated when the stirring time was increased to 10 min (white), suggesting that two-dimensional (2D) growth occurred. The NSs were several microns in length and 150–200 nm in thickness. The 2D growth observed in the WO₃ nanostructures was activated with increasing stirring time over 10 min, resulting in a mixture of NSs and NPs obtained from the solution with a stirring time of 10–40 min. Jointed-NSs with some attached NPs and randomly aggregated jointed-NSs were obtained from the solutions stirred for 60 min and 120 min, respectively. These results suggest that stirring time is a critical processing parameter for controlling the characteristics of WO₃ nanostructures. Hence, the sequential production of (1) NPs (stirring times of 1 and 5 min), (2) mixture of NSs and NPs (stirring time of 10–40 min), (3) jointed-NSs (stirring time of 60 min), and (4) three-dimensionally clustered joined-NSs (stirring time of 120 min) was due to the variation in the nucleation and growth processes during solvothermal synthesis.

The overall reaction to generate WO₃ nanostructures from the precursors is as follows [53]:

\[
\text{WO}_6 + 2\text{H}_2\text{O} \rightarrow \text{WO}_3 \times (\text{OC}_2\text{H}_5)_x + x\text{HCl} \quad (1)
\]

\[
\text{WO}_6 \times (\text{OC}_2\text{H}_5)_x + 3\text{O}_2 \rightarrow \text{WO}_3 + \text{H}_2\text{O} + \text{CO}_2 + \text{HCl} + \text{Cl}_2 \quad (2)
\]

However, the varying stirring times influenced the chemical state of the WCl₆ precursor in solution, which then resulted in the changes in morphology and dimensions of the WO₃ nanostructures. Consequently, it has been reported that oxygen plays a crucial role in these reactions [39,41]. Therefore, based on these reports, each step reaction of our samples, up to the overall reaction, can be approximately divided into four steps: Formation of (1) tungstic acid (H₃WO₄) at 5 min (yellow), (2) WO₃ by
dehydration at 10 min (white), (3) tungsten bronze (HₓWO₃ₓ, 0 ≤ x ≤ 1) at 10 min 10s (blue), (4) tungsten bronze (HₓWO₃ₓ, x ≤ y ≤ 1) at 40 min (dark blue). At shorter stirring times (1–5 min), the conversion of the kinetic energy from mixing to heat caused the separation of Cl from WCl₆ and the W central atom then combined with O, resulting in the formation of NPs. Increasing the stirring time triggers another growth mechanism (2D growth) as heterogeneous growth is a simpler mode of growth than homogeneous [34,55]. Here, since heterogeneous growth involves the use of the pre-generated WO₄ new precursors can help in reducing the resistance to the growth of WO₃ through continuous chemical adsorption on the surface of WO₃.

On the other hand, homogeneous growth is energy-intensive because each time, the energy barrier required for WO₃ nucleation must be overcome through a specific redox chemical method [55].

Figure 2(a) shows the XRD patterns of the WO₃ nanostructures fabricated from the solutions prepared with different stirring times. All the peaks were fully indexed against the reference peaks of monoclinic WO₃ (JCPDS No. 43–1035), suggesting that a single phase of WO₃ was formed in all the samples. It is noted that the ratio of the intensity of (002) to that of (020) or (200) (denoted as I_{002}/I_{020} or I_{002}/I_{200}) increased with stirring time until 60 min, since there was a preferential 2D growth along the (200) plane. The decrease in I_{002}/I_{200} in WO₃ with a stirring time of 120 min was due to the random directional agglomeration of jointed WO₃ NPs, as clearly shown in Figure 1(b). Hence, we can determine whether the solution reached nucleation [56,57] for WO₃ or remained in the embryo [58,59] depending on the stirring time, and found the stirring time is one of the key process variables to control the probability of nucleation in the same solution.

3.3. Gas sensing properties of WO₃ nanostructures

We studied the response of WO₃ nanostructures to 1 ppm NO₂ gas at different temperatures to demonstrate the effects of the crystallographic and morphological characteristics of WO₃ nanostructures on the surface chemistry. As shown in Figure 3(a), the response of the WO₃ nanostructures obtained from the solutions prepared with stirring times of 1, 40, 60, and 120 min to 1 ppm of NO₂ at 200°C were at 17.04, 68.33, 15.52, and 21.40, respectively. The highest surface reactivity was observed for the mixture of NSs and NPs (stirring time of 40 min). To clarify this, we examined the gas sensing behavior for oxidizing and reducing gases (Figure 3(b)). WO₃ nanostructures is a typical n-type semiconductor where the majority charge carriers are electrons. When NO₂ gas (2.28 eV), which has a higher electron affinity than O (0.43 eV), reacts with the O in WO₃, it extracts electrons from O [60,61] and the following reactions occur [62,63].

\[
\text{NO}_2 + e^- \rightarrow \text{NO}_2^- 
\]

(3)

\[
\text{NO}_2 + \text{O}^- \rightarrow \text{NO}_2^- + 1/2\text{O}_2
\]

(4)

Reactions (3) and (4) determine the thickness of the electron depletion layer (EDL) formed on the surface of WO₃ nanostructures, as illustrated in Figure 3(c) [64,65]. A relatively thin EDL was formed on the surface of the material in the vacuum state; however, both the thickness of the EDL and the corresponding conduction band interface increased when the oxygen ion species adsorbed on the surface of the WO₃ nanostructures. Therefore, the movement of electrons in the conduction band became more difficult and the resistance consequently increased. When NO₂ gas (an oxidizing gas) was introduced and adsorbed on the surface of the WO₃ nanostructures, it extracted electrons from O and the EDL of WO₃ became thicker. That is, since the mobile

![Figure 2](image-url)  
**Figure 2.** (a) XRD patterns of WO₃ nanostructures obtained from solutions of different colors (1–120 min stirring time). (b) Intensity ratio of (002) to (200) of the WO₃ nanostructures as a function of stirring time.
Figure 3. (a) Comparison of responses to 1 ppm NO₂ gas at 200°C for various types of WO₃ nanostructures obtained from solutions of different colors (1–120 min stirring time). (b) Selectivity under different gases with a concentration of 20 ppm at 200°C. (c) EDL thickness under vacuum, air, and target gas (NO₂) and the corresponding changes in the conduction energy band.

Figure 4. Responses of the WO₃ sample (stirring time: 40 min) to 1 ppm NO₂ gas based on the operating temperature of the sensor: (a) 8.41 at 30°C, (b) 26.04 at 100°C, (c) 68.33 at 200°C, (d) 11.87 at 250°C.
electron carriers moved from the internal WO₃ to the external oxygen or NO₂, the EDL by immobile charges becomes thicker on the surface of the existing WO₃. Therefore, the surface area is an important factor in determining the NO₂ sensing properties, and NPs are more suitable for gas sensing [66,67]. Additionally, the process temperature may be an important factor in semiconductor-based gas sensing, as the number of activated carriers involved in the chemical reaction during gas sensing may change sensitively with the process temperature. As shown in Figure 4, the process temperature of 200°C provides the best response owing to the highly activated carrier transport phenomenon. The oxygen vacancies formed on the surface of WO₃ are another important factor in gas sensing applications because these can activate the adsorption of the target gas [68,69]. Figure 5 shows the types of oxygen defects and their fractions generated at different stirring times. For example, first, oxygen defects associated with the oxygen lattice correspond to 83.32%, 68.19%, 77.37%, and

| Type of oxygen                  | Stirring time | 1 min    | 40 min   | 60 min   | 120 min  |
|--------------------------------|--------------|----------|----------|----------|----------|
| O_L, 530.6eV (lattice oxygen)  | 1 min        | 83.32%   | 68.19%   | 77.37%   | 64.49%   |
| O_V, 532eV (vacancy oxygen)   | 40 min       | 15.98%   | 30.54%   | 20.09%   | 13.22%   |
| O_C, 533.1eV (Chemisorbed oxygen species) | 60 min | 0.70%    | 1.27%    | 2.54%    | 22.29%   |

Figure 5. XPS spectra showing O1f on the surface for WO₃ nanostructures obtained from solutions of different colors (1–120 min stirring time) and types of oxygen defects in each condition.
64.49% for stirring times of 1 min, 40 min, 60 min, and 120 min, respectively. Second, oxygen vacancies typically develop in the WO$_3$ nanostructures prepared under 40 min of stirring. Despite the smaller surface area ($-2.89$ m$^2$/g) of the mixture of NSs and NPs than that ($-16.27$ m$^2$/g) of NPs alone (Figure 52), the highest response is obtained for the former (Figure 3(a)). In other words, in gas sensing, the disadvantage of the surface area can be overcome because the role of defects such as oxygen vacancies on the surface is more dominant. For example, Shouli Bai et al. [70] and Yihan Liu et al. [71] reported that the more oxygen vacancy occurs, the more W$^{5+}$ and W$^{6+}$ in the non-equilibrium state lacking oxygen are generated on the surface of WO$_3$ from W$^6^+$ of WO$_3$ in equilibrium. Therefore, oxygen vacancies prevent the movement of electrons, which are main carriers, from the WO$_3$ point of view in NO$_2$ gas sensing, and ultimately plays a role in increasing the response to resistance. Finally, the oxygen defects related to chemical adsorption are greatest at a stirring time of 120 min. Selectivity was also confirmed using different target gases (NO$_2$, H$_2$S, C$_2$H$_5$OH, C$_2$H$_6$O, H$_2$, and NH$_3$, each with a concentration of 20 ppm) at 200°C for WO$_3$ nanostructures prepared by 40 min of stirring (mixture of NSs and NPs). The responses for NO$_2$, H$_2$S, C$_2$H$_5$OH, C$_2$H$_6$O, H$_2$, and NH$_3$ were 801.93, 2.54, 2.23, 2.17, 2.19, and 2.88 (Figure 3(b)), respectively. These findings indicate that the WO$_3$ nanostructures were able to discriminate NO$_2$ from other interfering gases. Furthermore, the response and recovery times are much shorter for NO$_2$ than the other gases (Table S1). We simultaneously evaluated the stability and repeatability of the WO$_3$ gas sensor by exposing it to 1 ppm NO$_2$ gas after storage periods of 2 weeks and 5 weeks, respectively. Figure S3 compares the responses of the as-synthesized and stored WO$_3$ sensors. As-synthesized WO$_3$ shows a response of 68.33 (Figure 4), whereas WO$_3$ after 2 and 5 weeks of storage shows responses of 47.65 and 43.01, respectively. Over time, the response decreases compared to that of the initial sample; nevertheless, it is still acceptable for the sensing device to show a response of 40 or more at a low concentration (1 ppm NO$_2$). Table S2 shows the average responses of stored WO$_3$ obtained from 9 repeatability tests. Each response is stable without significant deviation from the average response. The main cause of the decrease in the response of the WO$_3$ sample over time is moisture in the atmosphere. Therefore, the effect of the relative humidity (RH) on gas sensing was investigated and compared (Figure S4). The responses of WO$_3$ samples exposed to 0%, 30%, and 60% RH to NO$_2$ gas are 68.33, 57.51, and 70.91, respectively. When the RH is low, the response slightly decreases, whereas when the RH is high, the response slightly increases. It can be considered that the WO$_3$ sample is not significantly affected by the humidity.

4. Conclusions
In this study, we found that the nucleation and growth of WO$_3$ nanostructures can be controlled during solvothermal synthesis by varying the stirring time of the precursor solution. Various WO$_3$ nanostructures with different morphologies and dimensions, including 0D nanoparticles, 0D-2D mixture of NSs and NPs, 2D jointed-NSs, and 3D randomly clustered jointed-NSs, were fabricated. This simple approach was also effective in controlling the concentration of surface oxygen vacancies in WO$_3$ nanostructures and triggering the (002) plane-oriented growth in WO$_3$ nanosheets. The surface reactivity according to the characteristics of the obtained WO$_3$ nanostructures was confirmed by measuring their NO$_2$ gas sensing properties. Our results show that a fine control of the stirring conditions is a simple yet promising way of fabricating shape-, dimension-, and crystal orientation-controlled nanostructures of metal oxides through solvothermal synthesis.

Disclosure statement
No potential conflict of interest was reported by the author(s).

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Availability of data and materials
All the data are available from the corresponding author on reasonable request.

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Ethics declarations

Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article.

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