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*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 $8.97 \pm 2.36$ 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 $H_2S$, $(NH_4)_2S$ [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 $In(ClO_4)_3$ 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) tertoctylphenyl 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 $0.02^\circ s^{-1}$ in a $2\theta$ range from 10° to 60° with Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å). Ultraviolet-visible spectroscopy (UV-Vis) was carried out at room temperature using a Perkin Elmer Lamda-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 $6.04 \pm 1.20$ nm and $8.93 \pm 1.37$ 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 $8.97 \pm 2.36$ nm and an average length of ~100 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 $20.04 \pm 3.75$ 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.

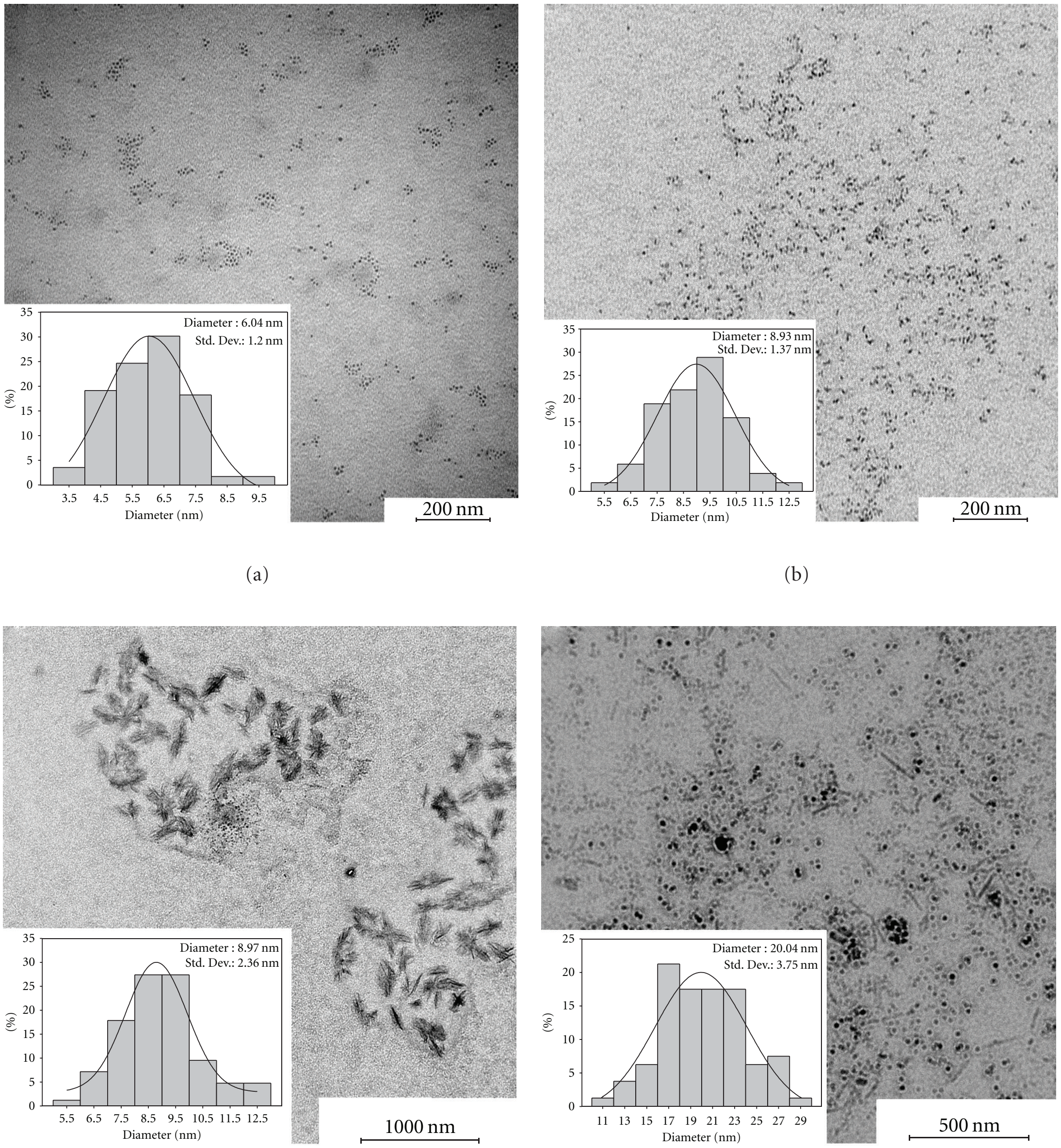
Figure 2 shows the X-ray diffraction (XRD) pattern of indium sulfide nanocrystals after the reaction time of 2 days. The peaks at $2\theta = 28.82^\circ$, $33.64^\circ$, $47.95^\circ$ and $56.99^\circ$ are attributed to (111), (200), (220), and (311) crystal planes, which are indexed to $In_2S_3$ with cubic crystal structure (JCPDS file no. 05–0731). Based on the lattice constant calculation using spacing ($d_g$) of the (220) plane and equation $1/d_g^2 = (h_2+k_2+l_2)/a^2$, the value a = 5.353 Å nm is close to the reported value of a = 5.358 Å 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 lain 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]

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

where $\alpha$ is the absorption coefficient, $\nu$ is frequency, $h$ is Planck's constant, $E_g$ is the gap energy of the nanoparticles, and $k$ equals a constant.



(a)

(b)

(c)

(d)

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]

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

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.

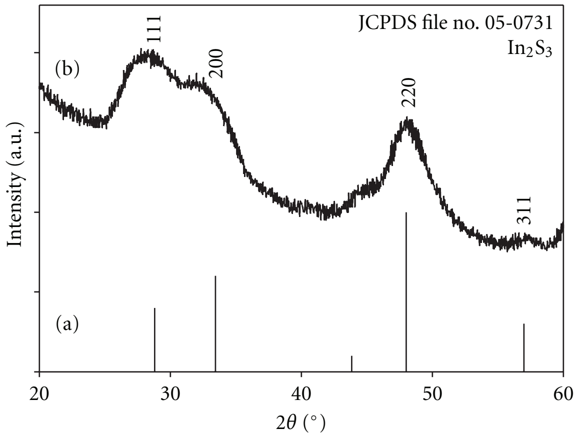
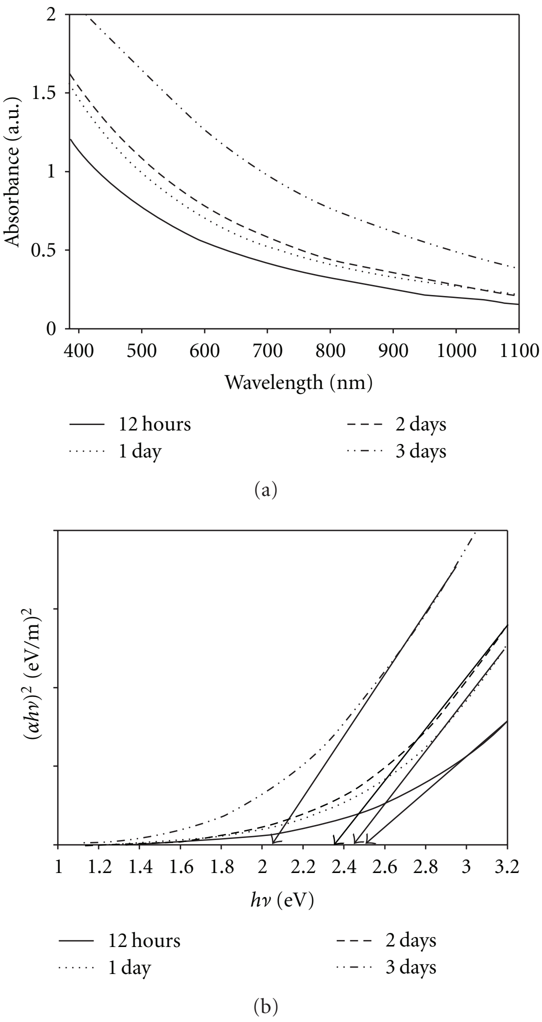


Figure 2: XRD patterns for (a) standard $In_2S_3$ cubic crystal structure diffraction peaks as per JCPDS files (05–0731) and (b) $In_2S_3$ nanorods synthesized in sucrose ester microemulsion after 2 days of reaction time.



(a)

(b)

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).

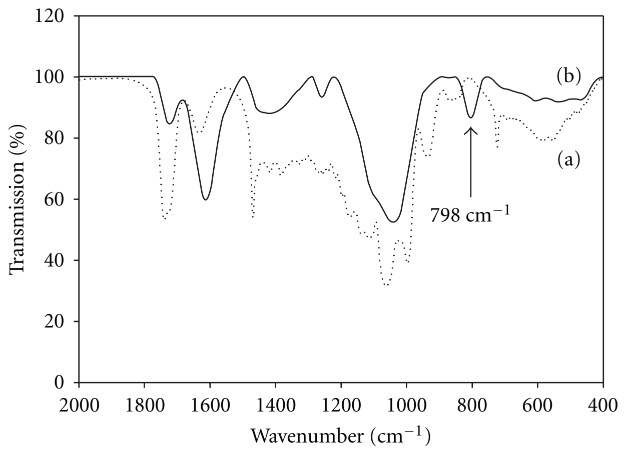


Figure 4: FTIR spectra for (a) pure sucrose ester and (b) $In_2S_3$ nanorods synthesized in the sucrose ester microemulsion system after 2 days of reaction time.

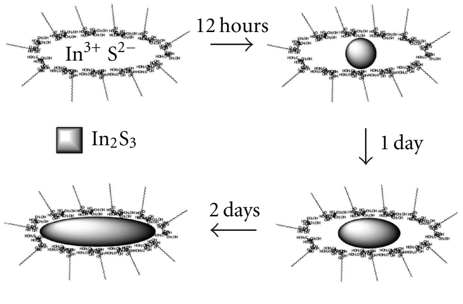


Figure 5: Schematic formation mechanism of $In_2S_3$ nanoparticles in sucrose ester water-in-oil microemulsion.

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 pH > 2. TAA released $S^{2-}$ ions slowly by the following stoichiometry [28]:

$$CH_3CSNH_2 \Longleftrightarrow CH_3C(SH)NH. \tag{3}$$

Protonation from $H^+$:

$$CH_3C(SH)NH + H^+ \Longleftrightarrow CH_3C(H_2S^+)NH. \tag{4}$$

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

$$CH_3C(H_2S^+)NH \longrightarrow CH_3CNH^+ + H_2S. \tag{5}$$

In the aqueous solution, $H_2S$ hydrolyzes:

$$H_2S + H_20 \longrightarrow HS^- + H_3O^+, \tag{6}$$

$$HS^- + H_2O \longrightarrow S^{2-} + H_3O^+. \tag{7}$$

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

$$In^{3+} + S^{2-} \longrightarrow In_2S_3. \tag{8}$$

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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## References

[1] C. H. Huang, S. S. Li, W. N. Shafarman et al., “Study of Cd-free buffer layers using $In_x(OH,S)_y$ on CIGS solar cells,” *Solar Energy Materials and Solar Cells*, vol. 69, no. 2, pp. 131–137, 2001.

[2] C. D. Lokhande, H. M. Pathan, M. Giersig, and H. Tributsch, “Preparation of Znx(O,S)y thin films using modified chemical bath deposition method,” *Applied Surface Science*, vol. 187, no. 1-2, pp. 101–107, 2002.

[3] D. K. Nagesha, X. Liang, A. A. Mamedov et al., “$In_2S_3$ nanocolloids with excitonic emission: $In_2S_3$ vs CdS comparative study of optical and structural characteristics,” *Journal of Physical Chemistry B*, vol. 105, no. 31, pp. 7490–7498, 2001.

[4] S. Gorai, D. Ganguli, and S. Chaudhuri, “Synthesis of 1D Cu2S with tailored morphology via single and mixed ionic surfactant templates,” *Materials Chemistry and Physics*, vol. 88, no. 2-3, pp. 383–387, 2004.

[5] E. Dalas, S. Sakkopoulos, E. Vitoratos, G. Maroulis, and L. Kobotiatis, “Aqueous precipitation and electrical properties of $In_2S_3$: characterization of the $In_2S_3$/polyaniline and $In_2S_3$/polypyrrole heterojunctions,” *Journal of Materials Science*, vol. 28, no. 20, pp. 5456–5460, 1993.

[6] T. Asikainen, M. Ritala, and M. Leskela, “Growth of $In_2S_3$ thin films by atomic layer epitaxy,” *Applied Surface Science*, vol. 82-83, no. C, pp. 122–125, 1994.

[7] M. Afzaal, M. A. Malik, and P. O’Brien, “Indium sulfide nanorods from single-source precursor,” *Chemical Communications*, vol. 10, no. 3, pp. 334–335, 2004.

[8] B. Yahmadi, N. Kamoun, R. Bennaceur, M. Mnari, M. Dachraoui, and K. Abdelkrim, “Structural analysis of indium sulphide thin films elaborated by chemical bath deposition,” *Thin Solid Films*, vol. 473, no. 2, pp. 201–207, 2005.

[9] C. Kaito, Y. Saito, and K. Fujita, “Studies on the structure and morphology of ultrafine particles of metallic sulfides,” *Journal of Crystal Growth*, vol. 94, no. 4, pp. 967–977, 1989.

[10] R. Nomura, S. Inazawa, K. Kanaya, and H. Matsuda, “Thermal decomposition of butylindium thiolates and preparation of indium sulfide powders,” *Applied Organometallic Chemistry*, vol. 3, pp. 195–197, 1989.

[11] J. C. Fitzmaurice and I. P. Parkin, “Self-propagating routes to Ga and In chalcogenides,” *Main Group Metal Chemistry*, vol. 17, pp. 481–490, 1994.

[12] P. N. Kumta, P. P. Phule, and S. H. Risbud, “Low-temperature wet-chemical synthesis of amorphous indium sulfide powders,” *Materials Letters*, vol. 5, no. 10, pp. 401–404, 1987.

[13] Y. Nosaka, N. Ohta, and H. Miyama, “Photochemical kinetics of ultrasmall semiconductor particles in solution: effect of size on the quantum yield of electron transfer,” *Journal of Physical Chemistry*, vol. 94, no. 9, pp. 3752–3755, 1990.

[14] P. V. Kamat, N. M. Dimitrijevic, and R. W. Fessenden, “Photoelectrochemistry in particulate systems—VII: electron-transfer reactions of indium sulfide semiconductor colloids,” *Journal of Physical Chemistry*, vol. 92, no. 8, pp. 2324–2329, 1988.

[15] A. Datta, S. K. Panda, S. Gorai, D. Ganguli, and S. Chaudhuri, “Room temperature synthesis of $In_2S_3$ micro- and nanorod textured thin films,” *Materials Research Bulletin*, vol. 43, no. 4, pp. 983–989, 2008.

[16] V. Uskokovic and M. Drofenik, “A mechanism for the formation of nanostructured NiZn ferrites via a microemulsion-assisted precipitation method,” *Colloids and Surfaces A*, vol. 266, no. 1–3, pp. 168–174, 2005.

[17] W. Zhang, X. Qiao, and J. Chen, “Synthesis and characterization of silver nanoparticles in AOT microemulsion system,” *Chemical Physics*, vol. 330, no. 3, pp. 495–500, 2006.

[18] A. Pal, S. Shah, S. Belochapkine, D. Tanner, E. Magner, and S. Devi, “Room temperature synthesis of platinum nanoparticles in water-in-oil microemulsion,” *Colloids and Surfaces A*, vol. 337, no. 1–3, pp. 205–207, 2009.

[19] M. Chen, Y. G. Feng, L. Y. Wang, L. Zhang, and J. Y. Zhang, “Study of palladium nanoparticles prepared from water-in-oil microemulsion,” *Colloids and Surfaces A*, vol. 281, no. 1–3, pp. 119–124, 2006.

[20] J. Solla-Gullón, A. Rodes, V. Montiel, A. Aldaz, and J. Clavilier, “Electrochemical characterisation of platinum-palladium nanoparticles prepared in a water-in-oil microemulsion,” *Journal of Electroanalytical Chemistry*, vol. 554-555, no. 1, pp. 273–284, 2003.

[21] P. S. Khiew, S. Radiman, N. M. Huang, and M. S. Ahmad, “Studies on the growth and characterization of CdS and PbS nanoparticles using sugar-ester nonionic water-in-oil microemulsion,” *Journal of Crystal Growth*, vol. 254, no. 1-2, pp. 235–243, 2003.

[22] N. Asim, S. Radiman, and M. A. B. Yarmo, “Synthesis of WO3 in nanoscale with the usage of sucrose ester microemulsion and CTAB micelle solution,” *Materials Letters*, vol. 61, no. 13, pp. 2652–2657, 2007.

[23] N. M. Huang, S. Radiman, H. N. Lim et al., “Synthesis and characterization of ultra small PbS nanorods in sucrose ester microemulsion,” *Materials Letters*, vol. 63, no. 3-4, pp. 500–503, 2009.

[24] H. Lim, A. Kassim, N. Huang et al., “Fabrication and characterization of 1D brushite nanomaterials via sucrose ester reverse microemulsion,” *Ceramics International*, vol. 35, no. 7, pp. 2891–2897, 2009.

[25] O. Glatter, D. Orthaber, A. Stradner et al., “Sugar-ester nonionic microemulsion: structural characterization,” *Journal of Colloid and Interface Science*, vol. 241, no. 1, pp. 215–225, 2001.

[26] S. D. Sartale and C. D. Lokhande, “Preparation and characterization of nickel sulphide thin films using successive ionic layer adsorption and reaction (SILAR) method,” *Materials Chemistry and Physics*, vol. 72, no. 1, pp. 101–104, 2001.

[27] T. Chen and K. Tang, “$\gamma$- Ga2O3 quantum dots with visible blue-green light emission property,” *Applied Physics Letters*, vol. 90, no. 5, Article ID 053104, 2007.

[28] G. Hodes, *Chemical Solution Deposition of Semiconductor Films*, Marcel Decker, New York, NY, USA, 2003.