

Studies on the phase transitions and properties of tungsten (VI) oxide particles by X-Ray diffraction (XRD) and thermal analysis

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Tungsten (VI) oxide, WO₃ particles were synthesized by colloidal gas aphrons technique. The resultant WO₃ particles were characterized by thermogravimetric-differential thermal analysis (TG-DTA) and X-Ray diffraction (XRD) measurements in order to determine the phase transitions, the crystallinity and the size of the WO₃ particles. The result from XRD and DTA show that the formation of polymorphs WO₃ particles have the following sequence: orthorhombic (β -WO₃) \rightarrow monoclinic (γ -WO₃) \rightarrow triclinic (δ -WO₃) \rightarrow monoclinic (ϵ -WO₃) with respect to the calcination temperature of 400, 500, 600 and 700°C. No diffraction peaks were found in the X-Ray diffraction measurements for the sample heat treated at 300°C (as-prepared), suggesting that an amorphous structure was obtained at this temperature whereas the crystallinity had been obtained by the other samples of the WO₃ particles at the calcination temperatures of 400, 500, 600 and 700°C. It is also found that the X-Ray diffraction measurements produced an average diameter of (30 \pm 5), (50 \pm 5), (150 \pm 10) and (200 \pm 10) nm at calcination temperatures of 400, 500, 600 and 700°C respectively by using Debye-Scherrer formula. The TG curve revealed that the WO₃ particles is purely anhydrous since the weight loss is insignificant (0.3-1.4)% from 30 until 600°C for the WO₃ particles calcined at 400°C. Finally, the composition and the purity of the WO₃ particles have been examined by X-Ray photoelectron spectroscopy (XPS). The results indicate no significant changes to the composition and the purity of the WO₃ particle produced due to the temperature variations.

I. INTRODUCTION

WO₃ particles had recently receiving a lot of attention because of their important applications such as in catalysis [1], surface acoustic wave gas sensor [2] and detecting of hazardous pollutants such as NO_x [3], H₂S [4] and other alcohol gases, for example CH₄, CO, and NH₃ [5-7]. The chemical and physical properties of metal oxides particles, including WO₃ particles are generally dependent on the route of their synthesis [8-10]. There are many techniques that have been developed for the preparation of particles, which include microemulsions [11], laser ablation [12], sol-gel [13], UV irradiation [14] and solvothermal process [15]. In the present work we have focused on the colloidal gas aphrons (CGA) technique to produce WO₃ particles.

CGA are surfactant gas micro bubbles of 10-100 μ m in diameter produced by a high intensity stirring (4000-10000 rpm) in a vessel of a surfactant solution composed of a gaseous inner core surrounded by a thin surfactant film. These bubbles, due to their small size, exhibit some colloidal properties as described by Sebba [16]. CGA method is used in order to template metal-oxide semiconductors materials such as SnO₂, AlO₃, ZnO, TiO₂, CdS and WO₃ [17]. Such CGA system as

shown schematically in Fig. 1 can form a suitable template for the formation of the particles.

In this study, the phase transitions of WO₃ particles due to temperature variations have been studied, using X-Ray diffraction measurements. The sequence of temperature-induced phase transitions from lower to higher temperature for crystallized WO₃ is the following: orthorhombic (β -WO₃) \rightarrow monoclinic (γ -WO₃) \rightarrow triclinic (δ -WO₃) \rightarrow monoclinic (ϵ -WO₃) (refer to Table I) which is consistent with the reported by others in Ref. [18-22].

TABLE I. Size and phase structure of WO₃ particles at various calcination temperature as obtained from XRD.

Temperature (°C)	Phase Structure	Size (nm) XRD	Size (nm) TEM
As-prepared	-	-	30-45
400	Orthorhombic	(30 \pm 5)	35-65
500	Monoclinic	(50 \pm 5)	60-80
600	Anorthic (triclinic)	(150 \pm 10)	170-185
700	Monoclinic	(200 \pm 10)	220-240

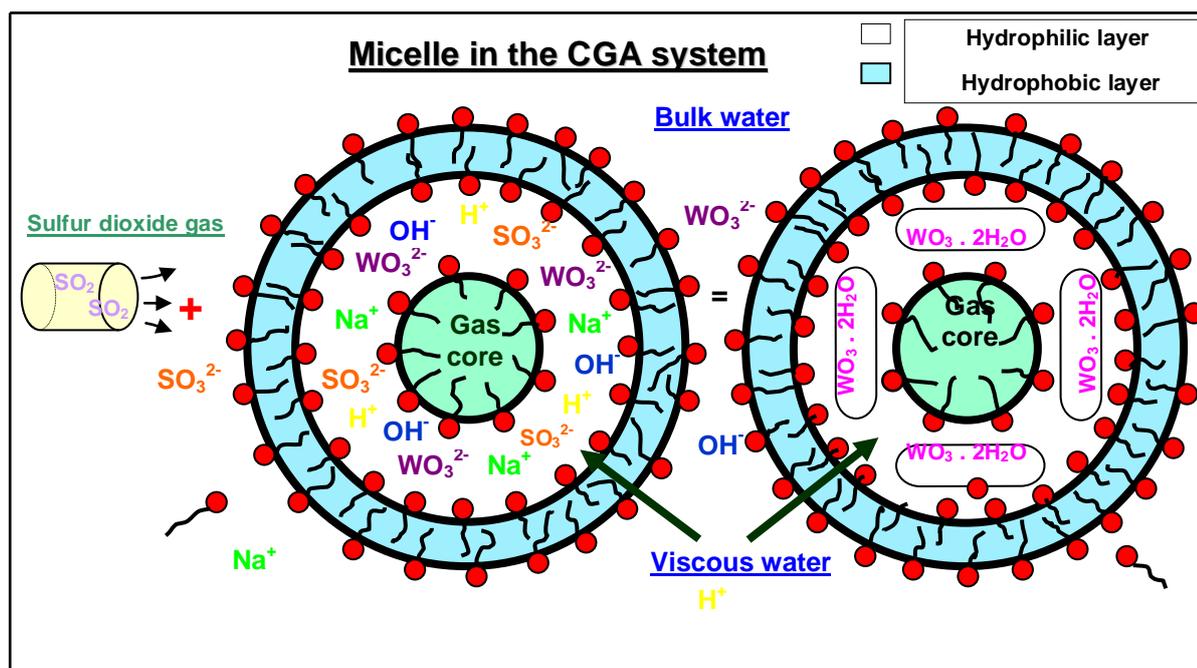


FIG. 1. A schematic flow chart of CGA technique for the synthesis of $\text{WO}_3 \cdot 2\text{H}_2\text{O}$.

II. MATERIALS AND METHOD

Ila. Materials

Sodium sulfite (Na_2SO_3 , 98%, SigmaUltra) and inorganic tungsten compound, sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$) were purchased from Sigma-Aldrich. Alkyl polyglucosides (commercially known as GlucoPone 650 EC Solution, 65%) was supplied from Fluka whereas hydrochloric acid (37%) and ethanol (99.8%) were both obtained from Scharlau. Double-distilled and deionized water (Purelab Prima Elga, having 18.2 M Ω electrical resistivity) was used throughout the samples preparation. All the chemicals and solvents were of analytical purity and were used as received without further purifications.

Ilb. Preparation Of WO_3 Nanoparticles

The solution which consisted of GlucoPone (60% wt. in water) was prepared. A 10.0 g of sodium tungstate dihydrate was then added to the solution. Finally, the CGA system was produced by stirring at 13500 rpm using a high speed stirrer (M. Zipper GmbH D-7813 Staufen, model X 620 CAT). All preparations were carried out at temperature of 28°C. This method is described in Ref. [17]. The solutions which contain the precipitate were washed with deionized water and pure ethanol before centrifugation at 4000 rpm in order to remove the surfactant, residual reactants and other byproducts. This process was repeated at least five times. Finally, the resultant product was heated in a

furnace at 300°C, for 3 h in order to remove water molecules from tungsten (VI) oxide dihydrate ($\text{WO}_3 \cdot 2\text{H}_2\text{O}$) to the anhydride (WO_3). The temperature at 300°C was chosen as the high peak started to appear from the XRD spectrum. This is followed by calcination for 4h at four different temperatures, i.e., 400, 500, 600 and 700°C.

Ilc. Characterization

The TG-DTA measurements were done on a Seiko 220U Thermogravimetry system with the temperature programming software of the furnace. The purge gas was N_2 , supplied at a constant rate of 400 mL/min. The sample weight loss (TG signal) and the energy loss (DTA signal) as functions of time and temperature were recorded continuously under dynamics conditions in the range of 30-600°C for the temperature measurements. In this investigation, TG-DTA data were used to determine the thermal decomposition, crystallization temperature which was found to be about 300°C and the effect of phase transitions of the samples.

Pyrolysis was carried out non-isothermally using 10.672 mg of WO_3 nanoparticles with the average size of (30 ± 5) nm placed in the platinum crucible which was then put on the sample pan hanging down in the reaction tube, in which the atmosphere could be controlled. The furnace tube was then raised to close the system. The pre-programmed control-unit regulates all the automatic functions of the recorder (e.g. the continuous change in the mass of the sample is measured), as well as the temperature programming of the furnace. After the

furnace temperature had achieved its set value, the sample was allowed to cool slowly to room-temperature.

The X-Ray diffraction (XRD) measurements were performed by a Bruker X-Ray diffractometer at a scanning rate of 1°/min in the range of 10-70°, using a monochromatized Cu K α radiation ($\lambda = 0.154$ nm). The silicon standard peak (111) was used to evaluate the instrumental broadening.

The X-Ray photoelectron spectroscopy (XPS) was carried out by a Kratos XSAM X-ray photoelectron spectrometer having a base pressure of 10⁻⁹ Torr. The Mg K α X-radiation was used as the excitation source. The binding energy of C1s (284.5 eV) was used as the reference in order to correct any charging shifts. A linear background subtraction has performed and the peaks in each spectrum were fit using a mixed Gaussian-Lorentzian function.

III. RESULTS AND DISCUSSION

The TG curve in Fig. 2 shows that the sample is purely anhydrous since the weight loss is insignificant 0.3-1.4% from 30 up to about 300°C with almost no further weight loss observed until 600°C. The line (almost plateau) formed between 300 and 600°C on the TG curve indicates the formation of crystalline WO₃ as decomposition product, as confirmed by XRD in Fig. 3. The DTA curves of thermal decomposition of WO₃ particles calcined at 400°C was shown in Fig. 2, a wide exothermic effect was observed with a peak at about 440°C, indicating that some phase transitions occurred which is from orthorhombic (β -WO₃) to monoclinic (γ -WO₃) as identified in Ref. [23] and [24]. The DTA curve for the others calcination temperature which is 500, 600 and 700°C were not shown since they gave a consistent phase transitions that is from monoclinic (γ -WO₃) \rightarrow triclinic (δ -WO₃), triclinic (δ -WO₃) \rightarrow monoclinic (ϵ -WO₃) and monoclinic (ϵ -WO₃) (only) respectively as can be referred in Ref. [23-26].

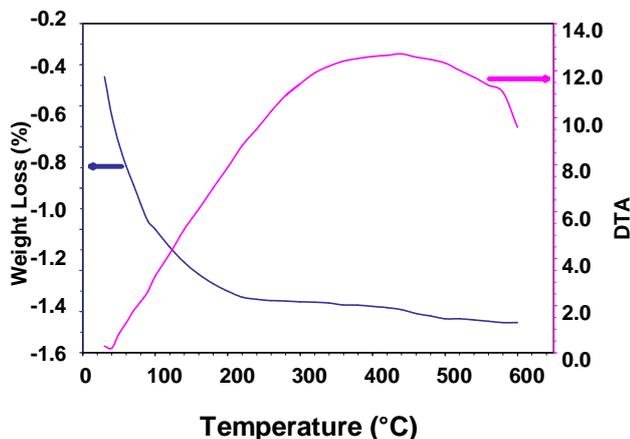


FIG. 2. The TG-DTA curves of thermal decomposition of WO₃ nanoparticles calcined at 400°C.

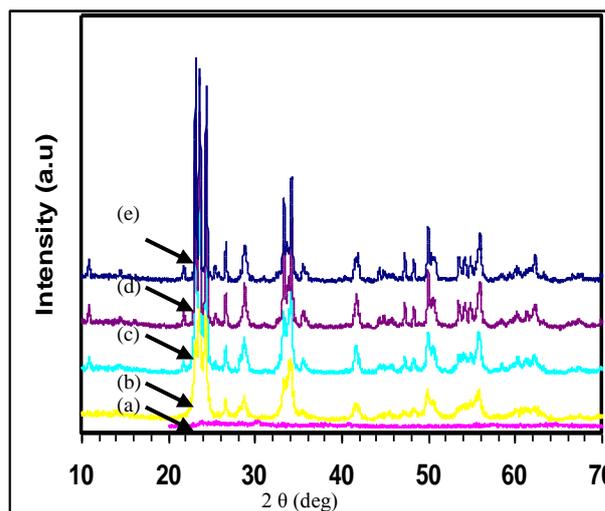


FIG. 3. The powder XRD patterns of WO₃ particles at various temperature: (a) as-prepared, (b) 400°C, (c) 500°C, (d) 600°C, (e) 700°C.

The X-Ray diffraction (XRD) patterns of the WO₃ are depicted in Fig. 3. All peaks (Table II) could be indexed to the standard patterns reported by the Joint Committee on Powder Diffraction Standards (JCPDS) [23-26], indicating a very high purity of the powder in all cases. It shows that all the calcined WO₃ produced are in crystalline form whereas as-prepared WO₃ particles are in amorphous form.

The average crystallite sizes of the nanoparticles can be obtained from the full-width half-maximum (FWHM) of the diffraction peaks by using Debye-Scherrer formula [27]. $D = (0.89 \lambda) / (B \cos \theta)$, where D is the diameter of the crystallites, 0.89 is the shape factor, λ is the X-Ray wavelength, B is the breadth of the diffraction lines in radian and θ is the diffraction angle in degree. The reflecting peak at the crystal planes of (0 0 2) for all the samples is chosen to estimate the average size of the nanocrystals.

Table I shows the phase transitions and the size with respect to the various calcination temperature [28-33]. Besides that the size of the WO₃ particles with TEM observation is compared [17]. For instance, at calcination temperature of 500°C the values is (50 \pm 5) nm by Debye-Scherrer formula but (60-80) nm with TEM observation. The only significant observation was the size by using TEM gave higher measurement than Debye-Scherrer formula. This is due to the fact that XRD measures crystallite size while TEM measures grain size. Grain size is normally bigger than crystallite size as it comprises several crystallite sizes of the particle.

TABLE II. Shows twenty-two broaden peaks and their respective Miller indices as obtained from XRD.

Peak (°)	Miller indices
23.1	(002)
23.6	(020)
24.4	(200)
26.5	(120)
28.6	(112)
33.2	(022)
34.0	(202)
34.2	(220)
35.3	(122)
41.4	(222)
49.6	(400)
49.7	(140)
49.7	(232)
50.1	(114)
50.2	(322)
55.3	(402)
55.4	(142)
55.6	(420)
59.1	(224)
60.9	(422)
60.9	(015)
62.3	(314)

XPS analysis was carried out to examine the electronic binding energy of the sample. Fig. 4(a) is the spectrum for the WO₃ nanoparticles sample at calcination temperature of 400°C. The intensity of the C (Auger) and O (Auger) peaks is high due to the organic molecule residue in the sample even after five times of washing process. Apart from these peaks, no other impurities were detected. Narrow scan for the W_{4f} in Fig. 4(b) shows peaks at 35.8 and 38.0 eV corresponding to the W_{4f}^{7/2} and W_{4f}^{5/2}, respectively. While the O_{1s} scan (Fig. 4(c)) shows peaks at 530.8 eV. These results are consistent with the data observed for the binding energy of WO₃ samples [33].

In the study on the XPS, the calcination temperature at 400°C is chosen for the presentation since the others gave almost similar results.

IV. CONCLUSION

The colloidal gas aphanons system has been developed to produce WO₃ particles. The increment of particle size and several phase transitions occurred when the WO₃ nanoparticles were heated from 30 to 600°C. The crystallization temperature for WO₃ particles was found to be above 300°C. The results from XPS show that no significant changes to the composition and the purity of the WO₃ particles at various calcination temperature. In addition, the nonionic surfactant,

Glucopone, that has been employed to form CGAs system in an aqueous solution in this present work is biodegradable and nontoxic to the environment.

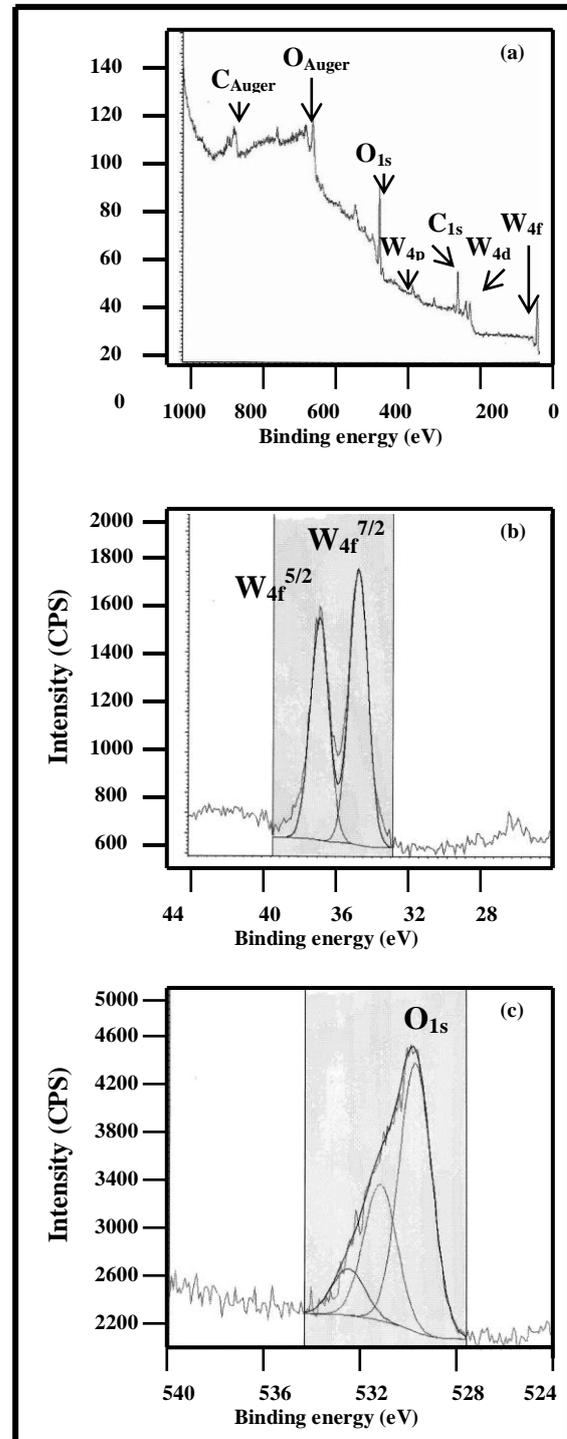


FIG. 4. (a) The wide XPS spectrum of the WO₃ nanoparticles at 400°C, (b) narrow scan for W_{4f} peaks and (c) narrow scan for O_{1s} peak.

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