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Effect of Surfactant Types on the Size of Tin Oxide Nanoparticles

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In this study, tin oxide (SnO_2) nanoparticles were synthesized by hydrothermal method in the presence of hydrazine and ammonia by adding surfactant for 12 h in a Teflon autoclave at 100 °C reaction temperature. Tin(II) chloride hydrate as an inorganic precursor, hexadecyl trimethyl ammonium bromide (CTAB), and tetrapropyl ammonium bromide (TPAB) as cationic, and sodium dodecyl sulfonate (SDS) as anionic surfactants were used. The results showed that the size and shape of nanoparticles depended on the surfactant types. The nanoparticles sizes between 17.5 and 19.7 nm were obtained by changing types of surfactants. Synthesized tin oxide nanoparticles were characterized by field emission scanning electron microscopy, transmission electron microscopy, X-ray diffraction, and the Fourier transform infrared spectroscopy.

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1. Introduction

The nanostructured materials have great significance in various areas of material engineering due to physical, mechanical, magnetic, and chemical properties [1]. The shape, small sizes and high surface-to-volume ratios are vital parameters for nanostructured materials. At the same time, the unique morphology and structure of semiconductor oxides can offer a lot of promising applications. Among them, as n-type of semiconductor, tin oxide has attracted great interest due to its properties such as wide-band-gap (E_g = 3.6 eV, at 300 K), unique optical and electrical properties [2, 3]. SnO_2 has great significance in widely technological applications such as dye-based solar cells, electrochromic devices [4], photovoltaics [3], transparent electrodes, catalysts, gas sensing, lithium-ion batteries [2] and transistors [5]. There are several research methods to synthesize SnO_2 nanostructures with high purity level, well dispersibility and controllable sizes, such as spray pyrolysis, hydrothermal process, evaporating tin grains in air, chemical vapor deposition, thermal evaporation of oxide powders, rapid oxidation of elemental tin and the sol-gel method, and hydrothermal method. Among these processes, hydrothermal method is a simple, energy economical and environmentally friendly process. The geometrical morphologies of nanoparticles that are synthesized with via hydrothermal process depend on the organic surfactant types. Also, the organic surfactants can be easily removed from the structure of the synthesized product by washing via alcohols or by calcination. Up to now, SnO_2 nanostructures have been synthesized using surfactants with different charge (cationic, anionic, non-ionic) and dosage, involved various geometrical morphologies such as nanorod, nanocube, nanowire, nanosheet, and nanoparticle. Therefore, it is very important to investigate the effect of surfactant types on the polar surfaces of SnO_2 nuclei [2, 6]. However, no previous research has been found that examines the effect of surfactant types on the size of SnO_2 nanoparticles obtained by hydrazine-assisted hydrothermal process at low temperature.

This study attempts to provide some findings to this research area. Here, we aimed to obtain the smallest SnO_2 nanoparticles with homogeneous distribution and different geometrical morphologies by hydrazine-assisted hydrothermal process including cationic and anionic surfactants.

2. Experimental

$SnCl_2 \cdot 2H_2O$ (10 mmol g) was dissolved in 100 ml deionized water at room temperature. 4 ml ammonia solution (26%) and 2.5 ml hydrazine were added. After 20 min of stirring, the solution was subjected to ultrasonication for 1 h. Then 0.5 mmol CTAB, TPAB, and SDS were added to the solution. After ultrasonically dispersing the solution for 30 min, hydrothermal treatment was carried out in a Teflon autoclave (120 ml) at 100 °C for 12 h. Finally, the autoclave was cooled naturally to room temperature, the sample was filtered and washed with deionized water and pure ethanol until the effluent pH became 7. The final product was dried at 60 °C for 24 h and calcined at 500 °C for 2 h.

The morphologies of the tin oxide nanoparticles were observed by transmission electron microscopy (TEM, FEI Tecnai G2 Spirit Biotwin, 20–200 kV) and field emission scanning electron microscopy (FESEM, FEI Quanta 450 FEG, 20–30 kV). The crystal structure of the ob-

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tained nanoparticles was defined by X-ray power diffraction (XRD, Rigaku DMAX IIIC) with a Cu K_α X-ray source (λ = 1.541871 Å) and the data were collected in the 2θ of 10–70° at a scanning rate of 2°/min. The Fourier transform infrared (FTIR)analysis was conducted using Mattson 1000 model FTIR spectrometer over a range from 400 to 4000 cm^{-1}.

3. Result and discussion

Figure 1 shows the XRD patterns of the SnO_2 nanoparticles by different surfactant assisted. All the diffraction peaks are attributed to the SnO_2 rutile structure without observable impurity peaks (JCPDS card no. 41-1445) [6]. The three peaks at 2θ values of 26.6°, 33.9° and 51.9° are associated with (110), (101) and (211) reflection planes of a tetragonal lattice of tin oxide [7]. The diffraction peaks at around 37.9°, 54.7°, 61.9°, and 65.9° are associated with (200), (220), (310), and (301), respectively [6]. When XRD diagrams of SnO_2 nanoparticles prepared using surfactant and no surfactant are compared, it is seen that the peak intensities are increasingly narrowing by adding surfactant. According to the results, SnO_2 nanoparticles can be synthesized at different sizes using various surfactants.

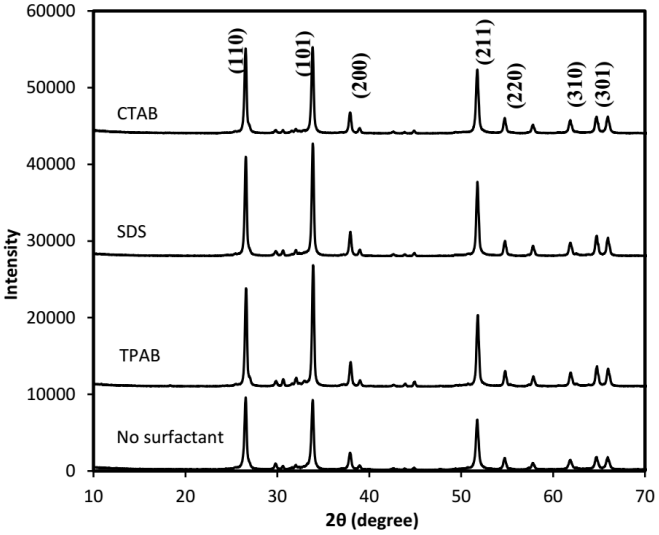

Fig. 1. XRD patterns of SnO_2 nanoparticles by different surfactant assisted.

In Fig. 2, the FTIR spectrum of SnO_2 nanoparticles by different surfactant assisted is illustrated. The band at 620 cm^{-1} can be attributed to a characteristic peak of the oxide-bridge functional group (O–Sn–O). In addition, the peaks around 3430 cm^{-1} appeared due to stretching vibration of adsorbed water at the surface of tin oxide [7].

The effect of surfactant types on the surface morphology and size of SnO_2 nanoparticles was observed by FESEM (Fig. 3) and TEM (Fig. 4). As shown in Fig. 3, densely packed and irregularly spherical-like SnO_2 nanoparticles were noticed. But, the exact shape of each

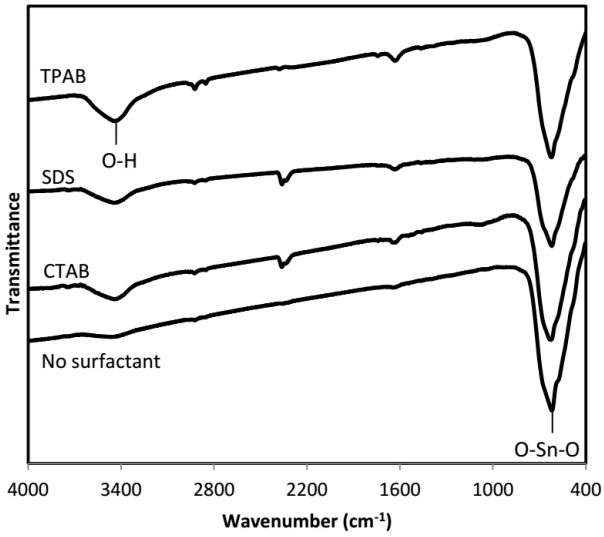

Fig. 2. FTIR spectra of SnO_2 nanoparticles by different surfactant assisted.

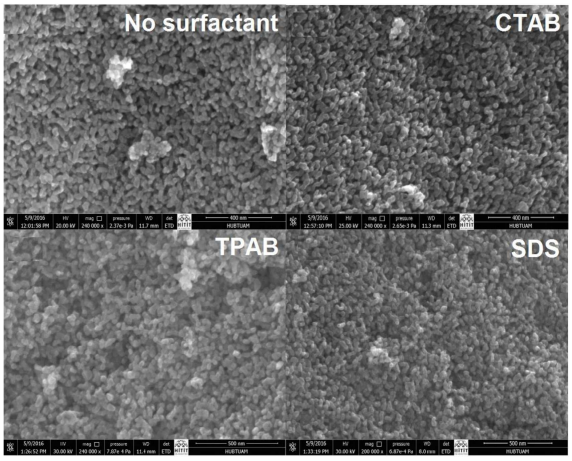

Fig. 3. FESEM micrograph of SnO_2 nanoparticles by different surfactant assisted.

particle cannot be understood from the FESEM photos. In addition, as seen in Fig. 4, the SnO_2 nanoparticles synthesized without surfactant were stacked together and composed mainly of nanospheres structures. The shape of SnO_2 nanoparticles were also influenced by varying surfactant type such as nanorectangles and nanohexagons when we used SDS, CTAB, and TPAB, respectively. Shapes of the particles were formed in nanohexagonal structures by the addition of CTAB and TPAB cationic surfactants to the synthesis medium. But, it was observed that the effect of adding the surfactants formed much SnO_2 nanoparticles stacked together. By adding SDS anionic surfactant to the synthesis medium, nanorectangles were obtained and the particle accumulation could be avoided at some point. As a result of that, particles in shape of nanorectangles were obtained. According to TEM results, the sizes of SnO_2 nanoparticles were determined using the UTHSCSA Image Tool 3 image analysis program [8]. The average

size of SnO_2 nanoparticles was obtained as 19.7, 18.2, 19.2, and 17.5 nm by changing surfactant types as no surfactant, CTAB, SDS, and TPAB, respectively. The smallest particle size and the best particle distribution were achieved by using TPAB (17.5 nm) as cationic surfactant and SDS as anionic surfactant, respectively (Fig. 4). These results are due to the combined interplay between the electrostatic interaction and the Van der Waals' forces [2].

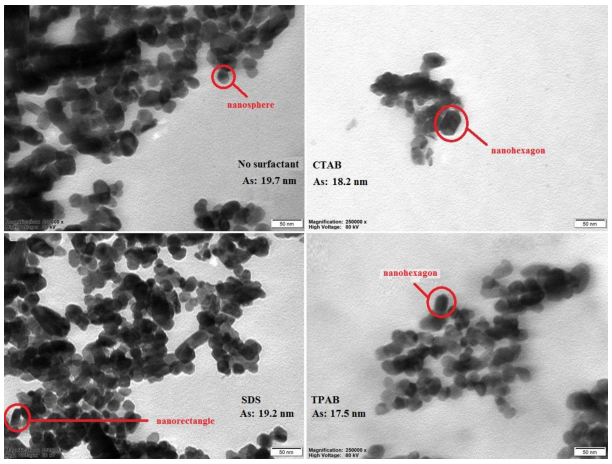

Fig. 4. TEM images of SnO_2 nanoparticles by different surfactant assisted.

4. Conclusion

We have successfully prepared SnO_2 nanoparticles with homogeneous distribution and different geometrical morphologies by hydrazine-assisted hydrothermal process including cationic (CTAB, TPAB) and anionic (SDS) surfactants. The effects of surfactant types on the surface morphology and size of SnO_2 nanoparticles were investigated. The average particle size was obtained in the range of 17.5 to 19.7 nm. While SnO_2 nanospheres was prepared without surfactant, the shape of SnO_2 nanoparticles was achieved as nanorectangles and nanohexagons using anionic and cationic surfactants, respectively. TPAB and SDS provided the smallest particle size and the better particle distribution of SnO_2, respectively.

Acknowledgments

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