Without capping agent

Glucose

irregular nanoparticle

Sucrose

uniform nanoparticle

Starch

nano plate

agglomerated particle

Effect of carbohydrate sugars as a capping agent on the size and morphology of pure Zn₂SnO₄ nanostructures and their optical properties

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ABSTRACT

Pure Zn₂SnO₄ nanostructures were prepared via simple and rapid co-precipitation approach in presence of different carbohydrate sugars as a green capping agents. The effect of different carbohydrate sugars such as glucose, sucrose and starch on the size, morphology and optical properties of Zn₂SnO₄ nanostructures were investigated. The results demonstrated that applying the appropriate amount of sugars could be effective in particle size, morphology and optical properties control.

Keywords: Nanoparticles; Semiconductor; Electron microscopy; Optical properties

1. Introduction

Zinc stannate (Zn₂SnO₄) as a ternary semiconductor is widely used in applications such as dye-sensitized solar cells [1], photocatalysis [2], lithium ion batteries [3] and gas sensing systems [4]. Zn₂SnO₄ has a wide band gap of 3.6 eV with excellent optical properties, great chemical sensitivity and low visible absorption. Different possible routes have been proposed for preparing nanocrystalline Zn₂SnO₄ including hydrothermal [5], co-precipitation [6], microwave-assisted hydrothermal [2], solid state calcinations [8] and thermal evaporation [9]. Among of these methods, co-precipitation is simple, rapid, cost effective approach, potential for large-scale production and simply control the shape and particle size for preparing of Zn₂SnO₄ nanostructures. For size and morphology

controlling, many efforts have been done. One of the significant ways of preparing nanostructures with optimum properties is choosing appropriate carbohydrate sugar shell. This shell is a molecular monolayer encapsulating the core. The carbohydrate sugar perform the task of adsorbent and stabilizer. The Zn_2SnO_4 surfaces are occupied by hydroxy groups. The carbonyl and hydroxyl groups of sugars will form hydrogen bonds with hydroxyls of Zn_2SnO_4 surface. As the capping agent molecules have many carbonyl and hydroxyl groups and Zn_2SnO_4 has many hydroxy groups on the surface, sugar molecules will entwine the Zn_2SnO_4 surface tightly. From these possible mechanism results, it can be concluded that probably a proper amount of sugar is attached to the surface of nanoparticles which may have an effective role in preventing nanoparticles agglomeration. In this way, these kind of capping agents have an advantageous role on controlling size, shape, and uniformity of final products. Beside the common surfactants, recently our team has focused on the effect of carbohydrate sugars as a capping agent on the properties of obtained products [10, 11]. Moreover, Due to the environmental pollutions, the use of natural capping agent instead of chemical compounds has developed in the past decades [12, 13]. For the first time, pure Zn_2SnO_4 nanostructures were prepared at the short time by using different sugars such as glucose, sucrose and starch with various steric hindrances as monosaccharide, disaccharide and polysaccharide, respectively. The effect of different carbohydrate sugars on the size, morphology and optical properties of Zn_2SnO_4 nanostructures were investigated. The results demonstrated that applying the appropriate amount of sugars could be effective in particle size, morphology and optical properties control.

2. Experimental

Materials and physical measurements: All the chemical reagents for the synthesis of Zn_2SnO_4 nanostructures such as $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, glucose, sucrose, starch, Na_2CO_3 were commercially available and employed without further purification.). X-ray diffraction (XRD) patterns were recorded by a Philips-X'pertpro, X-ray diffractometer using Ni-filtered $\text{Cu K}\alpha$ radiation. GC-2550TG (Teif Gostar Faraz Company, Iran) were used for all chemical analyses. Scanning electron microscopy (SEM) images were obtained on LEO-1455VP equipped

with an energy dispersive X-ray spectroscopy. The EDX analysis with 20 kV accelerated voltage was done. Transmission electron microscopy (TEM) image was obtained on a Philips EM208 transmission electron microscope with an accelerating voltage of 200 kV. Optical analyses were performed using a V-670 UV–Vis–NIR Spectrophotometer (Jasco).

Synthesis of Zn_2SnO_4 nanostructures: Zn_2SnO_4 nanostructures were prepared by co-precipitation method. First, glucose solution was added dropwise into the zinc nitrate solution under magnetic stirrer and then $SnCl_2 \cdot 2H_2O$ solution was added into the above solution (with molar ratio of Zn:Sn = 2:1). Then, Na_2CO_3 as a mineralizer was added dropwise into metal solutions. The pH solution was adjusted to 7-8 to preserve the hydroxide phases of Zn and Sn. The white precipitates obtained were collected by centrifugation at 4000 rpm for 5 min, washed repeatedly with distilled water several times. The as-obtained products were dried at 80 °C under vacuum for 4 h and then were calcined at 1000 °C for 3 h. The preparation conditions of Zn_2SnO_4 nanostructures have been illustrated in Table 1. To study the effect of capping agent on the morphology and size of the products, an experiment as blank tests were carried out without capping agent at room temperature.

Table 1. Preparation conditions for the synthesis of Zn_2SnO_4 nanostructures.

Sample No	Types of sugar	Morphology	Particle size (SEM) / nm	Band gap (eV)
1	glucose	nanoparticle	30-250	-
2	sucrose	nanoparticle	30-100	3.68
3	starch	nanoplate	thickness<100	3.6
4		nanoparticle	60-300	3.62

3. Results and discussion

XRD patterns of the products synthesized before and after calcination at 1000 °C are shown in Fig. 1a and b, respectively. The diffraction peaks observed in Fig. 1a and b can be indexed to pure cubic phase Zinc Tin Hydroxide (JCPDS card no. 73-2384) and cubic phase Zinc Tin Oxide (JCPDS card no. 24-1470),

respectively. The crystallite size diameter (D) of the Zn_2SnO_4 product calculated by Debye–Scherrer equation [14] have been found to be 35.4 nm for sample No.2.

EDS spectrum of Zn_2SnO_4 nanoparticles (sample No. 2) is illustrated in Fig. 1c. The lines of Zn, Sn and O are obviously observed.

To examine the role of the different carbohydrate sugars on the morphology and size of the products, Zn_2SnO_4 nanostructures were synthesized by monosaccharide, disaccharide and polysaccharide sugars. Fig. 2a-d show the SEM images of the Zn_2SnO_4 nanostructures synthesized in presence of glucose, sucrose, starch and without capping agent, respectively. These results show that using glucose and sucrose sugars lead to synthesis of Zn_2SnO_4 nanoparticles. However, by using starch sugar, nano plate products are obtained. By comparing SEM images of Fig. 2a and b, it can be seen that particle sizes of the Zn_2SnO_4 synthesized by sucrose are smaller than those produced by glucose due to higher steric hindrance effect of sucrose. The carbonyl and hydroxyl groups of sugars will form hydrogen bonds with hydroxyls of Zn_2SnO_4 surface. In this way, the sugars as a shell are adsorbed on the surface of Zn_2SnO_4 nanoparticles. Nano plate products were synthesized by using starch sugar, as starch sugar has a long chain of hydroxyl groups. But glucose and sucrose sugars with having less carbonyl and hydroxyl groups, synthesize nanoparticle products. To investigate the effect of the sugar on the morphology and size of the products, the blank test was carried out without using the sugar. According to the Fig. 2d, it can be seen that the morphology of the product is agglomerated and irregular. The corresponding TEM for samples No. 1-3 were synthesized in presence of glucose, sucrose and starch are shown in Fig. 2 e-g. As shown in Fig 2e-g, Zn_2SnO_4 products prepared in presence of glucose and sucrose are nanoparticles and in presence of starch are nanoplates. Fig. 2h, i show the HRTEM image and SAED pattern of Zn_2SnO_4 nanostructures prepared in presence of the sucrose sugar, respectively. Fig. 2h shows representative HRTEM image of the specimen. In the HRTEM image, the distance between the two adjacent planes, d , is measured to be 0.34 nm. Fig 2i shows the selected area

electron diffraction (SEAD) pattern of Zn_2SnO_4 nanostructures. The ring-like SAED pattern indicates that the nanostructures are polycrystalline.

Fig. 1. XRD patterns of as-prepared products (a) before and (b) after calcination and (c) EDS pattern of the Zn_2SnO_4 nanoparticles (sample No. 2).

The UV-Vis Diffuse Reflectance spectroscopy of sample Nos. 2-4 are shown in Fig 3a-c. As shown in this figure, the position of absorption edges are various. In comparison to the blank product (Fig. 3c), the absorption edge of prepared sample by sucrose (Fig. 3a) shift to blue region. The fundamental absorption edge in most semiconductors follows the exponential law. Using the absorption data, the band gap was estimated by Tauc's relationship:

$$\alpha = \frac{\alpha_0 (h\nu - E_g)^n}{h\nu}$$

where α is absorption coefficient, $h\nu$ is the photon energy, α_0 and h are the constants, E_g is the optical band gap of the material, and n depends on the type of electronic transition and can be any value between $1/2$ and 3 [15]. The energy gaps of the samples have been determined by extrapolating the linear portion of the plots of $(\alpha h\nu)^{1/2}$ against $h\nu$ to the energy axis (Fig. 3d-f). The E_g values are calculated 3.68, 3.6 and 3.62 eV for the samples Nos. 2-4, respectively. By decreasing of particles size (sample No. 2 and 4), energy gap increased. The difference of band gap values of samples have been attributed to variations size and morphology of nanostructures and the type of electronic transition [16, 17].

Fig 2. (a-d) SEM images of the samples No. 1-4, (e-g) TEM images of the samples No. 1-3, (h) HRTEM image and i) SAED pattern of Zn₂SnO₄ nanostructures (sample No. 2).

Schematic diagram of formation of Zn_2SnO_4 product by different sugars is depicted in Fig 3g. The influence of photocatalytic activity of Zn_2SnO_4 nanoparticle prepared by sucrose as a capping agent were investigated by monitoring the degradation of eosin Y as water pollutant in an aqueous solution under UV light irradiation. The obtained results are shown in Fig. 3h. According to photocatalytic calculations, the eosin Y degradation was about 94 % by Zn_2SnO_4 nanostructures after 120 min irradiation of UV light.

Fig. 3. (a-c) UV-Vis diffuse absorption spectra, (d-f) linear portion of the plots of $(ah\nu)^{1/2}$ against $h\nu$ of sample No.2-4, respectively, (g) Schematic diagram of formation of Zn_2SnO_4 nanostructures and (h) Photodecolorization eosin Y degradation of Zn_2SnO_4 nanostructures.

4. Conclusion

In summary, an eco-friendly, rapid and simple method to synthesize Zn_2SnO_4 nanostructures by carbohydrate sugars as a capping agent is developed. The effect of different carbohydrate sugars such as glucose, sucrose and starch on the size, morphology and optical properties of Zn_2SnO_4 nanostructures were investigated. The results demonstrated that applying the appropriate amount of sugars could be effective in particle size, morphology and optical properties control. The difference of band gap values of samples have been attributed to variations size and morphology of nanostructures.

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