SYNTHESIS AND APPLICATION OF WO₃ AS MATERIAL FOR POISONOUS CO GAS SENSOR

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ABSTRACT

Carbon monoxide (CO) is a poisonous and hazardous gas to human. A sensitive sensor device as an early indicator is necessary to prevent human from being poisoned by this gas. Therefore in this research a CO gas sensor was prepared from WO₃ synthesized via sol-gel method followed by calcination. Precursors WCl₆ and C₂H₅OH were used to synthesize WO₃ by sol-gel method. Sensor chip was prepared by spin-coating technique to deposit WO₃ thin film on alumina (Al₂O₃) substrate. Then the samples were calcined at various temperatures of 300, 400, 500, dan 600 °C for 1 hour. The sensitivity of the sensor was measured by potentiostat mode based on the electrical resistance changes in the absence and presence of CO gas at concentration of 50 ppm and 200 °C to find the sample which gave the optimum sensitivity. The sensitivity measurements were continued to the optimum sample at different CO gas concentrations of 100 and 200 ppm and different sensor operating temperatures of 30 and 100 °C. Scanning Electron Microscope (SEM) and High Resolution Transmission Electron Microscope (HRTEM) equipped with Energy Dispersive X-Ray Spectrometer (EDX) were used to observe the material morphology and chemical composition. X-Ray Diffraction (XRD) was used to observe the material structure and crystalline size. Thermo Gravimetric Analysis/Direct Thermal Analysis (TGA/DTA) was used to measure the moisture content and to inspect the structural changes due to temperature increase. BET analysis was used to measure the active surface area of WO₃. Raman Spectroscopy was used to identify the functional groups in WO₃ sample. WO₃ had two different structures of hexagonal after calcined at 300 °C and monoclinic after calcined at 400 °C and above. The crystallinity was enhanced along with the increasing of calcination temperatures. From the sensitivity measurement toward CO gas, it was found that the sensor prepared from WO₃ calcined at 500 °C gave the optimum sensitivity. This fact was supported by the TGA analysis showed that WO₃ calcined at 500 °C had the highest gas adsorption capability. Besides, the sensitivity increased with the increasing of CO gas concentration and operating temperature.

Keywords: WO₃ nanomaterial, sol-gel, calcination, CO gas sensor, sensitivity

I. INTRODUCTION

Carbon monoxide (CO) is a hazardous gas which is colorless, odorless, tasteless, and difficult to dissolve in water. CO gas is harmful to human health. To early detect the availability of CO, a sensitive sensor is needed. Tungsten trioxide (WO₃) is an n-type semiconductor metal oxide which has many applications including sensors for various gases, such as NO₂ [1], CH₄, CO [2], NH₃ [3], methanol, t-butanol, dimethyl methylphosphonate (DMPP), isopropanol, hexanol [4], electrochromic devices (smart windows) [5], and electrochemical capacitor [6]. The optimal performance on those mentioned applications depends on WO₃ nanomaterial electrical conductivity and surface adsorption properties, which are closely related to material structure, morphology, and size.

For its various applications and advantages many methods to synthesize WO₃ nanomaterials have been
reported and resulted in different structures, morphologies and sizes. Some of them include sol-gel process [1], spray pyrolysis [2], hydrothermal process [3], laser ablation [7], solvothermal synthesis [8], chemical vapor deposition [9], and reactive sputtering [10]. Among those methods sol-gel process offers relatively cheap, simple and easy procedures since it does not need strict controls on temperature and pressure. Besides it has been successfully applied in industries for thin and thick film mass productions with controllable size, shape, and homogeneity.

Although many papers have reported the applications of WO₃ as various gas sensors as mentioned above, the application of WO₃ as a CO gas sensor is rarely reported. Therefore in this research we tried to synthesize WO₃ nanomaterial by sol-gel method followed by calcination and applied as a CO gas sensor. X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), High Resolution Transmission Electron Microscope (HRTEM) equipped with Energy Dispersive X-Ray Spectroscopy (EDX), Raman Spectroscopy, Brunauer Emmet Teller (BET), and Differential Thermal Analysis/Thermo Gravimetry Analysis (DTA/TGA) analysis were used to characterize and compare the structures and morphologies of the resulted nanomaterials. The sensitivity of the sensor towards CO gas was measured using potentiostat mode of electrochemical measurement device based on the resistance changes of the chip sensor before and after CO gas exposure.

II. EXPERIMENTAL

Seven grams of tungsten (VI) hexachloride (WCl₆) (Acros Organics) were mixed with 100 ml of ethanol (C₂H₅OH) to produce tungsten alkoxide precursor of W(OC₂H₅)₆. 10 ml of 0.5 M ammonia hydroxide (NH₄OH) solution was added to the precursor as a catalyst and stirred for 24 hours under ice cooling to carry out hydrolysis and condensation processes. The chloride ions were carefully removed from the precipitation by de-ionized-water washing and centrifuging until no white precipitation of AgCl appeared when titrated with 0.1 M AgNO₃ solution. The washed precipitate was peptized by ammonia hydroxide, then 50 ml of surfactant (Triton X-100) was added into the solution and finally WO₃ gel was formed.

The gel was spin-coated on the polished surface of alumina (Al₂O₃) substrate of 2 cm x 2 cm x 0.2 cm at a rate of 500 rpm for 30 seconds and continued at 2000 rpm for 90 seconds. The alumina substrate was cleaned by de-ionized water and acetone prior to use. Next step was calcination process of the sample at various temperatures: 300, 400, 500 and 600 °C for 1 hour. The sample was slowly cooled in the furnace to allow the particles to array in well-ordered and form crystalline solids.

Scanning Electron Microscope (SEM FEI S-50) and High Resolution Transmission Electron Microscope (FEI Tecnai G²) were used to observe the morphology of the material. X-Ray Diffraction (XRD Philips X-Pert XMS) using Cu K-α X-ray source with wavelength 1.54056 Å was used to observe the material structure and crystalline size. Thermo Gravimetric Analysis/Direct Thermal Analysis (TGA/DTA Mettler Toledo) was used to measure the moisture content and to inspect the structural changes due to temperature increase.

To assembly a sensor chip, WO₃ which has been spin-coated on top of alumina wafer was sputtered by Palladium (Pd) in the both end-sides of 2 mm in width for 3 minutes to form current collectors. The back side of alumina substrate was also sputtered by Pd in zigzag line shape of 1 mm wide to form a heater. To measure the sensitivity towards CO gas, the sensor chip was placed in a chamber. Both current collectors were connected with Cu wires which extended out of the chamber to connect with electrochemical measurement device (Solartron Instrument). Both ends of Pd heater were also connected with Cu wires to thermo controller device outside of the chamber. Figure 1 shows the schematic diagram of the sensor chip arrangement.

To measure the sensitivity, initially the chip temperature was set at 200 °C and the resistance of the chip in air (denoted as R₀ (Ohm)) was measured by applying a constant potential difference of 3 V on potentiostat mode of Solartron instrument. Then CO gas with concentration of 50 ppm was introduced into the chamber and the resistance of the chip in the presence of CO gas was recorded. The resistance was denoted as Rₖ (Ohm). This measurement was applied to all of the 4 samples resulted from calcination at 300, 400, 500, and 600 °C.

\[
S = \frac{|R_k - R_o|}{R_o}
\]

Figure 1. Schematic Diagram of the Sensor Chip Arrangement

The sensitivity (S) was defined as the ratio of the difference between Rₖ and R₀ to R₀. It is mathematically expressed as [1]:
After the optimum sample which gave the highest sensitivity was found, the measurements were continued to the optimum sample to observe the sensitivity changes towards CO gas concentration variations of 100 and 200 ppm at constant temperature of 200 °C and towards operation temperature variations of 30 and 100 °C at constant CO gas concentration of 200 ppm.

III. RESULT AND DISCUSSION

Figure 2 depicts the secondary electron SEM images of WO₃ film coated on top of alumina wafer after calcined at various temperatures of 300, 400, 500, and 600 °C. WO₃ particles have grainy and thin transparent slab shapes. A number of particles tend to agglomerate to make a cluster. However as the temperature increases the aggregation tends to decrease. At lower temperature, moisture contents and volatile matters such as HCl, C₆H₅OH, NH₄OH, H₂O and surfactant in WO₃ bonded some particles to make clusters. At higher temperature, they were vaporized and removed from WO₃. Meanwhile, the size of particle increases along with the increasing of calcination temperature. For example, at 300 °C the size of particles ranges from 161-322 nm and at 600 °C it increases into 407-1142 nm. Higher temperature gives more energy for particles to grow larger.

The XRD patterns of WO₃ materials are shown in Figure 3. Generally the XRD peaks become sharper and show higher intensities as the calcination temperature increases. Hence, the crystallinity is enhanced along with the increasing of calcination temperature. The XRD patterns of the samples which calcined at 300 and 400 °C show broadened and less intense peaks as the indication of semicrystalline materials.

Two different structures of WO₃ material are identified based on XRD analysis. At 300 °C the XRD patterns are consistent with WO₃ of hexagonal structure (PDF No 85-2459) [11]. The three dominant crystalline plane orientations are (002), (112) and (321) at 2θ = 23.197°, 33.832°, and 65.2° respectively. At 400 °C and above, the XRD patterns show WO₃ of monoclinic structure (PDF No 83-0950) [12] with three dominant planes of (002), (200), and (020) at 2θ = 23.117°, 23.583°, and 24.367° respectively. The highest peak at 2θ = 41.7° belongs to alumina substrate of (006) plane (PDF No 41-1230) [13]. WO₃ has polymorphism in the crystalline structure as a function of temperature. The hexagonal phase is metastable, while the stable phase in room temperature is monoclinic or orthorhombic [14].

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D = \frac{0.9\lambda}{B \cos \theta}
\]

where \( \lambda \) is X-ray radiation wave length (nm), B is Full Width at Half Maximum/FWHM (radian), and θ is Bragg angle (degree) [15].

The XRD peaks show that the crystalline sizes of WO₃ were 6.4, 10.9, 21.8, and 39.3 nm at 300, 400, 500, and 600 °C respectively. It is obvious that the crystalline size increases with the increasing of calcination temperature. To observe more detail on the morphology of the material,
HRTEM analysis was performed on the sample which calcined at 600 °C and the results were displayed on Fig. 4.

![Figure 4. Bright field TEM images of WO₃ material calcined at 600 °C. a) A WO₃ cluster, b) a higher magnification image of a square region in (a), c) and d) magnified WO₃ images taken from the square region in (b)1 and (b)2 respectively.](image)

Figure 4a displays a cluster of WO₃ material which consists of ~ 30 particles of ~ 100 – 250 nm in width and ~ 400 – 600 nm in length. Figure 4b shows the higher magnification of a square region in (a). The square regions (1) and (2) in Figure 4b are magnified in Figure 4c and 4d. The lattice spacings are 0.35 nm and 0.37 nm which correspond to plane (020) and (200) respectively. These planes are also identified in XRD analysis showed in Figure 3.

Figure 5 shows the TGA/DTA results of WO₃ powder. TGA/DTA analysis was performed to WO₃ gel sample as shown in Figure 5a to explore the weight and heat changes of material due to heating. The material weight decreases sharply as much as 70% below 90 °C as a result of water and other volatile contents removal.

This process is indicated by the first endothermic peak at 90 °C showing the energy absorption to vaporize a large amount of physically bonded water and volatile matters. Further, there are no significant weight changes observed from 90 – 170 °C. The second endothermic peak at 230 °C is the indication of a small amount (~5%) of chemically bonded water vaporization. Above 230 °C the material weight loss is only 0.8%, which is probably due to oxygen removal [3]. In Figure 5b, the sample calcined at 300 °C shows more weight removal than other samples do.

Totally it loses 7% of its weight on heating, while that of 400 °C loses 0.64% on heating below 343 °C and regains 0.12% above 343 °C due to gas adsorption. Hence, they show semicrystalline structures based on the XRD analysis due to water and other volatile matter contents. Figure 5c is different from the other two figures, since the TGA graphs show the increasing of sample weight. The weight of sample calcined at 500 °C increases 2.5% on heating from room temperature to 600 °C, while that of sample calcined at 600 °C decreases 0.25% below 60 °C and increases 2% above 60 °C. The increasing of the sample weight is caused by gas adsorption since the DTA result in Figure 5a does not show any endothermic or exothermic peaks other than vaporization process as discussed above. Hence, WO₃ sample calcined at 500 °C shows the best ability in gas adsorption and it is suitable for gas sensor application. Wang
et al also reported that the WO$_3$ sample calcined at 550 °C showed the best sensitivity towards NO$_2$ gas [Wang et al., 2003].

Figure 6a depicts the sensitivity of sensors prepared by calcination at various temperatures. It shows that the sensor calcined at 500 °C showed the best sensitivity towards NO$_2$ gas. This result is supported by TGA data in Figure 5c showing the best ability of 500 °C sample in gas adsorption.

The sensitivity is increased along with the increasing of operating temperature. The CO gas adsorption mechanism at WO$_3$ surface is a reversible chemisorptions process based on the reaction:

$$\text{CO} + e^{-} \rightleftharpoons \text{CO}^-$$ (3)

The potential theory states that a potential barrier is formed between the surface of the semiconductor film and the ambient environment. As CO gas in contact with WO$_3$ surface, the oxygen of CO as the accepter will attract electrons from the conduction bands of WO$_3$. Therefore, the barrier of the WO$_3$ is increased and the resistance of the WO$_3$ film is also increased whenever CO is adsorbed on WO$_3$ surface. The density of electrons at the tungsten oxide surface increases with the operating temperature. Therefore, the sensitivity of WO$_3$ towards CO gas increases with the operating temperature as shown in Figure 6b. [Wang et al., 2003]

Figure 6c depicts the sensitivity of WO$_3$ sensor to various CO gas concentrations. It is obvious that sensitivity increases as CO gas concentration increases as a consequence of the increasing of WO$_3$ resistance towards more CO gas adsorbed onto the surfaces.

IV. CONCLUSION

WO$_3$ nanomaterials have been synthesized by a sol-gel method followed by calcination process at various temperatures of 300, 400, 500 and 600 °C for 1 hour and have been applied as CO gas sensors. The sensitivity of the material towards CO gas depended on the calcination temperature which affected the material structures. WO$_3$ calcined at 500 °C showed the optimum sensitivity towards CO gas due to its prominent performance in adsorbing gas. Meanwhile, the sensitivity also depended on the sensor operating temperature. It increased as operating temperature increased.

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