

Influence of Reaction Time on the Size of SnO₂ Nanospheres and Its Sensing Properties to VOC Gases

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Abstract: Tin Oxide (SnO₂) nanoparticles were synthesized using a simple hydrothermal technique at 100°C reaction temperature in a Teflon lined autoclave without adding any surfactant. A systematic study has been conducted by varying the reaction time between 6 and 72 hours using Tin (II) Chloride hydrate as an inorganic precursor. The influence of reaction time on the morphology, distribution and crystallite size of SnO₂ nanoparticles were analysed by transmission electron microscopy (TEM), X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy. The microscopy studies showed that the morphology of SnO₂ nanoparticles are spherical and SnO₂ nanospheres have an average size of 21.7-34.4 nm at different reaction times. The best combination of size and morphology was obtained at 21.7 nm at 12 hours reaction time. The gas sensing properties of SnO₂ nanospheres to the vapors of various Volatile Organic Compounds (VOC), such as Ammonia, Ethanol, Methanol, Acetone, Chloroform and Toluene were also investigated by two probe resistivity unit in a closed vessel at room temperature. The response of SnO₂ nanospheres to Ammonia vapor at different concentrations (1000-5000 ppm) was measured and SnO₂ nanospheres are observed to have a good sensitivity (98%). These results indicate that SnO₂ nanospheres exhibit to be an important alternative material for the detection of ammonia present in the environment at room temperature.

1. Introduction

Volatile Organic Compounds (VOCs) as toxic compounds, especially ethanol, acetone, ammonia and methyl benzene, are extra harmful to human health. But, they have been widely used in various industries [1]. Nowadays, many semiconductive metal oxides such as SnO₂, WO₃, ZnO, TiO₂, In₂O₃, Fe₂O₃ etc. have been extensively studied for detection of VOCs [2, 3]. Among various metal oxide, tin oxide appears to be one of the most important material because of its high sensitivity to reduce, large surface area, wide-band-gap (E_g= 3.65 eV), dielectric constant, environmental friendliness and easy synthesis [4, 5]. Although there are many studies on synthesis process of SnO₂ nanoparticles, there is no report that focuses on the importance of reaction time to get the smallest particle of SnO₂ nanospheres. To alleviate this deficiency to the extent possible, the influences of reaction time on the size of SnO₂

nanospheres and its sensing properties to the VOCs gases are investigated in this study.

2. Experimental

SnCl₂·2H₂O (2 g) was dissolved in deionized water and 4 ml ammonia solution (%26) was added to this under stirring at room temperature. After that, the solution was transferred into a 120 ml Teflon-lined autoclave and kept at 100 °C for varying reaction time between 6 and 72 hours. After naturally cooling to room temperature, the sample was filtered, washed with distilled water and ethanol several times, and then dried at 60°C for 24 h. Finally, SnO₂ nanospheres were obtained by annealing the as-prepared precursor in a muffle furnace at 500°C for 2 h.

The SnO₂ nanospheres were examined by using powder X-ray diffraction (XRD) performed on a Rigaku DMAX

III C diffractometer with a Cu K α radiation (1.541871 Å). Fourier transform infrared (FTIR) spectroscopy was carried out on a Mattson 1000 model FTIR spectrometer in the range of 400-4000 cm⁻¹. The morphology of the synthesized samples was observed by transmission electron microscopy (TEM, FEI Tecnai G2 Spirit Biotwin). The gas sensing measurement was performed by subjecting the synthesized sample pellet to the VOCs vapours in a glass closed test chamber using two probe technique with a Thurlby electrometer. The synthesized sample pellet was pre-prepared by keeping it under 7 t pressure for 3 min. The gas sensitivity is defined as shown in equation 1.

$$\%S = \frac{(\rho_a - \rho_v)}{\rho_a} \times 100 \quad (1)$$

Here, ρ_a and ρ_v are the electrical resistivity of the pellet in air and target VOC vapour, respectively [4].

3. Result and Discussion

3.1. Characterization

X-ray diffraction patterns of SnO₂ nanospheres synthesized at different reaction times are presented in Fig. 1. All the synthesized samples can be indexed to SnO₂ rutile structure without observable impurity peaks. The observed narrow and strong peaks in all the samples indicate the good crystallinity.

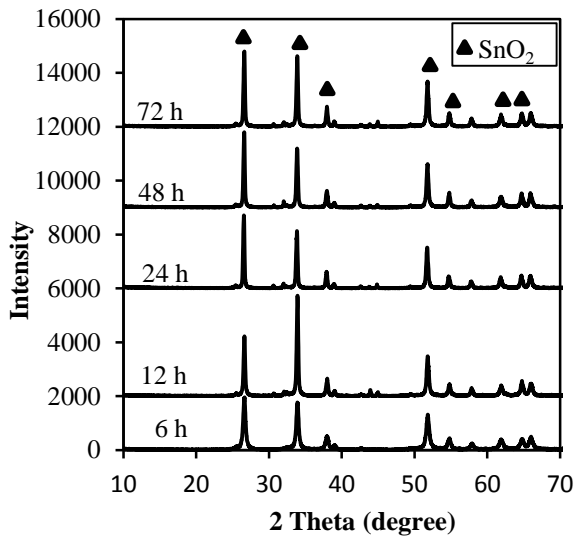


Figure 1. XRD patterns of SnO₂ nanospheres synthesized at different reaction times.

The XRD patterns exhibited that the peaks at 2 θ 26.6°, 33.9° and 51.9° are associated with (110), (101) and (211) reflection planes of the tetragonal SnO₂ [5]. The characteristics peaks of SnO₂ at around 37.9°, 54.7°, 61.9° and 65.9° corresponding to the (200), (220), (310), and (301) planes respectively were observed [6].

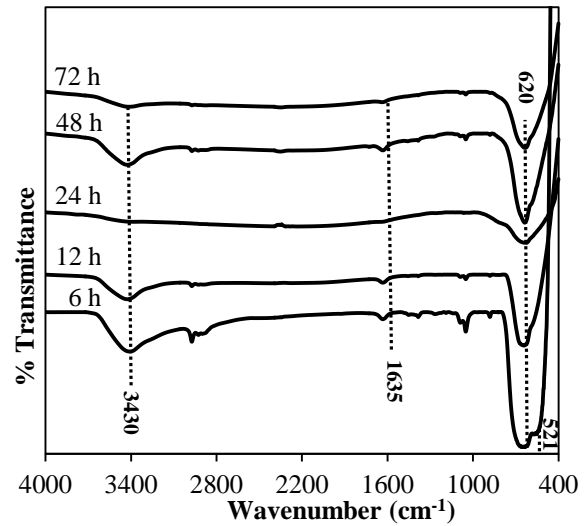


Figure 2. FT-IR spectrum of SnO₂ nanospheres synthesized at different reaction times.

Fig. 2 shows the FTIR spectrum of as synthesized SnO₂ nanospheres at different reaction times. The FTIR signals have been attributed to stretching vibration of O-H bending (3430 cm⁻¹, 1635 cm⁻¹), O-Sn-O (620 cm⁻¹) and Sn-OH (521 cm⁻¹). The peak at 521 cm⁻¹ disappeared after 12 h due to the transformation of all Sn(OH)₄ to SnO₂ [6, 7]. According to these results, we can say that the most appropriate reaction time is 12 hours to form SnO₂.

TEM images of SnO₂ nanospheres synthesized at different reaction times are presented in Fig. 3. The microscopy studies showed that the morphology of SnO₂ nanoparticles are spherical and the crystallite size of the five synthesized samples at different reaction times (6, 12, 24, 48, 72 hours) were 22 nm, 21.7 nm, 34.35 nm, 28.35 nm, 25.37 nm respectively. While at 6 and 24 hours reaction time, the SnO₂ nanoparticles agglomeration are more dominant, the particles show better distribution for reaction time at 12, 48 and 72 hours. The best combination of size and morphology was obtained at 21.7 nm at 12 hours reaction time.

3.2. Gas sensing properties

The response of SnO₂ nanospheres synthesized at 12 hours for saturated ammonia, ethanol, methanol, acetone, chloroform and toluene at room temperature is 98, 26, 28, 30, 47 and 57%, respectively (Fig. 4). In the results, the sample exhibits a remarkably high response to NH₃. Figure 5 shows the gas response towards various concentrations of NH₃ in the range of 1000-5000 ppm and the response is about 14, 25, 32 and 39%, respectively.

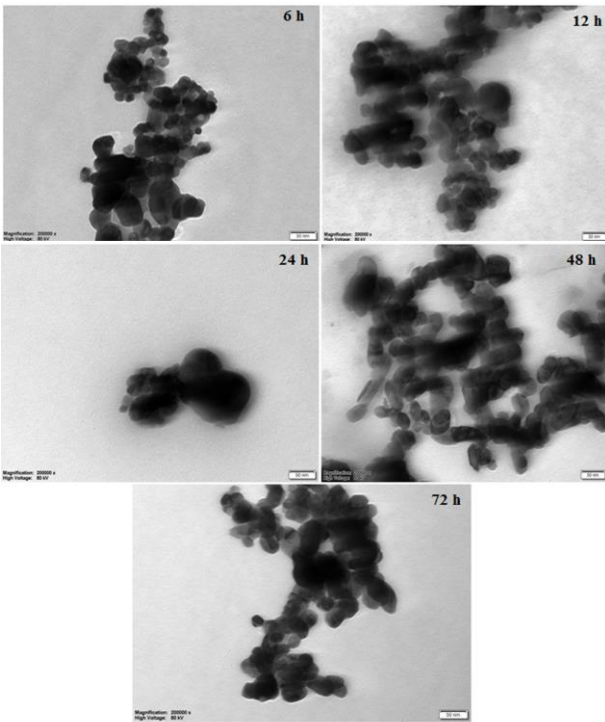


Figure 3. TEM image of SnO_2 nanospheres synthesized at different reaction times [Scala Bar: 50 nm].

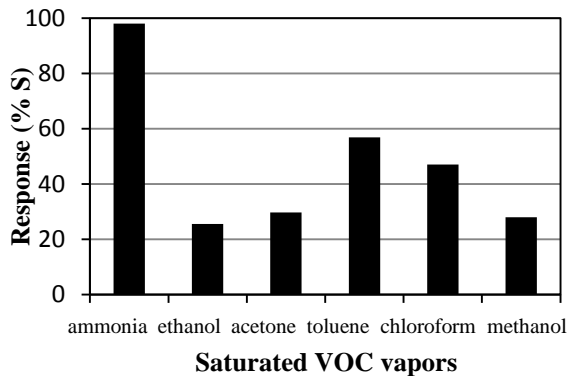


Figure 4. Gas sensing properties of SnO_2 nanospheres synthesized at 12 hours to various VOCs saturated vapours at

4. Conclusions

The SnO_2 nanospheres were successfully synthesized through controlling reaction time. The results showed that the reaction time has effect on size and morphology of SnO_2 during the hydrothermal synthesis and the best combination of size and morphology was obtained at 21.7 nm at 12 hours reaction time. Sensing properties of SnO_2 nanospheres exhibit the desirable sensing characteristics towards NH_3 at room temperature. The study showed that SnO_2 nanospheres are promising sensing material for an ammonia vapour sensor.

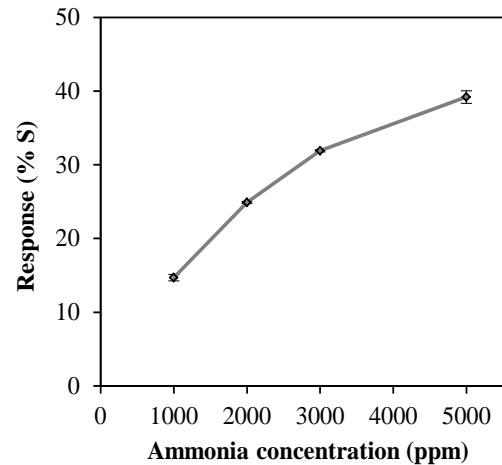


Figure 5. Gas sensing response towards 1000-5000 ppm of NH_3 at 25°C of SnO_2 nanospheres synthesized at 12 hours

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