

Research Article

Synthesis and Characterization of In_2S_3 Nanorods in Sucrose Ester Water-in-Oil Microemulsion

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We report the synthesis of In_2S_3 nanorods in a nonionic sugar-based water-in-oil (w/o) microemulsion system using food grade sucrose ester as biosurfactant. In_2S_3 was formed by mixing indium (III) chloride and thioacetamide in the water core of the microemulsion system. The as-prepared yellowish In_2S_3 was characterized by X-ray diffractometry (XRD), UV-visible absorption spectroscopy (UV-Vis), transmission electron microscopy (TEM), and Fourier transform infrared spectroscopy (FTIR). Formation of spherical or rod-like In_2S_3 nanomaterials was dependent on reaction time. Rod-like In_2S_3 , arranged in bundles, was formed only after 2 days of reaction time. Upon longer aging time, a mixture of rod-like and spherical In_2S_3 was formed. A plausible formation mechanism of the In_2S_3 nanorods in the sucrose ester microemulsion was postulated. The diameter of the In_2S_3 nanorods was found to be very small, which is 8.97 ± 2.36 nm with aspect ratio of 20 : 1 (length : diameter).

1. Introduction

Due to the toxicity of transition metals like Cd and Pb, alternative metals have been studied for the production of metal sulfides like ZnS, SnS_2 , and In_2S_3 [1, 2]. In_2S_3 is an interesting semiconductor with band gap energy of ~ 2.0 eV for bulk material [3, 4]. In_2S_3 is a metal sulfide group III–VI with potential application in optoelectronic, solar cells, and photoelectric [5, 6]. Many different types of techniques have been introduced for the synthesis of In_2S_3 in thin film or powder form with various morphologies [7, 8].

Conventionally, In_2S_3 was synthesized through direct reaction between indium and sulfur in a quartz chamber under high temperature [9], thermal treatment by In_2O_3 in the presence of H_2S gas at high temperature, thermal degradation of butylindium at the temperature of 300°C [10], or self-propagation with metathesis reaction between InCl_3 and Li_2S at the temperature of 500°C [11]. There are a lot of reports on the solution synthesis method, which includes precipitation in aqueous solution that yields amorphous or low crystalline indium sulfide from reaction between InCl_3 and H_2S , $(\text{NH}_4)_2\text{S}$ [5], or NaHS [12], In_2S_3 formation in sodium polysulfide solution using laser ablation technique; In_2S_3

nanoparticles precipitation method by adding Na_2S into the InCl_3 solution in the presence of polymeric stabilizing agent [13], injection of H_2S into the $\text{In}(\text{ClO}_4)_3$ solution [14], and precipitation of In_2S_3 nanoparticles in microemulsion system. However, few works reported on the formation of 1-D In_2S_3 nanomaterials [15], thus, synthesis of 1-D In_2S_3 remains a great challenge.

W/o microemulsion systems have been employed for some time now as media for the preparation of nanoparticles. More popular surfactants including cetyltrimethylammonium bromide (CTAB) [16], sodium dodecylsulfate (SDS) [17], polyoxyethylene (10) tertocetylphenyl ether (Triton-X) [18], sodium bis(2-ethylhexyl)sulphosuccinate (AOT) [19] and polyethylenglycol-dodecylether (Brij 30) [20] have been used for the synthesis of nanomaterials. Our group had reported on the synthesis of spherical-shaped metal sulfides [21], tungsten oxide [22], PbS nanorods [23], and brushite nanofibers [24] using sucrose ester-based microemulsion.

In this paper, we utilized sucrose ester S1670 as the nonionic food grade surfactant to form w/o microemulsion (water/heptan-1-ol/sucrose ester) as a soft template for the synthesis of In_2S_3 nanorods. Sucrose ester is a green and biodegradable biosurfactant with raw material that comes

from renewable sources like fatty acids and sugar. To the best of our knowledge, this is the first report on the formation of In_2S_3 nanorods synthesized using sucrose ester microemulsion system.

2. Experimental

The sucrose ester used in this work is a commercially available sucrose monoester of stearic acid (S1670, denoted as SES, HLB = 16, at least 70% monoester of stearic acid) in a mixture with di-, tri-, and polyesters of stearic acids, which was purchased from Mitsubishi-Kagaku Food Corp. Indium (III) chloride (>99.0% in purity) and thioacetamide (>99.0% in purity) were from Fluka, and heptan-1-ol (>99.5% in purity) and absolute ethanol (>99.5% in purity) were obtained from BDH. All chemicals were used as received without further purification. Doubly distilled and deionized water was used throughout the sample preparation.

Thioacetamide solution was prepared daily prior to the sample preparation. In a typical synthesis of the In_2S_3 nanoparticles from the w/o microemulsion method, 50 wt% heptan-1-ol, 40 wt% sucrose ester S1670, and 10 wt% aqueous solution (with 0.2 M indium (III) chloride and 0.2 M thioacetamide) were vigorously mixed in well-sealed glass tubes at 30°C. This was followed by centrifugation to remove bubbles in the samples, giving viscous, isotropic, and optically clear solutions, which indicate homogeneity. The homogenous samples were kept at 30°C for reaction time of 12 hours, 1 day, 2 days, and 3 days for the formation of In_2S_3 nanomaterials. The isotropic sample turned yellowish in color but remains transparent, indicating homogenous formation of nanosized In_2S_3 particles in the w/o microemulsion system. The In_2S_3 nanoparticles were recovered by washing with absolute ethanol to remove byproducts and excessive surfactants at least four times. The yellowish In_2S_3 samples were left to dry at room temperature.

Transmission electron microscope, TEM (Philips CM12 operated at 100 kV) was used to examine the size and morphology of the In_2S_3 nanomaterials. A drop of the In_2S_3 solution was cast onto a 300 mesh carbon-coated copper grid using a micropipette and was allowed to dry in an oven at 40°C for 1 day. Measurement of the average diameter of the nanoparticles was carried out using I-Solution-DT (version 6.5, IMT) image analysis software with at least 200 nanoparticles being chosen as the sampling data. The crystallinity of the nanoparticles was determined by X-ray diffraction (XRD) using a Philip diffractometer employing a scanning rate of 0.02°s^{-1} in a 2θ range from 10° to 60° with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Ultraviolet-visible spectroscopy (UV-Vis) was carried out at room temperature using a Perkin Elmer Lambda-35 spectrophotometer in the range of 380 to 1100 nm.

3. Results and Discussion

Indium sulfide synthesized in the sucrose ester microemulsion is observed under the TEM as shown in Figure 1. From the TEM micrographs, spherical indium sulfide nanoparticles were formed after the reaction time of 12 hours

(Figure 1(a)) and 1 day (Figure 1(b)) with average diameters of $6.04 \pm 1.20 \text{ nm}$ and $8.93 \pm 1.37 \text{ nm}$, respectively. The particles enlarged after 1 day of reaction time. The indium sulfide nanoparticles formed have narrow size distribution and dispersed well without aggregations. Indium sulfide with rod-like morphology was obtained after 2 days of reaction time with an average diameter of $8.97 \pm 2.36 \text{ nm}$ and an average length of $\sim 100 \text{ nm}$ (Figure 1(c)). The indium sulfide nanorods, arranged in bundles, create a unique morphology. Formation of nanorods is due to the confinement of the inorganic materials in the aqueous prolate-shaped cores of sucrose ester [25]. After the reaction time of 3 days, the indium sulfide formed has a mixture of nanoparticles and nanorods with average diameter of $20.04 \pm 3.75 \text{ nm}$ (Figure 1(d)). This is because the aqueous nanocores could no longer restrict the growth of the particles and the instability of the sucrose ester microemulsion system caused the formation of a mixture of particle shapes.

Figure 2 shows the X-ray diffraction (XRD) pattern of indium sulfide nanocrystals after the reaction time of 2 days. The peaks at $2\theta = 28.82^\circ$, 33.64° , 47.95° and 56.99° are attributed to (111), (200), (220), and (311) crystal planes, which are indexed to In_2S_3 with cubic crystal structure (JCPDS file no. 05-0731). Based on the lattice constant calculation using spacing (d_g) of the (220) plane and equation $1/d_g^2 = (h_2^2 + k_2^2 + l_2^2)/a^2$, the value $a = 5.353 \text{ \AA}$ is close to the reported value of $a = 5.358 \text{ \AA}$ for In_2S_3 . No characteristic peaks of other indium compounds and impurities were detected. The broadening of the diffraction peaks is due to the finite size of the nanocrystals and indicates that the dimensions of the nanoparticles are very small. The relative intensity for the (111) crystal plane is higher than the standard In_2S_3 relative intensity. This suggests that In_2S_3 nanorods growth is along the (111) crystal plane direction.

In order to study the optical properties of In_2S_3 nanocrystallite, UV-Vis absorption spectra for the as-obtained In_2S_3 nanocrystallite are carried out at room temperature and are laid out in Figure 3(a). UV-Vis spectra for In_2S_3 synthesized after 12 hours and 1 day of reaction time show blue shift as compared to the reaction time of 2 days and 3 days due to the quantum confinement size effect of the In_2S_3 nanoparticles. This result is in agreement with observation under TEM which shows smaller particles size for reaction time of 12 hours and 1 day.

The bulk In_2S_3 is a direct semiconductor with band gap energy of 2.0 eV. Estimation of the direct absorption band gap energy of the In_2S_3 nanorods was done by transferring the absorption data to a quadratic equation. The optical absorption data of the spectra have been analyzed from the following equation in order to determine the optical band gap of the In_2S_3 nanocrystals [26, 27]

$$\alpha h\nu = k(h\nu - E_g)^{1/2}, \quad (1)$$

where α is the absorption coefficient, ν is frequency, h is Planck's constant, E_g is the gap energy of the nanoparticles, and k equals a constant.

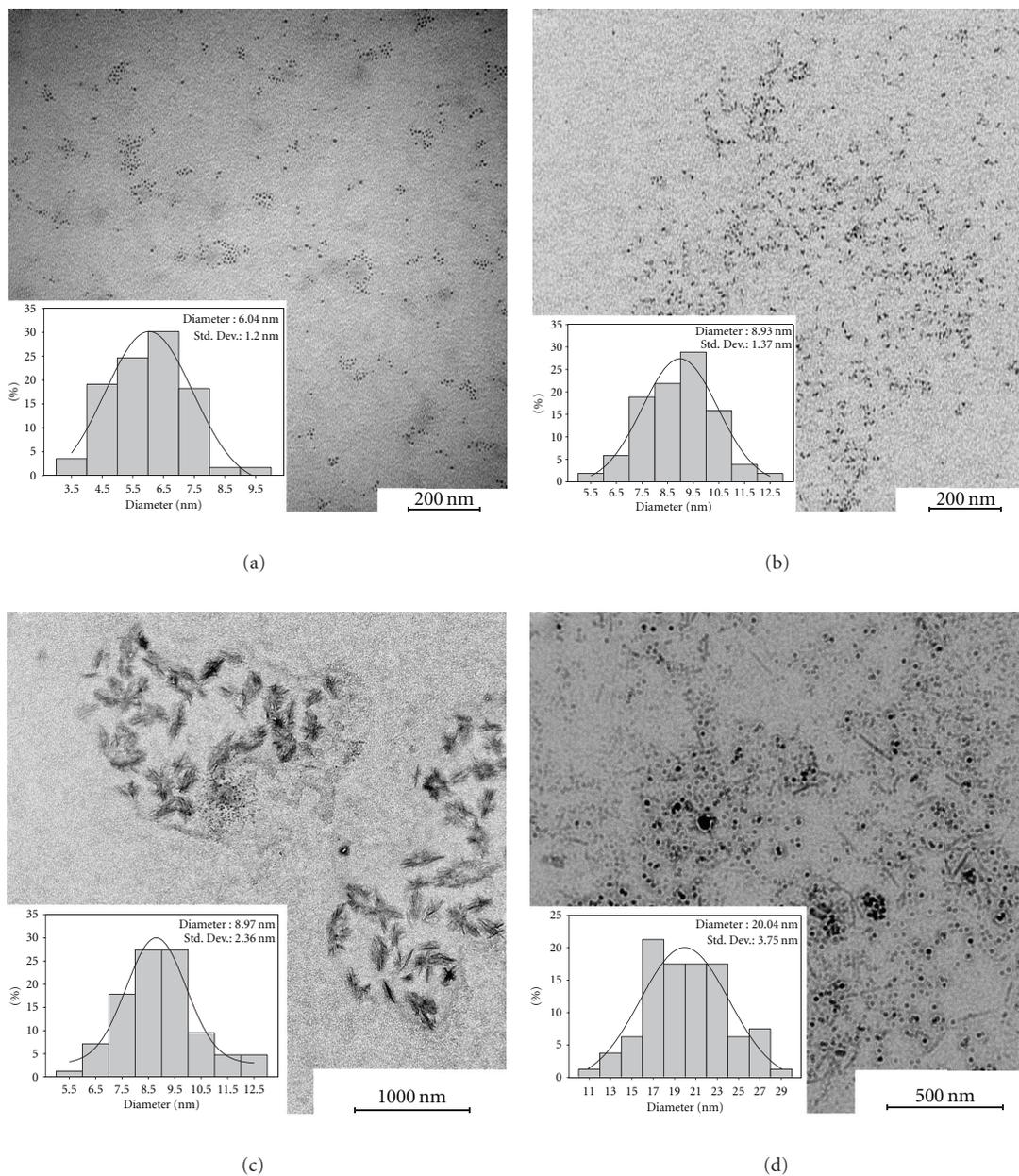


FIGURE 1: TEM images for In_2S_3 after reaction time of (a) 12 hours, (b) 1 day, (c) 2 days, and (d) 3 days. (Concentrations of In^{3+} and S^{2-} were 0.4 M).

The value of absorption coefficient can be calculated by (2) [21]

$$\alpha = \frac{1 - \log I_t/I_o}{t \log e} = \frac{1}{t} \frac{A}{\log e}, \quad (2)$$

in which t is the thickness of the quartz cell, I_t and I_o are the intensities of transmitted and incident lights, respectively, and A is the absorbance of the samples in UV-Vis measurements. The curves of $(\alpha h\nu)^2$ against $h\nu$ are shown in Figure 3(b). The band gap energy of In_2S_3 is estimated from the extrapolation of the curve to the energy axis for zero absorption coefficients. The optical band energies for In_2S_3 produced after the reaction time of 12 hours, 1 day, 2 days

and 3 days were 2.51, 2.45, 2.35, and 2.07 eV, respectively. The estimated band gap energies were larger than the bulk bandgap energy and consistent with values estimated from the literature [3, 4].

FTIR spectra for pure sucrose ester and In_2S_3 nanorods after 2 days of reaction time in sucrose ester microemulsion are shown in Figure 4. Close examination revealed that there is a band around 798 cm^{-1} , which is absent in the spectra for pure sucrose ester. This peak is due to the bonding of In-S. There is no other peak present in the spectrum except for the one that is contributed by the sucrose ester.

A mechanism formation of In_2S_3 in the aqueous droplet of the sucrose ester microemulsion is postulated in Figure 5.

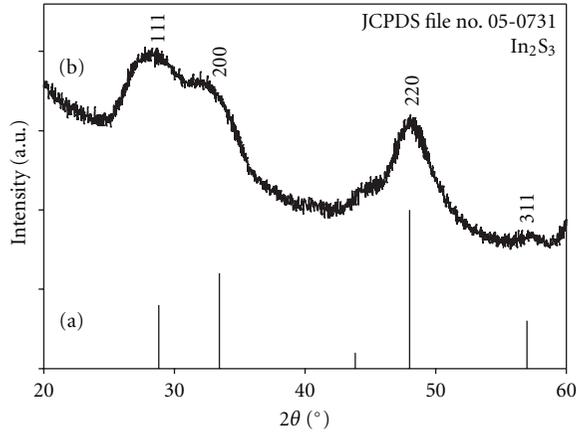


FIGURE 2: XRD patterns for (a) standard In_2S_3 cubic crystal structure diffraction peaks as per JCPDS files (05-0731) and (b) In_2S_3 nanorods synthesized in sucrose ester microemulsion after 2 days of reaction time.

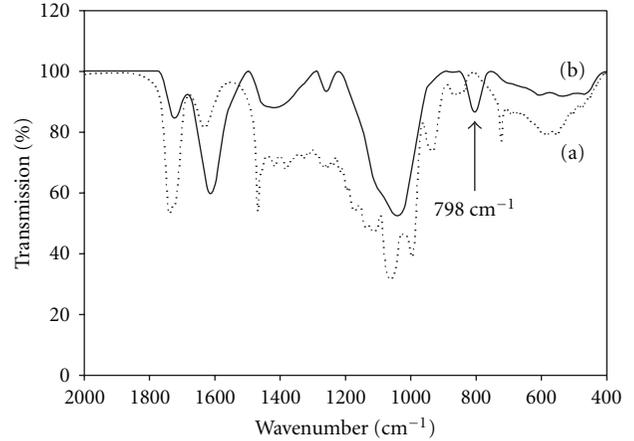


FIGURE 4: FTIR spectra for (a) pure sucrose ester and (b) In_2S_3 nanorods synthesized in the sucrose ester microemulsion system after 2 days of reaction time.

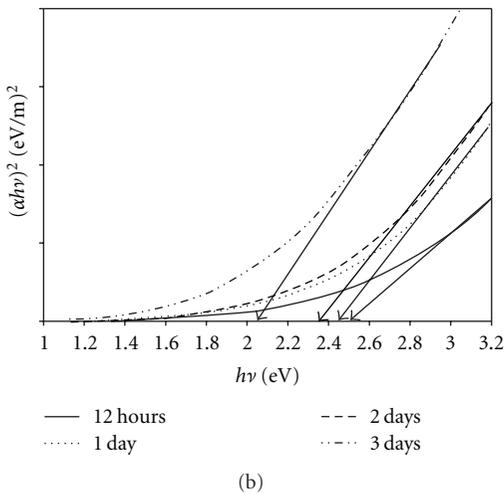
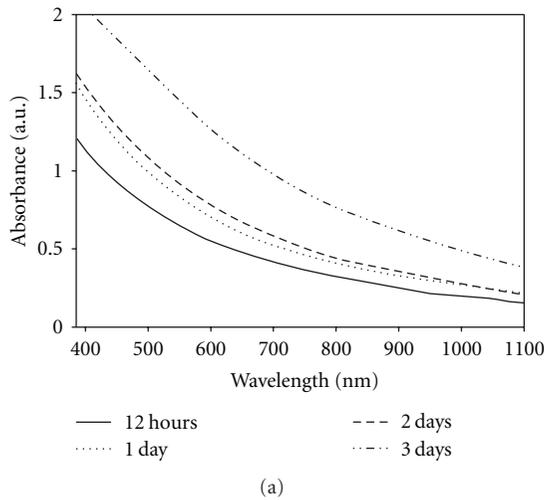


FIGURE 3: UV-Vis spectrum for In_2S_3 produced from sucrose ester microemulsion (a) and plot $(\alpha h\nu)^2$ against $h\nu$ for the estimation of bandgap energy (b).

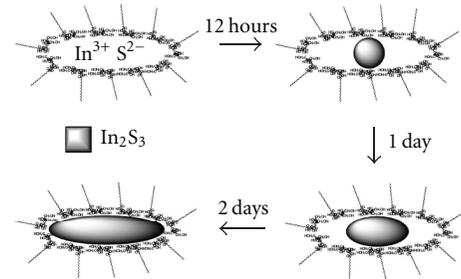


FIGURE 5: Schematic formation mechanism of In_2S_3 nanoparticles in sucrose ester water-in-oil microemulsion.

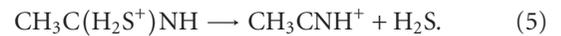
When indium chloride and thioacetamide are added into the microemulsion system, thioacetamide (TAA) hydrolyzes in the aqueous solution and releases H_2S slowly at room temperature at $\text{pH} > 2$. TAA released S^{2-} ions slowly by the following stoichiometry [28]:



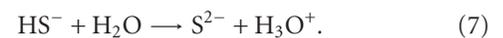
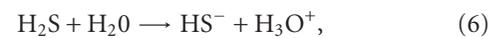
Protonation from H^+ :



This interspecies from stoichiometry (4) will decompose to form H_2S :



In the aqueous solution, H_2S hydrolyzes:



After the formation of S^{2-} ions, they will react with In^{3+} :



This property is exploited to decrease the rate of In_2S_3 formation in the aqueous cores as S^{2-} ions react with In^{3+} ions as shown schematically in Figure 5. After mixing the reactants with the microemulsion system thoroughly, TAA will hydrolyze and release S^{2-} ions slowly before reacting with In^{3+} ions to form In_2S_3 in the aqueous droplets of the microemulsion. After 12 hours of reaction time, spherical nanoparticles are formed in the prolate-shaped water droplets. After 1 day of reaction time, the particles grow larger and are slightly elongated. Rod-like particles are formed after 2 days of reaction time. The slow reaction kinetics of TAA allows efficient mixing of indium (III) chloride and TAA within the aqueous geometry of the microemulsion template.

4. Conclusion

In_2S_3 nanorods with diameter <10 nm were synthesized in a w/o microemulsion system using a food grade biosurfactant, sucrose ester S1670. Thioacetamide was exploited as a sulfur source that slowly reacts with In^{3+} ions in the water droplets of the microemulsion to form In_2S_3 nanoparticles. The prolate shape of the w/o microemulsion water droplets served as an excellent template for the synthesis of rod-like materials. The absorption spectra of the In_2S_3 nanorods shows blue shift compared to that of the bulk In_2S_3 with estimated band gap energy of 2.07 to 2.51 eV depending on the reaction time. This microemulsion templating synthesis method provides a convenient route for the formation of rod-like In_2S_3 nanoparticles with very small diameter, which serves the basis for further studies of quasi one-dimensional (1-D) nanostructure particles of other materials.

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