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RAPID COMMUNICATION

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Facile synthesis of nanocrystalline hexagonal tungsten trioxide from metallic tungsten powder and hydrogen peroxide

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Abstract

A hexagonal form of tungsten trioxide (h-WO_3, particle size: 15.9-57.1 nm) was found to be formed by a direct reaction between metallic tungsten powder (W, particle size: 0.45-0.59 μm) and 15%-30% hydrogen peroxide (H_2O_2) aq solution. Oxide film on the powder surface having the similar crystal structure as h-WO_3 was essential for the formation, and the surface oxide film was formed by aging the powder in air at 45°C, a relative humidity of 100% (P_{H2O} 96 hPa) for 3-28 days or in ambient atmosphere at room temperature for 12 years. The Rietveld analysis performed in the space group $P6_3/mcm$ ($Z = 6$) indicated the crystal structures were the same as those of the reported h-WO_3 and that the crystallographic characteristic was as follows: $a = 0.74219$ nm, $c = 0.77198$ nm for h-WO_3 from the 28-day aged powder, and $a = 0.74538$ nm, $c = 0.77194$ nm for h-WO_3 from the 12-year aged powder.

KEYWORDS
nanoparticles, oxides, synthesis, tungsten/tungsten compounds, X-ray methods

1 | INTRODUCTION

Tungsten trioxide, WO_3, has received much attention for a wide variety of applications such as photocatalyst in water splitting,[1-8] dye-sensitized solar cells,[9] electrode materials for lithium-ion batteries,[10] photochromic films,[11] and electrochromic displays.[12,13] Many methods have been reported for the preparation of WO_3 nanoparticles as well as their properties and applications.[14] Tungsten trioxide crystallizes in several polymorphic forms, which can be categorized into two general crystal structures. One is based on the ReO_3-type structure, i.e., WO_6 octahedra link together by corner sharing and form a three-dimensional framework. In this case, distortions of the octahedra bring about lower symmetries than ReO_3, and these polymorphs have been reported to be monoclinic phase (II) from 5 to 278 K, triclinic phase from 248 to 290-300 K, monoclinic phase (I) (γ-phase) from 290-300 K to 600 K, orthorhombic phase from 600 to 1010 K, and tetragonal phase from 1010 K to the melting point, 1746 K.[15] The other general crystal structure is a form with hexagonal symmetry first reported by Gerand et al,[16] i.e., WO_6 octahedra share their corners to form a framework with hexagonal channels along *c*-axis. This hexagonal WO_3 (h-WO_3) is a metastable phase, which has not been described in phase diagrams, and its synthetic routes are limited to low-temperature processes because high temperature causes transformation to the stable monoclinic phase (I).[17] The h-WO_3 was first prepared by dehydration of $WO_3 \cdot 1/3H_2O$, and this hydrate was obtained by hydrothermal treatment of an aqueous suspension of either tungstic acid gel or $WO_3 \cdot 2H_2O$ at 120°C.[16] The h-WO_3 has been also prepared by other methods such as hydrogen peroxide oxidation of hexagonal ammonium tungsten bronze,[18] and thermal decomposition of ammonium peroxo-polytungstate.[17] These preparation processes of h-WO_3 require precise control of experimental conditions and are not suitable for inexpensive large-scale production. As the h-WO_3 as well as the monoclinic phase (I) has attracted a lot of attention as an alternative material for photocatalyst,[3] a facile and inexpensive preparation method of h-WO_3 is highly desirable. Our research group has been investigating a soft-chemical synthesis of metal oxides starting from a

peroxo-metallic acid solution obtained by the direct reaction between metal powder and hydrogen peroxide.[19-26] Using such new methods we have successfully prepared K_xWO_3,[27] $BaTiO_3$,[28] $KNbO_3$,[29] $LiVO_2$,[30] Ramsdellite Li_xTiO_2,[31] etc. In this study, we found that a direct reaction between tungsten (W) powder and 15%-30% hydrogen peroxide (H_2O_2) aq gave a precipitate of h-WO_3 instead of a peroxo-polytungstic acid solution when metallic tungsten powder with smaller particle size, 0.45-0.59 μm, was used.

2 | EXPERIMENTAL PROCEDURE

2.1 | Raw materials

Two types of metallic tungsten powders with different particle sizes were used: 0.45-0.59 μm (99.9% purity, W-H, Japan New Metals Co., Ltd., Osaka, Japan), and 1.28 μm on average (99.9% purity, No. 64401, Mitsuwa Chemicals Co., Ltd., Osaka, Japan). As for the tungsten powder with particle size of 0.45-0.59 μm, we also used an old sample stored in a sample bottle in ambient atmosphere at room temperature for 12 years along with the new samples. Hydrogen peroxide solution (30.0 wt%, Kanto Chemical Co., Inc., Tokyo, Japan) was used as purchased without further purification.

2.2 | Pretreatment

Tungsten powders were pretreated before the reaction to enhance the formation of surface oxide film having the similar crystal structure as h-WO_3. We carried out either of the following pretreatments: heating in air at 45°C; water vapor pressure (P_{H2O}) 96 hPa (relative humidity, RH 100%) for 1, 3, 7, 14, 21, or 28 day(s); heating in air at 275°C, P_{H2O} 23 hPa for 12 hours; or keeping in water at 20°C for 7 days, 100°C for 12 hours, or 100°C at 1 MPa for 12 hours. The old tungsten powder stored for 12 years was used without any pretreatment.

2.3 | Synthesis

A vigorous reaction occurred by adding 11.0 g of tungsten powder into 50 mL of 15% H_2O_2 aq, and a precipitate was formed. After the vigorous reaction ceased, 20 mL of 30% H_2O_2 aq was added more to complete the reaction. The precipitate was filtrated using a membrane filter with pore size of 0.1 μm, rinsed with water, and dried at 45°C for 2 hours.

2.4 | Characterization

The X-ray diffraction (XRD) patterns of the products were measured with a diffractometer (XD-D1, Shimadzu, Kyoto, Japan) using graphite-monochromatized CuK_α radiation (λ = 0.15406 nm). The X-ray profiles were collected between 2° and 120° of 2θ angles with a step interval of 0.02° and a count time of 4 s/step. The crystalline parameters were refined by the Rietveld method using the RIETAN-FP program,[32,33] and the crystallite sizes were estimated by the Scherrer equation. The morphology was observed by a field emission scanning electron microscope (FE-SEM, JSM-7100F, JEOL, Tokyo, Japan) with an accelerating voltage of 10 kV. The specific surface area of h-WO_3 was measured by the Brunauer-Emmett-Teller (BET) method using the adsorption of nitrogen gas at the temperature of liquid nitrogen (Micrometrics Tristar 3020, Shimadzu, Kyoto, Japan). Prior to the measurements, the samples were degassed at 200°C for 2 hours under vacuum. The thermal behavior was investigated by thermogravimetry (TG) and differential thermal analysis (DTA; DTG-50, Shimadzu, Kyoto, Japan) at a heating rate of 20°C/min in air.

3 | RESULTS AND DISCUSSION

A pale blue precipitate was found to be formed after a vigorous reaction between the old tungsten powder (particle size: 0.45-0.59 μm) stored for 12 years and hydrogen peroxide, while the reaction between the tungsten powder (particle size: 1.28 μm) and hydrogen peroxide yielded yellow transparent peroxo-polytungstic acid solution as reported in literature.[21,22] As shown in Figure 1, the XRD pattern of the precipitate was in good agreement with that of h-WO_3 (PDF-000331387), and interestingly the old tungsten powder for the raw material showed weak broad peaks at the same angles with h-WO_3 as well as strong sharp peaks of metallic tungsten. Oxide film having the similar crystal structure as h-WO_3 was formed on the powder surface during the storage for 12 years, and this suggests that the oxide film grown on tungsten surface in ambient atmosphere at room temperature is the phase of h-WO_3. On the other hand, the pristine tungsten powder (particle size: 0.45-0.59 μm) showed no broad peaks at the angles of h-WO_3 in the XRD pattern, and the precipitate of the same reaction became the mixture of tetragonal $WO_{2.90}$ (PDF-000181417) and other oxides. These results suggest that the oxide film on the powder surface is an essential seed crystal for the formation of h-WO_3.

In order to prepare the surface oxide film artificially in a short time and to reproduce the formation of h-WO_3, we aged the pristine tungsten powders (particle size: 0.45-0.59 μm) in various conditions such as steaming and boiling at ordinary and high pressures. As shown in Table 1 and Figure 2, we successfully obtained h-WO_3 as a single-phase precipitate in the reaction with hydrogen

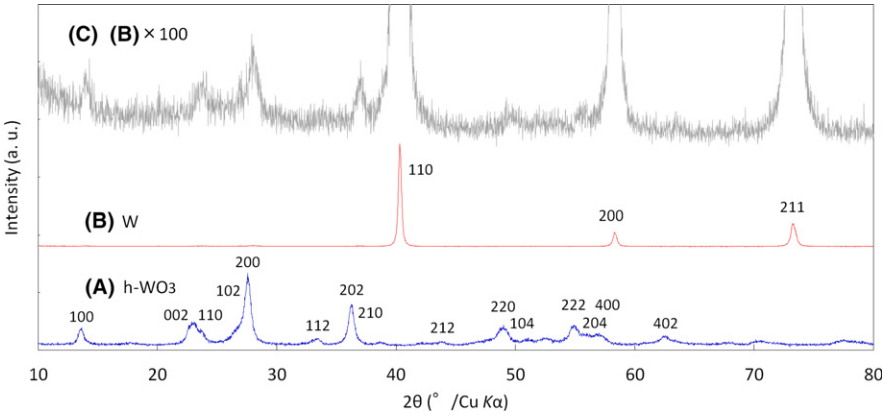

FIGURE 1 XRD patterns of (A) h-WO_3 obtained as a precipitate by the reaction between tungsten powder (particle size: 0.45-0.59 μm) stored in ambient atmosphere at room temperature for 12 years and hydrogen peroxide, (B) tungsten powder stored in ambient atmosphere at room temperature for 12 years, and (C) magnified view (×100) of (B) [Color figure can be viewed at wileyonlinelibrary.com]

peroxide by using the tungsten powder after aging at 45°C, RH 100% (P_{H2O} 9.58 kPa) for 3 days or more. Small amount of h-WO_3 (PDF-000331387) was observed along with $WO_3 \cdot H_2O$ (PDF-000430679) and metallic tungsten (PDF-000040806) in the XRD patterns of the samples after aging at 45°C, RH 100% for 3 days or more, while the sample after aging in the same condition for 1 day showed no peaks other than those of metallic tungsten. This indicates that surface oxide film consisting of $WO_3 \cdot H_2O$ and h-WO_3 was formed on the powder surface at 45°C in humid air and that this acted as a seed crystal for the formation of h-WO_3. After the reaction with hydrogen peroxide, $WO_3 \cdot H_2O$ and metallic tungsten completely transformed into h-WO_3, and they were not observed in the XRD patterns of the product. When tungsten powder was aged in water at 100°C, small amount of highly crystalline $WO_3 \cdot H_2O$ was observed together with small amount of h-WO_3 in the XRD pattern, and the highly crystalline $WO_3 \cdot H_2O$ on the powder surface presumably caused the predominant formation of $WO_3 \cdot H_2O$ compared with h-WO_3. On the other hand, when the tungsten powder was aged at 275°C in humidified air for 12 hours, small amount of triclinic WO_3 (PDF-000321395) was observed on the powder surface and the triclinic WO_3 was formed after reaction with hydrogen peroxide. Furthermore, when we used tungsten powder with larger particle size, 1.28 μm, only small amount of highly crystalline $WO_3 \cdot H_2O$ was observed together with those of W after aging at 45°C, RH 100% for 3 or 7 days, and $WO_3 \cdot H_2O$ was obtained alone as a precipitate by the reaction with hydrogen peroxide. The precipitation of h-WO_3 occurred only when ultrafine tungsten powder with particle size of 0.45-0.59 μm was used. The surface oxide film consisting of h-WO_3 was formed only on the surface of ultrafine tungsten powder, and the film was an essential seed crystal for the formation of h-WO_3. It can be considered that the crystal growth of

TABLE 1 Aging conditions of tungsten powders (particle size: 0.45-0.59 μm) and the products after aging and reaction with hydrogen peroxide

t (°C)	Atmosphere/solvent	P_{H2O} (hPa)	Duration	Product after aging	Main product after reaction
45	Air	96	1 d	$WO_3 \cdot H_2O$	$WO_3 \cdot H_2O_2 \cdot H_2O$
			3 d	$WO_3 \cdot H_2O$ + h-WO_3	h-WO_3
			7 d	$WO_3 \cdot H_2O$ + h-WO_3	h-WO_3
			14 d	$WO_3 \cdot H_2O$ + h-WO_3	h-WO_3
			21 d	$WO_3 \cdot H_2O$ + h-WO_3	h-WO_3
			28 d	$WO_3 \cdot H_2O$ + h-WO_3	h-WO_3
275	Air	23	12 h	Triclinic WO_3	Triclinic WO_3
20	Water	—	7 d	$WO_3 \cdot H_2O$	$WO_3 \cdot H_2O$
100	Water	—	12 h	$WO_3 \cdot H_2O$ + h-WO_3	$WO_3 \cdot H_2O$ + h-WO_3
100	Water, 1 MPa	—	12 h	$WO_3 \cdot H_2O$	$WO_3 \cdot H_2O$

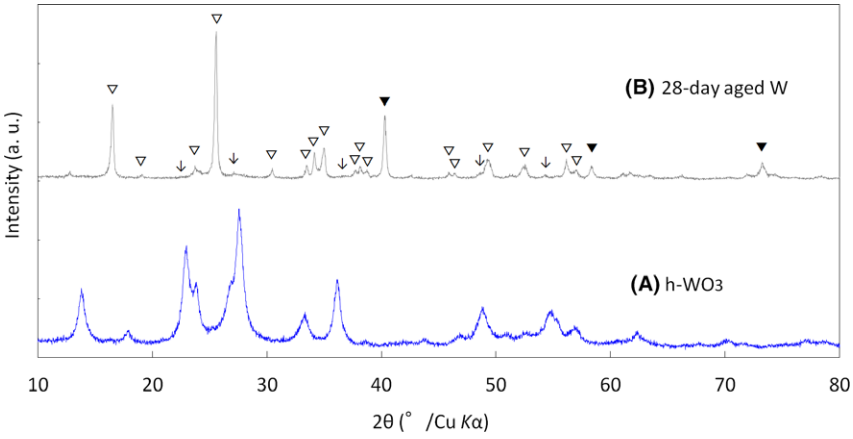

FIGURE 2 XRD patterns of (A) h-WO_3 obtained as a precipitate by the reaction between tungsten powder (particle size: 0.45-0.59 μm) aged in air at 45°C and a relative humidity of 100% (P_{H2O} 9.58 kPa) for 28 days and hydrogen peroxide, and (B) tungsten powder (particle size: 0.45-0.59 μm) aged in air at 45°C and a relative humidity of 100% (P_{H2O} 9.58 kPa) for 28 days. ▼: W, ▽: $WO_3 \cdot H_2O$, ↓: h-WO_3 [Color figure can be viewed at wileyonlinelibrary.com]

the metastable phase, h-WO_3, is easy to occur on the low crystalline metal surface of ultrafine powder rather than the high crystalline surface of the larger particles. The Rietveld refined structural parameters for h-WO_3 from two types of tungsten powders after storage for 12 years and after aging for 28 days at 45°C, RH 100% are summarized in Table 2. All the data were well fitted with the space group $P6_3/mcm$ ($Z = 6$), and the crystal structures proved to be similar to those in the earlier reports.[11,12] Gerand et al described the structure using the space group $P6/mmm$ ($Z = 3$), and the O(1) atoms between the W layers were fixed at 3 *g* sites (1/2, 0, and 1/2) with high symmetries. We located the O (1) atoms at 6*g* sites (*x*, 0, 1/4) with lower symmetries in the space group $P6_3/mcm$ ($Z = 6$) and obtained the structural parameter, *x*: 0.500, as fitting results for the both samples. The O(1) atoms positions converged to the same atomic positions as the 3 *g* sites (1/2, 0, and 1/2) in the

TABLE 2 Refined crystallographic data of h-WO_3 obtained from tungsten powder aged for 12 years (A) and aged at 45°C, RH 100% for 28 days (B)

(a) Hexagonal; space group; $P6_3/mcm$ (193) a = 0.74538(16) nm, c = 0.77194(20) nm Z = 6			
Atom	**Site**	**Atomic position**	**Occupancy**
W	6*f* (1/2, 0, 0)		1.0
O(1)	6*g* (*x*, 0, 1/4)	*x*: 0.500(7)	1.0
O(2)	12*i* (*x*, 2*x*, 0)	*x*: 0.1982(16)	1.0
Interatomic distances/nm			
W-O(1)	2 × 0.1930	O(1)-O(2)	8 × 0.2765
W-O(2)	4 × 0.1980	O(2)-O(2)	2 × 0.2559
			2 × 0.3021
(b) Hexagonal; space group; $P6_3/mcm$ (193) a = 0.74219(13) nm, c = 0.77198(13) nm Z = 6			
Atom	**Site**	**Atomic position**	**Occupancy**
W	6*f* (1/2, 0, 0)		1.0
O(1)	6*g* (*x*, 0, 1/4)	*x*: 0.500(3)	1.0
O(2)	12*i* (*x*, 2*x*, 0)	*x*: 0.1913(15)	1.0
Interatomic distances/nm			
W-O(1)	2 × 0.1930	O(1)-O(2)	8 × 0.2783
W-O(2)	4 × 0.2003	O(2)-O(2)	2 × 0.2459
			2 × 0.3163

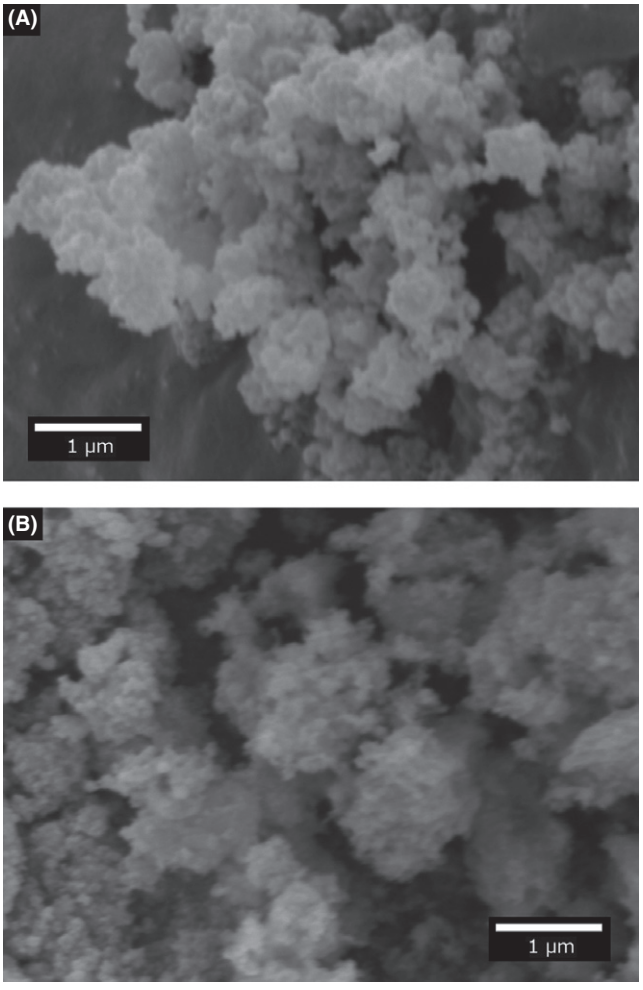

FIGURE 3 FE-SEM images of h-WO_3 powders prepared from tungsten powders stored for 12 years (A) and aged at 45°C, and RH 100% for 28 days (B)

space group *P6/mmm*, and consequently we obtained the same fitting results for the two space groups $P6_3/mcm$ and *P6/mmm*. The result for the space group $P6_3/mcm$ is presented here because this is more supportive of the atomic position of O(1). The interatomic distances between W and O were calculated at 0.1980-0.2003 nm along the *ab* plane and 0.1930 nm along the *c*-axis, and these are in good agreement with the reported W-O single bonding distances.[12,22] The O-O distances between neighboring oxygens vary from 0.2459 nm to 0.3163 nm, and this brings about the distortion of the WO_6 octahedra, which are stacked parallelly to the *c*-axis. Additionally, Oi et al used more general sites of the same space group $P6_3/mcm$ and reported remarkably distorted WO_6 octahedra. We also considered such atomic arrangement, but the fitting results were either almost the same as the above results or divergent. Thus, we adopted the present atomic arrangement. The crystallite sizes of h-WO_3 estimated from the peak profile parameters using the Scherrer equation were 14.2 nm and 12.6 nm, respectively, for the samples from 12-year-old tungsten powder and from 28-day aged tungsten powder. The BET specific surface areas of h-WO_3 were 16.9 m^2/g and 60.3 m^2/g, respectively, for the samples from 12-year-old tungsten powder and from 28-day aged tungsten powder. If we assume spherical particles, the average particle sizes are calculated at 57.1 nm and 15.9 nm, respectively. Figure 3 shows the FE-SEM images of h-WO_3 powders prepared from 12-year-old tungsten powder and from 28-day aged tungsten powder. The aggregates of nanocrystalline particles are observed for both of the samples. The crystallite size of h-WO_3 from 28-day aged tungsten powder was smaller than that from 12-year-old tungsten powder, and this is in good agreement with the results obtained from the BET analysis. The crystallite sizes of both of h-WO_3 were much smaller than the particle size of the raw material tungsten powder (0.45-0.59 μm) and varied depending on the preparation method. This suggests that the formation process of h-WO_3 is a topochemical oxidation through powder surface involving disruption to nanocrystalline particles. This room-temperature process allowed the formation of nanocrystalline and metastable phase by suppressing further crystal growth and transformation into more stable phase. This method is advantageous in preparation of nanocrystalline and metastable metal oxides because a high-temperature crystal growth process is not involved in the reaction unlike the solid-state reactions and the hydrothermal methods.

4 | CONCLUSIONS

Nanocrystalline h-WO_3 with crystallite size of 12.6-14.2 nm was facilely obtained as a precipitate in the direct reaction between tungsten powder and hydrogen peroxide. This new synthetic route necessitates surface oxide film having the similar crystal structure as h-WO_3, which can be obtained by aging the tungsten powder under conditions such as in air at 45°C, RH 100% for 3-28 days. The surface oxide film acts as a seed crystal for the crystal growth and leads to the formation of the metastable phase. The crystal structure of the present h-WO_3 was well fitted with the space groups $P6_3/mcm$ and *P6/mmm* in the Rietveld refinement and confirmed to be the same as that first reported by Gerand et al. Our method is advantageous over the conventional ones in that it is a facile room-temperature process and allows the formation of metastable and nanocrystalline phases. We consider the method will be applied to the preparation of the other metal oxides by using direct reactions of metallic powders such as titanium, molybdenum, niobium, and vanadium with hydrogen peroxide.

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