

Preparation of Nanosized WO_3 Powder by Chemical Vapor Condensation Process

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Abstract A chemical vapor condensation (CVC) process using the pyrolysis of metal-organic precursors was applied to produce the nanosized WO_3 powders. Morphology and phase changes of the synthesized WO_3 powder as a function of CVC parameters were investigated by XRD, BET and TEM. The agglomerated nanosized monoclinic WO_3 powders with nearly spherical shape and 10-38 nm in mean diameter could be obtained. Conditions to produce the WO_3 nanopowders are presented in this paper.

Keywords : Chemical vapor condensation, WO_3 nanopowders, Gas sensing materials

1. Introduction

In the recent years, much attention has been paid to synthesis and investigation of nanostructured powders because of their wide range of potential applications such as electronics, optics, catalysis, gas sensors and magnetic data storages^{1,2)}. Surface to bulk ratio of the nanostructured materials is much greater than that of coarse-grained materials. Therefore, the nanostructured materials exhibit a high specific surface area, and they have advantages to develop high-sensitivity chemical gas sensors. The Gas sensing applications of the nanostructured materials have been considerable interested in recent years. It is known well that SnO_2 and WO_3 metal oxides have been used for the effective gas sensor materials. Furthermore, the WO_3 is one of most variable materials for electrochromic devices, information displays, smart windows and rechargeable lithium batteries^{3,4)}.

A wide range of techniques to fabrication the nanosized powders such as inert gas condensation method, chemical vapor condensation process and sol-gel process has been developed rapidly over the past decades [5-7]. Particularly, the chemical vapor condensation (CVC) process is most attractive method because it is a direct route to produce the nanostructured powders with high purity and non-agglomeration properties as well as grain size of <30 nm. Like other materials, the nanostructured WO_3 powders could be produced by

various methods such as the evaporation of tungsten in the presence of O_2 or the sol-gel methods. However, no efforts have been made to synthesize the nanosized tungsten oxide powders by the chemical vapor condensation method so far. In this paper, we prepared the tungsten oxide (WO_3) nanopowder by the chemical vapor condensation process by the pyrolysis of metal-organic precursor of $W(CO)_6$. The effects of processing parameters on the microstructure and size of tungsten oxide nanopowders were investigated.

2. Experimental

The basic setup of the CVC is shown in Fig. 1. This is similar to that described in literature elsewhere⁸⁾. To produce tungsten oxide nanopowders, a carrier gas is fed through a heated bubbling unit containing the solid tungsten hexacarbonyl $W(CO)_6$ precursor. Three different Ar, O_2 , CO carrier gases were used to investi-

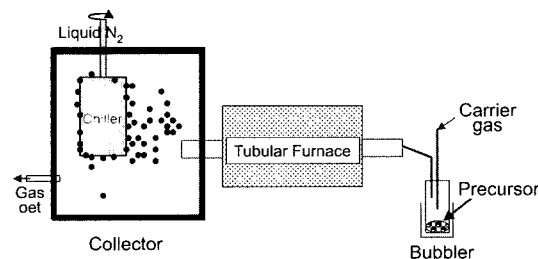


Fig. 1. Schematic of CVC process.

gate the phase changes of as-produced nanopowder. The flow of carrier gas entraining the precursor vapor passed through the heated tubular furnace to the collection chamber. The precursor decomposed and reacted in the furnace and condensed into the cluster or nanopowders. The experiment was conducted at temperature range of 700 to 1000°C. The nanopowders were synthesized and collected under room atmospheres in an air.

X-ray diffraction (XRD) with monochromatic $\text{CuK}\alpha$ radiation ($\lambda=0.1542$) was performed to identify the phases existing in as-prepared powders. The crystalline and particle size were evaluated by Scherrer formula from the half width of XRD peaks and BET specific surface area. The morphology and powder size were analyzed by field-emission scanning electron microscope (FE-SEM, Philips) and transmission electron microscope (TEM, JEOL, JEM-2000FXII). The powders for TEM investigations were ultrasonically dispersed in ethanol and dropped on a carbon-coated copper grid.

3. Results and Discussions

In the previous study, it was reported that the hexacarbonyl tungsten $\text{W}(\text{CO})_6$ precursor was pyrolyzed from $\text{W}(\text{CO})_6(\text{s})$ to $\text{W}(\text{g})+6\text{CO}(\text{g})$ at the temperature range of 120~205°C[9]. Therefore, in this experimental, the solid precursor was kept at the 120°C in the evaporator. In order to investigate the phase changes

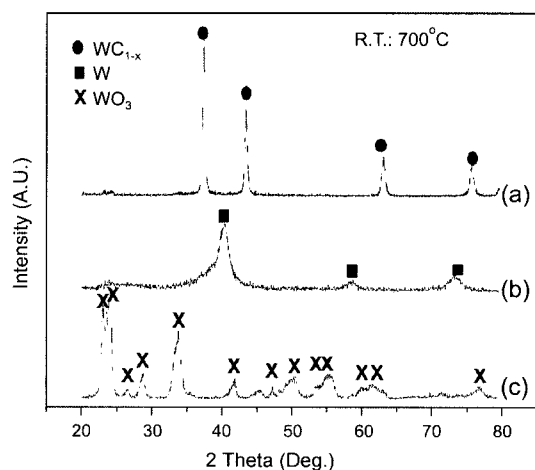


Fig. 2. XRD patterns of the as-CVCed nanopowders, which were prepared using (a) CO (b) Ar, and (c) O_2 carrier gases at 700°C.

with carrier gases, the as-synthesized nanopowders, which were collected in the chamber, were analyzed by XRD as shown in Fig. 2. XRD trace of the as-prepared nanopowders using of Ar and CO carrier gases Fig. 2(a, b) shows that the cubic-tungsten carbide (WC_{1-x}) and tungsten (W) nanopowders were synthesized by CVC methods, respectively. However, XRD spectra of Fig. 2(c) exhibits that the single phase monoclinic WO_3 nanopowders (JCPDS: 43-1045) were synthesized by using of O_2 carrier gas at 700°C.

In order to investigate the effect of reaction temperature, nanopowders were produced at 1000°C as shown in Fig 3. When the decomposition temperature increased to 1000°C using the CO carrier gas, new peaks, which are corresponded to the pure tungsten (W)

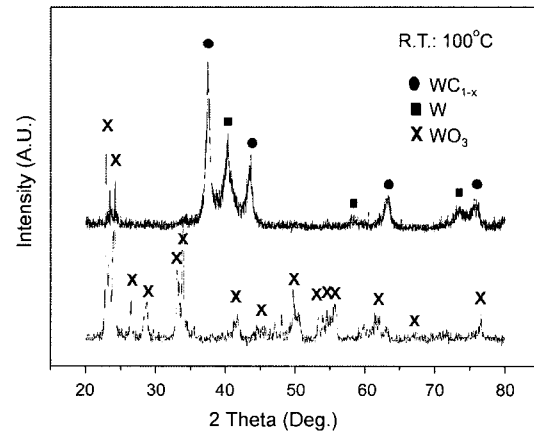


Fig. 3. XRD patterns of the CVCed powders prepared at 1000°C using (a) CO and (b) O_2 carrier gas.

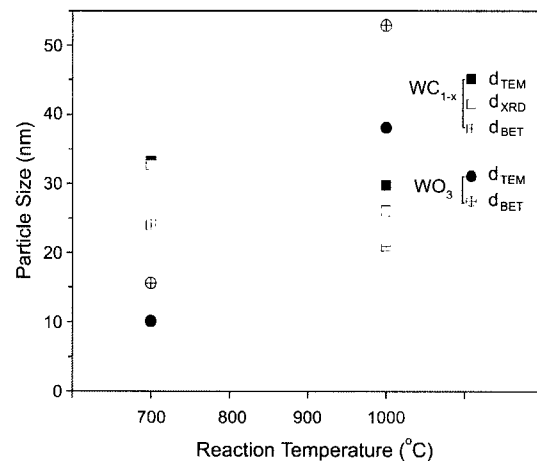
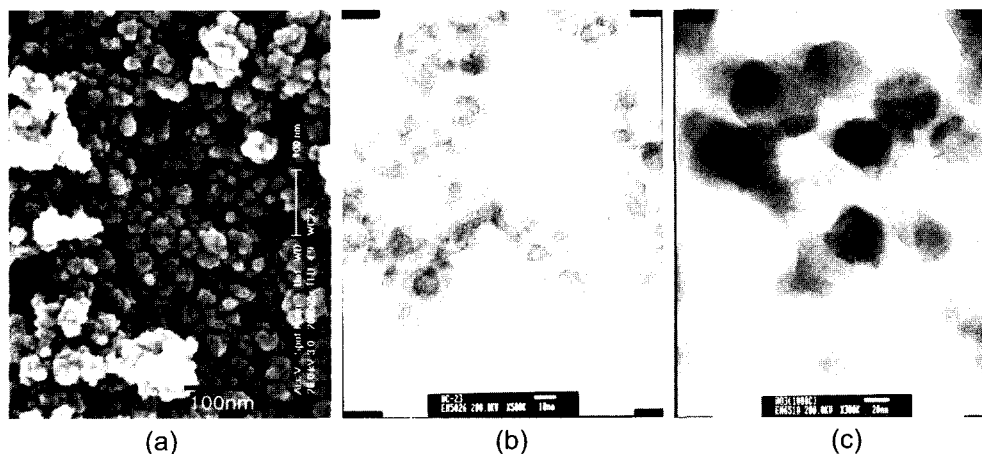


Fig. 4. Changes in size of WC_{1-x} and WO_3 nanopowders evaluated from XRD, TEM and BET.

Table 1. Characteristics of CVCed nanopowders with change of the carrier gas and the reaction temperature.

Reaction Temperature (°C)	Phase	CO gas Color	Shape	Phase	O ₂ gas Color	Shape
700	WC _{1-x}	Black	Rounded Rectangular	WO ₃	Light Yellow	Spherical
1000	W, WC _{1-x}	Black	Irregular Rectangular	WO ₃	Light Yellow	Spherical

**Fig. 5. FE-SEM and TEM micrographs of WO₃ nanopowders prepared at 700(a, b) and 1000°C(c).**

phase, appeared at this temperature, and the cubic tungsten carbide and pure tungsten were co-existed. However, under the condition of O₂ carrier gas, the monoclinic WO₃ phase was only confirmed at 1000°C as Fig. 2(c). The peak intensity of WO₃ increased and its width narrowed with increasing the reaction temperature, which indicates that the size of the as-prepared WO₃ nanoparticles increased during CVC reaction.

The crystalline and particle size, which measured by Sherrer formula from the XRD results, TEM observation, and BET surface area, were represented in Fig 4. As the reaction temperature increased from 700°C to 1000°C, the mean size of the CVCed cubic WC_{1-x} powders decreased a little from 33 nm to 30 nm. However, the mean size of the monoclinic WO₃ nanopowders drastically increased from 10 nm to 38 nm with reaction temperature. The mean crystalline size and powder size measured by XRD and TEM was well corresponded each other. But, the BET result of WC_{1-x} nanopowder showed smaller than XRD and TEM one because of the loose agglomeration of as-synthesized nanopowders. Chang *et al.* reported that the nanosized powders showing loose agglomeration, which lead to nanopores or sub-nanopores, had large BET specific surface area due to the formation of large aggregation,

and consequently have smaller grain size⁸⁾. To the contrary, the mean size of the WO₃ measure by BET is bigger than that of TEM results. Therefore, we thought this is resulted from the hard agglomeration of the WO₃ nanopowders. Characteristics of various samples prepared in this experiment are listed in Table 1. Color of the as-prepared powders was changed from black to light yellow when the carrier gas was changed from CO to O₂.

Fig. 5 shows FE-SEM and TEM micrographs of the CVCed WO₃ nanopowders prepared at 700 and 1000 °C. As shown in these pictures, with increasing the reaction temperature to 1000°C, the grains size of TEM was increased from 10nm to 38 nm. Recently, Y.B. Li *et al.* reported that monoclinic WO₃ nanorods or nanobelts could be synthesized via physical vapor deposition process, oxidizing W filaments and in-situ evaporating via infrared irradiation heat at 950-100°C in air⁴⁾. But, in this study, the as-prepared WO₃ nanopowders showed very smooth spherical shape because we used the direct evaporation and condensation method by the pyrolysis of tungsten metal-organic precursor under oxidation condition. In FE-SEM and TEM micrographs, no WO₃ nanorods or nanobelts are visual.

4. Conclusions

Nanostructured monoclinic tungsten oxide powders were prepared by chemical vapor condensation process by using of hexacarbonyl tungsten W(CO)₆ as precursor. The agglomerated tungsten oxide powders having smooth rounded shape were synthesized by the CVC process. The nanosized cubic-tungsten carbide (WC_{1-x}), pure tungsten and WO₃ powders were synthesized with change of carrier gases. Grain size of WO₃ powder was increased from 10nm to 38nm with the increasing the reaction temperature to 1000°C.

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