Effect of SiO₂ Doping on Growth Retardation of WO₃ Nanoplate*

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Abstract

Tungsten oxide (WO₃) is recently recognized as one of the most widely studied gas sensitive ceramics. To maintain good thermal stability at moderate operating temperature, the gas sensitive materials were typically heated at several hundreds degree Celsius. Such treatment caused grain growth, resulting to reduction of specific surface area which is considered to be one of the important properties determining gas sensor's performance. In this present work, grain growth of the WO₃ nanoplate was retarded by incorporation of silica (SiO₂) particle. To obtain homogeneous structure, the SiO₂ was incorporated by mixing tetraethyl orthosilicate into the W precursor during precipitation of the tungsten oxide. It was found that the SiO₂ dramatically retarded the particle growth, preserved the nanoplate structure, and resulted to more porous WO₃ powder. The effect was very significant when the powders were calcined at high temperatures.

Key words: Tungsten Oxide, Nanoplate, Silica, Growth Retardation

1. Introduction

Tungsten oxide (WO₃) is one of the most widely studied wide-band gap metal oxide semiconductors. It has been used in many applications such as electrochromic coating, photocatalyst and gas sensor.¹⁻⁴⁾ For the applications that rely on surface area such as photocatalyst and gas sensor, very fine powders with low particle agglomeration are favorable since they possess high specific surface area for gas adsorption and/or desorption. Due to simplicity of equipment employed, the WO₃ powders are typically prepared by wet chemical processes such as sol-gel⁵⁾ and precipitation.^{4,6)} Thermal decomposition and pyrolysis of tungsten salt are also common for preparation of the powder for gas sensor application.⁷⁻⁸⁾ For these methods, the powders are always subjected to heat treatment either during the synthesis step as in the case of thermal decomposition or pyrolysis, or post-synthesis step as in the case of wet chemical processes. Such heat treatment is important as it transforms the material into a desirable composition or crystalline structure. Heat-treated powder also has good thermal stability which is crucial for gas sensor which is typically operated at 200 – 350 °C.

However, there is a tradeoff for such heat treatment since the particle will grow leading to reduction of the specific surface area. This particle growth, known as “Ostwald ripening”, is very pronounced at higher temperature since the growth rate has exponential relationship with heating temperature.⁹⁾ Since the particle growth is unavoidable, it is therefore important to reduce its rate. Particle growth retardation is commonly achieved by addition small amount of the second phase material. For instance, by adding small amount of La₂O₃, the crystallite growth of SnO₂ sensing material was retarded and the resulting sensor showed improving sensitivity.¹⁰⁾ However, such improved sensitivity was not obtained when

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the amount of La_2O_3 exceeded 2 wt.%.

In this work, silica (SiO_2) particle was incorporated into the WO_3 nanoplate to retard the particle growth. The silica precursor, tetraethyl orthosilicate (TEOS), was mixed with the tungsten salt solution to ensure homogeneous mixing.

2. Experimental Procedure

2.1 Materials

Ammonium tungstate para pentahydrate $((\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 5\text{H}_2\text{O})$, Wako) and tetraethyl orthosilicate (TEOS, $\text{C}_8\text{H}_{20}\text{O}_4\text{Si}$, Sigma-Aldrich) were starting reagents used for the synthesis of WO_3 and SiO_2 , respectively. Nitric acid (HNO_3 , Scharlau) was used to adjust the solution's pH. All chemicals were analytical reagent grade (AR grade) and were used with no further purification. Precursor solution was heated and the precipitation temperature was kept constant by using a heater equipped with a temperature controller (IKA) with ± 1 °C deviation from the setting value.

2.2 Preparation of undoped and silica-doped WO_3 nanoplate

Pre-determined amount of ammonium tungstate para pentahydrate was dissolved in 6 M nitric acid solution at room temperature under vigorous stirring. The ammonium tungstate solution was heated to 80 °C and subsequently aged at this temperature for about 30 min under continuous stirring. Then, TEOS solution prepared by dissolving 1 g of TEOS in 5 mL ethanol was added slowly into the heated tungsten solution. The resulting solution was vigorously stirred for another 30 min, after which the precipitate was allowed to settle at room temperature overnight.

The precipitate was washed three times with de-ionized water. Each washing cycle was performed as follow. After a supernatant was decanted, large amount of de-ionized water was added and the resulting suspension was stirred for 1 h. The suspension was then left at room temperature overnight to allow complete settle of the precipitate. The next washing cycle was performed in similar manner. The precipitate was separated by ultrafiltration using a polymer membrane (pore sizes = 0.47 μ). After drying at 100 °C for at least 2 h, the precipitate was calcined in ambient air at temperatures ranging from 400 – 800 °C for 6 h. Finally, the dried and calcined precipitates both with and without TEOS addition were ground into very fine powders for further characterization.

2.3 Material characterization

Crystal structure was identified by using an x-ray diffractometer (XRD; JDX-3503). Particle morphology was directly observed by using a field-emission scanning electron microscope (FE-SEM; JSM-6301F) and a transmission electron microscope (TEM; JEM-2010). The crystallite size (D, in Å unit) was calculated from peak broadening using the Scherrer approximation, which is defined as

$$D = 0.9\lambda / B \cos\theta, \quad (1)$$

where λ is the wavelength of the x-ray (1.5418 Å), B is the full width at half maximum (FWHM, radian) and θ is the Bragg angle (degree). The average value of FWHM was obtained by performing profile fitting of (200), (202), and (002) peaks using an XRD pattern processing software (Jade 6.5). The instrumental line broadening was corrected by using an NIST 640A silicon standard.

The amount of SiO_2 present in the WO_3 powder was analyzed by using an x-ray fluorescence (XRF; PW-2404). A Fourier-transform infrared spectroscope (FT-IR; Perkin Elmer System 2000) was also employed to investigate the presence of functional groups and chemical bonding of the compound. For FT-IR analysis, the powders were mixed with KBr powder and then pressed into a disc. The specific surface area was measured by means of

nitrogen gas adsorption using a Quantachrome Autosorb-1 and then calculated by using a Brunauer, Emmett and Tellet (BET) method.

3. Results and Discussion

Figure 1 shows IR spectra of dried precipitates obtained from the tungsten precursor with and without the addition of TEOS. Broad absorption band centered at around 710 cm^{-1} is assigned to a W-O stretching,¹¹⁾ while broad absorption bands between $3,200$ to $3,600\text{ cm}^{-1}$ are assigned to an O-H vibration of physically adsorbed water. Sharp absorption band at around $1,400\text{ cm}^{-1}$ is attributed to a stretching vibration of N-H bond in ammonia.¹²⁾ Existence of this bonding indicates the presence of ammonium ion residue, and the as-precipitates required more thorough washing. Sharp peak at $1,620\text{ cm}^{-1}$ is assigned to an O-H bond of chemically bonded water (water of crystallization) of the $\text{WO}_3 \cdot \text{H}_2\text{O}$. The absorption bands at $1,400$ and $1,620\text{ cm}^{-1}$ disappeared upon heating due to removal of ammonia and water, respectively.

For the precipitate obtained from the precursor containing TEOS, absorption bands at 440 and $1,075\text{ cm}^{-1}$ assigned to a Si-O-Si stretching were clearly observed.¹³⁾ Note that sharp absorption band at around $3,000\text{ cm}^{-1}$ corresponding to a C-H stretching of ethyl group was not observed. It was believed that silicon alkoxide ($\text{Si}(\text{OC}_2\text{H}_5)_3$) groups were hydrolyzed to silicon hydroxide ($\text{Si}(\text{OH})_4$) and underwent subsequent condensation with each other or with unhydrolyzed alkoxide groups to give products containing Si-O-Si.¹⁴⁾ By products were ethyl alcohol and water which were eliminated during washing step.

Fig. 1 FT-IR spectra of dried precipitates obtained from the tungsten salt precursor with and without addition of TEOS.

Figure 2 shows XRD patterns of pure and silica-doped WO_3 powders calcined at various temperatures. These powders have monoclinic structure having (200), (020) and (002) as major reflections. According to the previous study on pure WO_3 nanoparticles¹⁵⁾, the three reflections have similar relative intensity for calcined particles. In this current work, the relative intensities observed on some specimens were significantly different. For instance, for the WO_3 calcined at 400°C the intensity of the (200) reflection was much lower than those of the (020) and (002) reflections, suggesting that this precipitate has preferred orientation. Heat treatment at higher temperatures promoted the growth in (200) plane. By incorporating the silica into the WO_3 , it was observed from XRD patterns that relative intensity of the (200) reflection was significantly reduced, particularly for the

specimen calcined at 400°C. Its intensity increased upon increasing calcination temperature, indicating the morphology change from the plates to more equiaxed particles but in lower extent compared to the undoped powder. However, morphology change was in lower degree compared to the undoped WO_3 , indicating that the silica suppressed the growth of the (200) plane.

Fig. 2 XRD patterns of (a) undoped WO_3 and (b) SiO_2 -doped WO_3 nanoplates.

Figure 3 shows SEM images of the undoped and SiO_2 -doped WO_3 calcined at 400 °C to 800 °C. In general, both sample series underwent particle growth upon calcinations. In both cases, dimension of the plate was in the range of about 100 – 200 nm wide and about 20 – 50 nm thick, depending on calcination temperature. However, it is evident from the images that by adding SiO_2 doping the growth of WO_3 nanoplates was significantly retarded. Moreover, plate structure of the WO_3 was preserved as the increase of plate thickness was not significant. This retardation effect was more significant when the powders were calcined at high temperatures. In contrast, the growth of the undoped plate resulted to more spherical particles. SEM results are in good agreement with XRD results that the doped WO_3 has plate-like structure. The SiO_2 content in the calcined powders as determined by XRF was 5.8 wt.%.

Fig. 3 SEM images of the undoped and SiO_2 -doped WO_3 calcined in air at 400 – 800 °C.

Figure 4 shows TEM images of the undoped and SiO_2 -doped WO_3 calcined at 500 °C. In these two images, individual plates both top and side views are clearly seen. Since the two images were recorded at the same magnification, plate size of the two samples can be visually compared. Nevertheless, an average dimension of the individual plate (width and thickness) was measured from many TEM images in which the individual plates were clearly seen. The average dimension of the undoped WO_3 was about 120 ± 10 nm wide and 30 ± 5 nm thick, while that of the SiO_2 -doped WO_3 was 60 ± 8 nm wide and 10 ± 3 nm thick. Aspect ratios (width/thickness) of the undoped and SiO_2 -doped plates were 4 and 6, respectively, indicating that the undoped plates were getting more rounded upon calcination. This result was in good agreement with the SEM result shown in Fig. 3.

Table 1 shows specific surface area of undoped and SiO_2 -doped powders calcined at various temperatures. The specific surface area of SiO_2 -doped powder was much higher than that of undoped powder. For instance, it was 22.7 ± 0.06 and 1.3 ± 0.01 $\text{m}^2\cdot\text{g}^{-1}$ for undoped powders calcined at 400 °C and 800 °C, respectively, and was 45.3 ± 0.03 and 15.1

$\pm 0.06 \text{ m}^2\cdot\text{g}^{-1}$ for SiO_2 -doped powders calcined at 400°C and 800°C , respectively. Upon the increase of calcination temperature, the difference of the specific surface area was more significant. That is, the specific surface area of the SiO_2 -doped WO_3 powder was about 2 times higher than that of the undoped powder when they were calcined at 400°C . The figure increased to about 4 and 12 times when the powders were calcined at 600°C and 800°C , respectively.

(a) Undoped WO_3 calcined at 500°C

(a) SiO_2 -doped WO_3 calcined at 500°C

Fig. 4 TEM images of the undoped and SiO_2 -doped WO_3 calcined at 500°C .
A scale bar represents the length of 40 nm.

Table 1 Specific surface area of the undoped and SiO₂-doped powders calcined at various temperatures.

Calcination temperature (°C)	Specific surface area (m ² ·g ⁻¹)	
	Pure WO ₃	SiO ₂ -doped WO ₃
400	22.73 ± 0.06	45.32 ± 0.03
600	8.51 ± 0.03	33.54 ± 0.03
800	1.27 ± 0.01	15.09 ± 0.06

Figure 5 shows the crystallite size of the WO₃ and SiO₂-doped WO₃ derived from the (200), (020) and (002) XRD peaks using a Scherrer formular (Eq. (1)) which relates the crystallite size and peak broadening. It is obvious that the crystallite growth was significantly retarded when the silica was incorporated. Retardation became more pronounced at higher calcination temperature which is in good agreement with direct observation with SEM (Fig. 3). Note that the crystallite size was smaller than the particle size observed in SEM and TEM images (Figs. 3 and 4) indicating that the particles were polycrystalline. By comparing the crystallite size derived from XRD peaks and the plate size measured from SEM images, it was found that for the undoped powder calcined at low temperature (e.g. 400 °C) the plate consisted of ~4 – 5 crystals. These crystallites grew and underwent Ostwald ripening which finally resulted to only one crystallite in an individual plate after they were calcined at 800 °C. Such phenomenon was not significant in SiO₂-doped powders. In all heat treatment temperatures, the SiO₂-doped plates consisted of ~ 4 - 5 crystallites.

Fig. 5 Calculated crystallite size of the undoped and SiO₂-doped WO₃ powders calcined in air at 400 – 800 °C

4. Conclusion

Growth of nanocrystalline WO₃ plate during heat treatment at temperature range of 400 – 800 °C were retarded by the incorporation of SiO₂ into the WO₃ matrix. In addition to reducing growth rate, such SiO₂ doping also preserved plate-like structure of the WO₃ powder since the increase of plate thickness was significantly suppressed compared to that of the undoped powder. The resulting powders were more porous which may be beneficial for some applications such as gas sensor.

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