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Synthesis of Mesoporous Tin Oxide with Cationic Surfactant as a Template in Aqueous Media

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Abstract Mesoporous tin oxide (SnO_2) with high surface area was synthesized in alkaline condition. The synthesis of the product was achieved using cationic surfactant (cetyltrimethylammonium bromide: CTAB) as template and hydrated tin chloride ($SnCl_4.5H_2O$) as inorganic precursor. Mesoporous SnO_2 was characterized by thermogravimetric analysis (TGA), X-ray diffraction (XRD), and N_2 adsorption-desorption experiment. The BET surface area of the sample calcined at 400°C is 164.9 m^2/g, with an average pore diameter of 4.1 nm.

Keywords Mesoporous tin oxide, Cationic surfactant, Hydrated tin chloride, High surface area

1. Introduction

Since the successful synthesis of MCM-41 [1], a number of mesoporous materials have been synthesized [2], employing the supramolecular assembly of surfactant molecules as templates. Mesoporous materials have attracted much interest, due to their large surface areas and narrow pores size distributions, which make them ideal candidates for catalyst, molecular sieve, and electrodes in solid-state ionic devices [3].

Tin oxide (SnO_2) is an n-type semiconductor with a wide energy band gap. SnO_2 is known as one of the promising metal oxides to be used as a catalyst, gas sensor, lithium ion batteries, and optical electronic devices [4]. Previously, several approaches using supramolecular templating mechanism have been reported for the preparation of mesoporous SnO_2 [5-8]. However, the mesoporous SnO_2 powders prepared so far are not always thermally stable and the poor thermally stability restricts their performance, especially in gas sensor field which have to be operated at elevated temperature [9].

In this paper, preparation of mesoporous SnO_2 using $SnCl_4.5H_2O$ as inorganic precursor, with cetyltrimethylammonium bromide (CTAB) as a template under alkaline condition was reported based on the modified Guo et al. [7] worked. This method of synthesizing mesostructured SnO_2 is much faster than previous worked and can produce high surface area of SnO_2, to the based on our knowledge. The as-synthesized product and its corresponding resultants calcined at different temperature were characterized.

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2. Experimental

2.1. Synthesis

The mesoporous SnO_2 were synthesized based on supramolecular templating mechanism by using cationic surfactant cetyltrimethylammonium bromide, (CTAB) as template and chemical materials ($SnCl_4.5H_2O$ and NH_4OH) as inorganic precursor and alkali source, respectively. The procedure was as follows: 1.6 g of CTAB was mixed with 100 ml of deionized water until a homogenous solution was obtained. A Sn^{4+} solution of 5 g $SnCl_4.5H_2O$ diluted with 100 ml deionized water was then added into the CTAB solution. 1 M of NH_4OH was introduced into the above mix solution under stirring till the pH value of the mixture was adjusted to 10 to promote hydrolysis process. After stirring for 3 h, the sol was aged for 3 days. The resulted white slurry was centrifuged and washed by deionized water for few times, and then dried overnight by using freeze dryer. The mesoporous SnO_2 were obtained by calcining the as-synthesized powders in a furnace at 400°C and 500°C for 2 h, respectively, and doted as Sn-400 and Sn-500. For the purpose of comparison, the commercial SnO_2 is selected and doted as Sn-C.

2.2. Characterization

The sample was characterized by thermogravimetric analysis (TGA, Parkin Elmer Pyris7) to analyse the amount of weight loss in the sample with a temperature increasing rate of 10°C/min. The phase transition and crystallite size of SnO_2 were characterized by X-ray diffraction (XRD, Philips PW 1710) using Cu Kα radiation (0.15418 nm). Specific surface area and pore size distribution were measured by a

BET method using N_2 sorption isotherm (Micromeritics, ASAP 2020).

3. Result and Discussion

3.1. Thermal Analysis

Figure 1 shows the TGA curve of the as-synthesized sample under N_2. At Stage I, the weight loss of water in the sample at the lower temperature range (<160°C) was about 6%. For stage II, the weight loss due to the surfactant begins at 160°C and it was greatly removed at about 320°C. From temperature 340°C to 800°C (Stage III), removal of carbon and little residual surfactant was occurred [10].

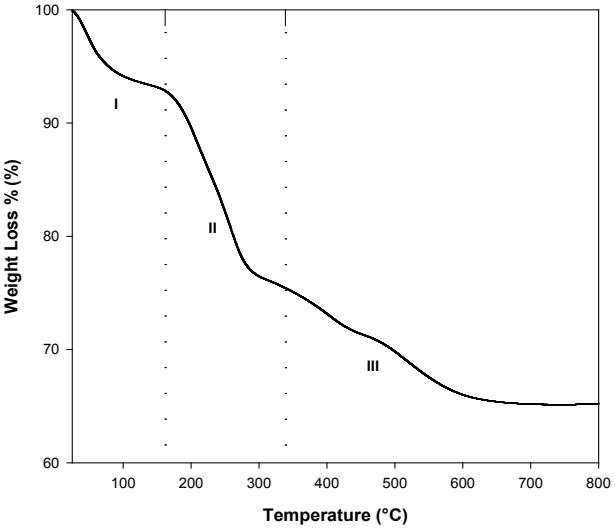

Figure 1. TGA curve of the as-synthesized sample

The analysis of the as-synthesized sample showed ~35% total weight loss on heating to 800°C. Since, the curve shows complete removal of surfactant at higher temperature range (>340°C), the calcination of the sample in air has been performed at 400°C and 500°C in order to determine the best mesoporous sample between two different calcination temperature.

3.2. XRD Analysis

XRD patterns are shown in Figure 2 for the commercial and synthesized mesoporous SnO2. It can be seen from the XRD patterns that all the samples are well crystallized and all diffraction peaks can be well indexed to the cassiterite tetragonal structure of SnO2 (JCPDS 41-1445). As observed from Figure 2, the diffraction peaks of the Sn-400 and Sn-500 are apparently broader than the peaks of the Sn-C, indicating the synthesized SnO2 sample have smaller particle size.

By using Scherrer equation, in the order of Sn-400, Sn-500 and Sn-C, the average crystallite size is calculated to be 4.9, 7.8 and 84.2 nm respectively. As expected, Sn-C possesses much larger crystallite size than the Sn-400 and Sn-500. In addition, the average crystallite size between Sn-400 and Sn-500 do not shows a huge different although they are being calcined at high temperature, which indicates that the addition of CTAB restrains the growth and coagulation of SnO_2 crystal particle [11].

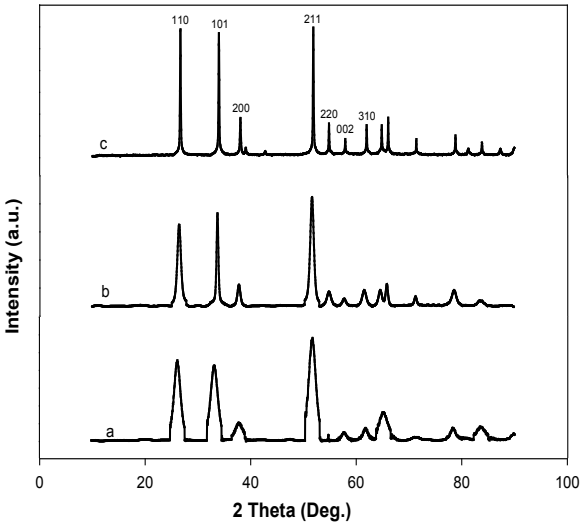

Figure 2. XRD patterns of Sn-400 (a), Sn-500 (b), and Sn-C (c)

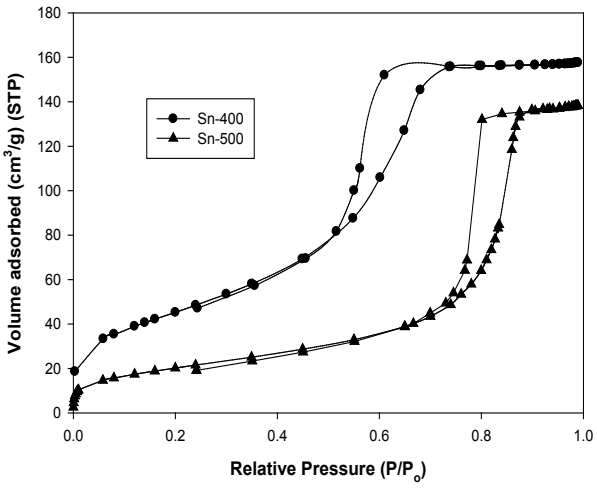

Figure 3. N_2 adsorption isotherm of mesoporous SnO_2

3.3. N_2 Adsorption and Desorption

Figure 3 shows the N_2 adsorption isotherms for sample Sn-400 and Sn-500. Both curve illustrates the sample have similar type IV adsorption isotherm with are typical for mesoporous materials [12]. The adsorption amount of N_2 on Sn-500 is much smaller than on Sn-400, indicating that Sn-500 has a much lower surface area than Sn-400 [13]. Sn-400 has a BET surface area of 164.9 m^2/g which is higher than Sn-500 (74.7 m^2/g). Both curves also show a H2 type of hysteresis loops according to the IUPAC classifications. Both isotherms show a strong hysteresis loop in the P/P_0 region from 0.5 to 0.7 and 0.7 to 0.9 for sample Sn-400 and Sn-500 respectively. This is related to the formation of bottleneck in the channels with the mesostructure framework

collapse in the process of calcination [11, 14, 15].

Based on Figure 4, Sn-400 has an average pore diameter of 4.1 and narrow pore size distribution while Sn-500 has an average pore diameter of 9 nm and broad pore size distributions. This suggests that as the calcination temperature increases, the pore size increases while at the same time the number of pores decreases as a result of sintering, thus lead in a decrease of surface area.

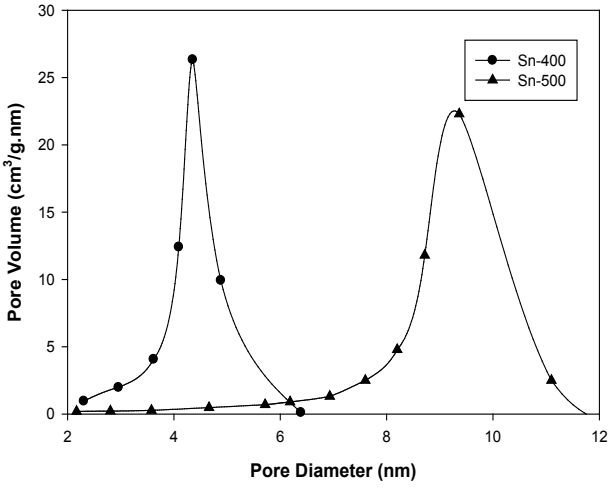

Figure 4. Pore size distribution of mesoporous SnO_2

For subsequent studies, the synthesized mesoporous SnO_2 nanopowders will be used as an active material in thick-film gas sensor application to detect different concentration of ethanol gas. The sensor performances in term of sensitivity, response and recovery time will be investigated.

4. Conclusions

In conclusion, the mesostructured tin oxide has been synthesized, employing cetyltrimethylammonium bromide as template and $SnCl_4.5H_2O$ as inorganic precurosor under alkaline condition. Sample with being calcined at 400°C (Sn-400) has high specific surface area which is 164.9 m^2/g and has an average pore diameter of 4.1 nm and narrow pore size distribution.

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