Synthesis of Tin Dioxide Nanoparticles and Nanorods by Hydrothermal Method and Gas Sensing Characteristics*

Vu Xuan Hien,† Dang Duc Vuong, and Nguyen Duc Chien

Department of Electronic material, Institute of Engineering Physics, Hanoi University of Technology, Community 1, Dai Co Viet Street, Hai Ba Trung District, Hanoi, Vietnam

Khuc Quang Trung

University of Fire fighting and Protection, Community 243, Khuan Duy Tien Street, Thanh Xuan District, Hanoi, Vietnam

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Tin dioxide nanoparticles and nanorods were successfully prepared by hydrothermal method using tin chloride, liquid ammonia, sodium hydroxide and cetyltrimethyl ammonium bromide (CTAB) as starting materials. The crystalline and structure features of the tin dioxide nanomaterial were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy dispersive X-ray analysis. Sensor devices were fabricated by coating SnO$_2$ nanomaterials on the front side of silicon substrates attached with Pt-interdigitated electrodes before annealed at 600°C for 30 minutes. Also, the films were measured to LPG and alcohol vapor at operating temperature in the range of 220-330°C. In addition, the sensitivity and selectivity of sensor were discussed. [DOI: 10.1380/ejssnt.2011.503]

Keywords: Tin dioxide; Nanorods; Nanoparticles; Hydrothermal

I. INTRODUCTION

Nowadays, with the development of nano-science and nano-technology, scientists have had a long jump on the way how to study the world, especially in material sciences. Nanomaterials, with a lot of feature properties, have been used widely in life. It should be noted that scientists have been taking their focus to prepare materials in nano-scaled with different morphologies by a lot of methods. Recently, one-dimension (1D) nanoscale materials have attracted many scientists because of their unique electronic, optical and mechanical properties [1, 2]. In this morphology, nanosized semi-conducting oxide materials seen to play the most important role with properties covering almost all aspects of material science, such as super-conductivity, ferro-electricity and magnetism etc.

In a number of metal oxides, tin dioxide in nano-scaled which was used in many fields, for instant dye-sensitized solar cells [3], optical waveguides [4], gas sensors [5], transparent conductive electrodes, transistors [6, 7] and Li ion batteries [8], is an important material with many interesting characteristics like chemical, thermal stability, inexpensive and high gas-sensing. In gas sensor area, SnO$_2$ has being considered as an unchangeable material in industrial scale production. When the noticeable disadvantage of this material is not selective to any gas, numerous researches and papers have been appeared. Up to now, two remarkable routes that solve this problem are preparing different morphologies and doping additives.

At this moment, several different morphologies of SnO$_2$ have been synthesized by self-catalytic vapor-liquid-solid (VLS) method [9], chemical vapor deposition [10], thermal evaporation [11], hydrothermal [12], laser ablation technique [6], solvothermal [13] and carbothermal reduction [14]. These studies all require high growth temperature (above 900°C) which makes them difficult for certain applications and which is difficult to control throw process. Guo et al. [15] has first reported a low-temperature hydrothermal synthesis of SnO$_2$ nanorods at 160°C from SnCl$_4$ aqueous solution with support of CTAB. After that, Lupan [16] reported a rapid hydrothermal synthesis of rutile SnO$_2$ nanowires using SnCl$_4$ without CTAB surfactant.

In this study, low temperature of synthesizing SnO$_2$ nanoparticles and nanorods by hydrothermal treatment was illustrated. It is also noted that SnO$_2$ nanorods were prepared using monodispersed sol suspension which contains SnO$_2$ nanoparticles. Also, the influence of morphology to tin dioxide gas sensing properties was analyzed by LPG and ethanol sensing experiments. Moreover, the possible formation mechanism of tin dioxide nanoparticles and nanorods prepared by hydrothermal was proposed.

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†Corresponding author: vxhien1986@gmail.com
II. EXPERIMENTAL

First, SnO$_2$ nanoparticles were fabricated by sol-gel method. In a typical synthesis, the SnCl$_4$-5H$_2$O crystal was introduced into de-ionized water under stirring for 30 minutes to receive SnCl$_4$ 0.2M solutions. Subsequently, liquid ammonia was dropped slowly into the solution making the vigorous reaction as follows:

$$\text{SnCl}_4 + 4\text{NH}_4\text{OH} \rightarrow \text{SnO}_2\cdot n\text{H}_2\text{O} + 4\text{NH}_4\text{Cl} + (2 - n)\text{H}_2\text{O}$$

The pH was adjusted approximate 7 to make sure that the reaction took place completely. After that, the white precipitation was filtered four times by de-ionized water to make stannic acid gel. A transparent suspension containing SnO$_2$ nanoparticles was received by dispersing the stannic acid gel back into the distilled water with support of NH$_4$OH. Then, as-solution was put into a Teflon-line stainless-steel autoclave (150 ml capacity), sealed and maintained at 180-200°C for 3h to make the treated sol.

The treated sol suspension was dried at 80°C for 12h to receive SnO$_2$ powder.

The proper treated sol 2wt% was added to 0.15 M NaOH solution by vigorous stirring to obtain an opaque solution to form Sn(OH)$_6^{2-}$ anions:

$$\text{Sn(OH)}_4 + 2\text{OH}^- \rightarrow \text{Sn(OH)}_6^{2-}$$

After that, 2 mmol of cetyltrimethyl ammonium bromide (CTAB) was added into above opaque solution, followed by heating to make CTAB dissolved completely. It should be noted that the ratio among treated sol, NaOH solution and CTAB was controlled to 1:25:2, respectively. Then the mixture was poured into a stainless Teflon-lined 200ml autoclave and treated at 140°C for 16h. After cooled down to room temperature, white precipitate was collected by centrifugation, washed by deionized water and ethanol for several times.

In order to investigate the structure and gas sensing properties of SnO$_2$ nanoparticles and nanorods, the powders after mixing with soluble water to make slurry, which were coated on Pt interdigitated electrodes by spin coating (1000 rpm for 5 minutes). Then, the electrodes were dried and annealed at 600°C for 3h. The morphology and composition were characterized by Field emission scanning electron microscopy image (FE-SEM) and Energy dispersive X-ray analysis (EDX). Gas sensing tests were performed on a static test system. A glass chamber with 20l volume stays on a substrate which is designed to outside communicate by a supplying and a releasing valve. An external electric heater inside the chamber plays a role as a heating furnace which can reach up to 500°C is controlled by a powerstat. The sensor position was fixed on the heating plate and we used two needles to obtain the signal which assembles serial to a power supply and rheostat at a constant test voltage of 5V. The Signal from rheostat was then received by Keithley Instrument and saved the data to computer though gpib interactive card. Target gas such as LPG was injected into the testing chamber by a syringe (50 ml).

III. RESULTS AND DISCUSSION

The XRD patterns of treated sol 2 wt% calcined at different temperatures in Fig. 1 show that samples indi-
cate three strong peaks at scanning angles 26.5°, 33.7° and 51.7° which are correlative to faces (110), (101) and (211). This result not only proves the existence of SnO₂ in tetragonal structure with parameters \( a = 4.7 \text{Å} \) and \( c = 3.2 \text{Å} \), but also shows the crystal size which can be calculated by Scherrer formula: \( d = k\lambda/(\beta \cos \theta) \). In this formula, \( \lambda \) is the wavelength of X-ray; \( k = 0.89; \beta \) is the full width at half maximum of peak and \( \theta \) is diffraction angle. The slight growth of SnO₂ crystal size calculated by Scherrer formula to different calcination temperatures is indicated in table I. Besides, the TEM image of treated sol 2 wt% which coated on an interdigitated-electrode and calcined at 600°C for 3 hours, shows the sphere-like shape and the narrow range in diameter (4 to 6 nm) of SnO₂ nanoparticles. It should be pointed out that the particles seem to be the same in crystal size and grain size and exist in sol solution as mono-dispersion grains. This result is important since our experiment of synthesizing SnO₂ nanorods uses treated sol as precursor. Thus, by controlling the crystal size of SnO₂ nanoparticles, the dimension of received nanorods may be controlled in the same synthesis conditions.

It is different from the result of SnO₂ nanoparticles preparation process, product which is derived from SnO₂ nanorods process is powder. This powder after annealed at 600°C for 3 hours was characterized by XRD and SEM as introduced in Figs. 3 and 4. The XRD pattern proclaims that all the diffraction peaks are perfectly indexed to the standard XRD data file of SnO₂ (JCPDS-041-1445) (ICSDdata) [17] without other impurities like NaCl or cetyltrimethyl ammonium bromide (CTAB) in sample.

By controlling the ratio of treated sol, NaOH solution and CTAB to 1:25:2, SnO₂ nanorods with diameter in the range of 400-500 nm were prepared under hydrothermal treatment condition (T=140°C for 16h) as shown in Fig. 5. It can be observed that the SnO₂ nanorods were prepared with high density and well uniform shape. Interestingly, this result seems to be the same with the synthesis of SnO₂ nanowires of Lupan’s group [16], while it is different from the precursors and treated conditions. That may be caused of behavior of CTAB which can unite the separated Sn(OH)₆²⁻ anions as reported by Guo’s report.

Table I. SnO₂ crystalline size at different calcination temperatures.

| Anneal temperature (°C) | \( \beta \)  | \( \theta \) | Crystalline size (nm) |
|-------------------------|-----------|-----------|---------------------|
| 120                     | 3.666     | 26.545    | 3.5                 |
| 400                     | 2.725     | 26.545    | 4.3                 |
| 600                     | 2.038     | 26.545    | 5.2                 |
| 800                     | 1.356     | 26.545    | 6.5                 |

FIG. 5: SEM images of SnO₂ nanorods treated at 140°C for 16h by hydrothermal.

FIG. 6: The response of LPG sensing between SnO₂ nanoparticles and nanorods to temperature.

FIG. 7: The response of ethanol sensing between SnO₂ nanoparticles and nanorods to temperature.
FIG. 8: The LPG and ethanol sensing comparison between SnO$_2$ nanoparticles and nanorods.

FIG. 9: The response-recovery time curves of SnO$_2$ nanoparticles and nanorods to ethanol.

[15]. In that study, the possible formation mechanism of SnO$_2$ nanorods is based on the formation of W nanowires [18], in which the Sn(OH)$_6^{2-}$ anions are connected to each other between the head of groups of CTA$^+$ to form CTA$^+$ - Sn(OH)$_6^{2-}$ ion pairs by electrostatic interactions. This effect leads to an aptitude that the length of SnO$_2$ nanorods can be raised by increase the quantity of CTAB.

The response comparison of LPG and ethanol sensing between SnO$_2$ nanoparticles and nanorods is illustrated in Figs. 6 and 7. It can be seen that the response of SnO$_2$ nanoparticles is approximate five times higher than SnO$_2$ nanorods to LPG at peaks. Besides, the optimum operating temperature can be observed at 300$^\circ$C exposing LPG and a slight shift to 310$^\circ$C when exposing to ethanol. Moreover, the influence of gas concentration to response of the nanoparticles and nanorods samples was carried out with the result is introduced in Fig. 8. Interestingly, SnO$_2$ nanorods do not provide high response to experimental gas, but it is better sensitivity to ethanol while comparing with SnO$_2$ nanoparticles. In another side, it can be observed that the response-recovery time curves of SnO$_2$ nanoparticles and nanorods when exposing to ethanol (Fig. 9) differ insignificantly to each other. Astonishingly, the gas sensing properties of SnO$_2$ nanorods is previously predicted to be better than particle morphology because of the remarkable feature in transition function. In fact, the low of response to target gas of SnO$_2$ nanorods comparing to SnO$_2$ nanoparticles may be brought about the large size of SnO$_2$ rods (400-500 nm in diameter) since their sensing properties depended mainly on surface area to react with target gas. This hypothesis seems to open a new study in which sensing properties of SnO$_2$ nanorods are improved by controlling the rod’s dimension, namely the ratio of treated sol : NaOH : CTAB, the temperature and operation time in hydrothermal process.

IV. CONCLUSION

In conclusion, SnO$_2$ nanoparticles and nanorods were successfully synthesized by hydrothermal at low temperature. Also, the XRD, SEM and TEM results indicate the tetragonal structure and prove the uniform shape, density of SnO$_2$ material nanosized. Besides, the LPG and ethanol sensing experiments show the better response of nanoparticles and better selectivity of nanorods to ethanol while comparing to each other. Thus, this leads to open a new study of improvement gas sensing properties of tin dioxide nanorods by modifying the process factors to control its dimension.

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