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Preparation of Indium−Tin Oxide Particles in Shear-Induced Multilamellar Vesicles (Spherulites) as Chemical Reactors

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Spherulites, spherical multilamellar vesicles (300−10 000 nm in diameter), were formed by applying shear force to the mixture of two lamellar phases, containing inorganic salts (indium nitrate and tin chloride) in one lamellar phase (I) and a precipitating agent (ammonium hydroxide) in another lamellar phase (II). These spherulites were employed as a reaction medium to prepare the indium−tin hydroxide nanoparticles. The chemical reaction for the formation of indium−tin hydroxide particles took place in the hydrophilic layers of lamellar phase I in spherulites composed of AOT (dioctyl sulfosuccinate sodium salt), because the vesicle wall is selectively permeable to the anions but practically impermeable to cations. Inorganic salts were encapsulated within the hydrophilic layers of spherulites. Indium−tin hydroxide particles were collected by breaking the spherulite structures by adding acetone after reaction, and spherical indium−tin oxide (ITO) particles of about 10−30 nm in size were obtained after calcination of indium−tin hydroxide particles at 700 °C for 2 h.

Introduction

Because of their amphiphilic nature, surfactant molecules tend to self-assemble into various types of large aggregates in a solution (in either water or oil). These aggregates such as micelles, vesicles, microemulsions, and lyotropic liquid crystals were well-characterized by many authors and have been used in a wide variety of applications in science and technology.[1,2]

The preparation of ultrafine monodispersed particles has attracted a great deal of attention due to their technological applications such as for ceramics, magnetic particles, semiconductors, superconductors, and metallic catalysts. Surfactant aggregates can offer an interesting reaction medium for the preparation of these particles with a certain shape and size distribution because they can solubilize, concentrate, localize, and even organize the reactants. The synthetic methods and characterization of particles prepared in surfactant aggregates have been reported in numerous papers. In addition, we have reported that the shape and size of ITO (indium−tin oxide) particles prepared in AOT (dioctyl sulfosuccinate sodium salt)-based reverse microemulsions were in good agreements with those of water droplets in microemulsions.[3] Besides reverse microemulsions, various surfactant aggregates such as micelles, lamellar structures, vesicles, and monolayers can be used as synthetic medium for the preparation of particles. The particles of $Cu_4(OH)_6SO_4$ synthesized in CTAB/hexanol/water lamellar liquid crystals were spherical particles or sheets in shape and have narrow size distributions.[4] Particle size increased with reaction time, but the rate of growth of particles in aqueous solution was much faster than that in liquid crystals. The PbS ultrafine particles were synthesized in Triton X-100/$C_{10}H_{21}OH/H_2O$ lamellar liquid crystals, and the particles are spherical, with narrow size distribution and average sizes below 8 nm.[5]

Surfactant vesicles are long-lived entities that do not undergo the exchange of their water content. For this reason, they were widely used as encapsulating systems essentially referred to as "liposomes" (which is the common name for vesicles made of lipids). Liposomes have a variety of applications ranging from stabilization of the active agent in skin care lotions to the controlled delivery of drugs.[6,7] However, reactivity in liposomes is limited because of the aqueous nature of the internal core, the weak permeability of reactants through the membrane, and the poor encapsulation efficiency. Up to now, applications of liposomes as the reaction medium have mainly been limited to photochemical reduction of metallic salt dissolved in the aqueous core of vesicles or polymerized vesicles.[8,9] However, several vesicular systems have been employed as a reaction

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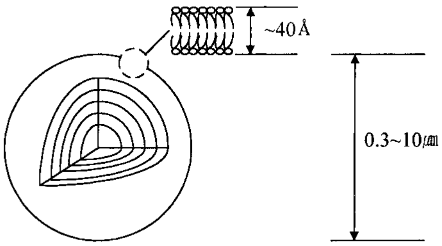

Figure 1. Schematic representation of spherulite (from Gauffre and Roux[9]).

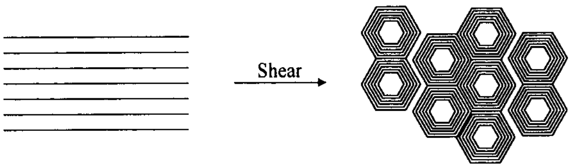

Figure 2. Schematic diagram for spherulites formation from lamellar structure by shear force.

medium for the preparation of nanoparticles. Bose et al. synthesized magnetic nanoparticles in unilamellar vesicles of anionic and cationic surfactant mixtures in aqueous solution. The particles have spherical shape of 2.6 nm diameter, which is smaller than that of particles prepared in reverse microemulsion.[10]

Recently, it was discovered that lamellar phase can undergo structural transformations into vesicular shape by application of external shear force.[11,12] At very low shear rate (typically below 1 s^{-1}), the layers are mainly parallel to the flow with defects (dislocations) in the two other directions. At very high shear rates, the orientations of lamellar phases are similar but the defects in the flow direction have been suppressed. For intermediate shear rates, the lamellar phase organizes itself into multilamellar vesicles, the so-called onions or spherulites (see Figure 1), which are closed and closely packed in space (see Figure 2).[9] Actually the cryo-fracture observation reveals that the structure of these closely packed spherulites is not spherical but polyhedral.[13]

One characteristic of this intermediate state is that all spherulites formed under shear flow have the same size. This size can be in a range from a few micrometers to a tenth of this size[14,15] It has been proposed that this size distribution is due to the balance between the viscous stress applied to lamellar structure and the elastic stress.[16] It has been proposed that the size of spherulites (D) can be correlated with shear rate (γ) by the following equation:[15,16]

$$D \sim \gamma^{0.5} \tag{1}$$

According to Van der Linden and co-workers' results,[17] the relationship between shear rate (γ) and viscosity of spherulite (η) can be expressed by eq 2 when the weight percent of AOT was 30% and the brine solution contains 10 g/L of NaCl.

$$\eta \text{ (in Pa·s)} = 8\{\gamma \text{ (in s}^{-1})\}^{-0.55} \tag{2}$$

Another feature of this intermediate state is that the spherulite structure can be quenched by quickly stopping the shearing. Then, the spherulite structures are relaxed very slowly over a few days to several months, depending particularly upon the composition of lamellar.[18]

The permeability of encapsulated cations through vesicle wall depends on the adsorption of ions into wall. The more adsorption into vesicle wall, the lower is the permeability of ions. Tricot and Fendler found that strong adsorption of Cd^{2+} ions on negatively charged DHP (dihexadecyl phosphate) vesicles took place up to a density of one Cd^{2+} per three DHP molecules. Therefore, at 2×10^{-3} M DHP concentration, up to about 6.5×10^{-4} mol of Cd^{2+} was adsorbed. Any excess remained in the outer bulk aqueous solution.[19]

In the case of lipid membranes, the diffusion rate of many anions is known to be ca. 10^5 times faster than that for cations which have very low permeability across membranes.[20] So actually, only small anions can diffuse down their chemical potential gradient into the vesicles.

In addition, leakage experiments have been carried out for various surfactant species in vesicles using different solutes. Despite considerable accumulations of experimental results, the mechanism of surfactant-induced vesicle leakage is far from understood.[21]

In this study, as a continuation of our previous research regarding the preparation of ITO particles in AOT-based reverse microemulsion,[3] ITO particles were prepared through intra- and intervesicular reaction of OH^- ions with aqueous solution of $In(NO_3)_3/SnCl_4$ in spherulites composed of AOT surfactant as nanoreactors.

Thin films formed by ITO powders have widely been used for transparent conducting layers in various optoelectronic devices such as liquid crystal displays, plasma display devices, and solar cells. The preparation processes of ITO films include spray, chemical vapor deposition, evaporation, and sputtering. Among these, the most preferred technique in a production line is sputtering method using ITO targets. The ITO targets for sputtering are made from ITO powders by a molding or sintering process. To obtain high-density ITO targets, it is compulsory to use ultrafine and monodispersed ITO powders.

The microstructure of spherulite employed as the reaction medium was investigated by cryo-SEM. The shape and size of particles were studied by FE-SEM (field emission-scanning electron microscopy), and the chemical compositions of particles were analyzed with EDS (energy dispersive X-ray spectrophotometer).

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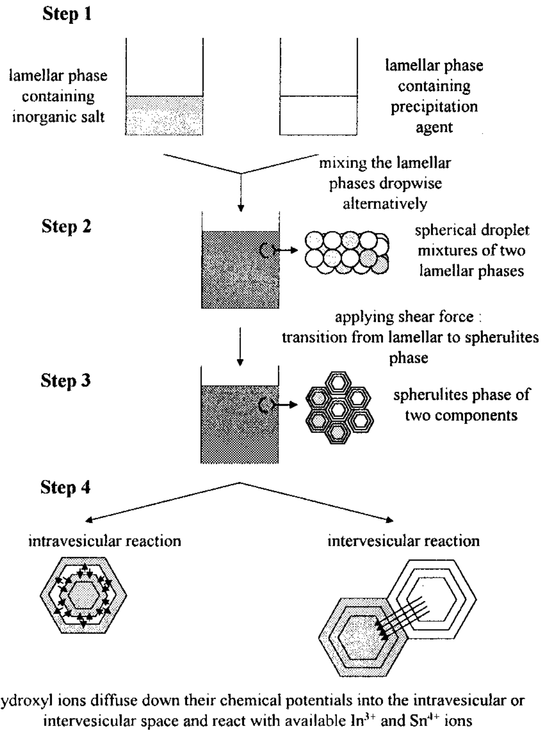

Figure 3. Schematic diagram of the reaction for the formation of ultrafine particles in spherulites.

Experimental Section

Materials. AOT (Sigma, 99.9%) and deionized water (electrical resistivity, 18.2 MΩ) were used to form lamellar structures. Indium nitrate pentahydrate ($In(NO_3)_3{\cdot}5H_2O$, High Purity Chemicals, Japan, 99.99%) and tin chloride pentahydrate ($SnCl_4{\cdot}5H_2O$, Katayama Chemicals, Japan, 99.9%) as inorganic reactants, NH_4OH (Mallinckrodt Chemicals, U.S.A., NH_3, 29.7%) as precipitating agent were used to prepare indium−tin hydroxide particles.

Formation of Spherulites for the Synthetic Reaction. Both 0.1 M of indium nitrate pentahydrate and 0.0099 M of tin chloride pentahydrate were dissolved in 1 L of distilled water to keep an atomic ratio of indium to tin of 9:1. AOT was added into this aqueous solution until the weight percent of AOT reached 40.0% in a glass vial to prepare lamellar structure I. This mixture was heated to 120 °C for 2 h to dissolve AOT, mixed thoroughly by a vortex mixer about 5 min, and kept at room temperature until an equilibrium state was obtained. Lamellar structure II was prepared by mixing 0.5 M NH_4OH aqueous solution with the same amount of AOT as lamellar structure I (step 1 in Figure 3).Drops of lamellar structure I and lamellar structure II were added alternately into glass beaker (step 2 in Figure 3). Because the two lamellar phases were very viscous, it would be impossible to have a homogeneous mixture if both lamellar phases I and II were mixed together in full. The lamellar mixture was converted into the spherulites structure by applying shear force into the mixture of lamellar phases I and II at room temperature (step 3 in Figure 3). The mixture was manually agitated using a bar in a glass beaker. While the shear force was being applied to the mixture, the mixed lamellar structures became turbid and more viscous. After about 2 h, the mixed lamellar structure becomes transparent. Finally, a transparent and birefringent mixture was obtained. Turbidity was caused due to both the relatively long time required to reach equilibrium and the high viscosities of structures I and II, and an increase in viscosity was observed upon applying shear force into the mixture.

The mixed lamellar structure was kept at room temperature for 2 days to allow enough reaction time (step 4 in Figure 3). The particles formed in spherulites were not sedimented due to the adsorption of surfactant molecules onto the surface of particles and the high viscosity of reaction medium. After the reaction, acetone was added to break the spherulite structures and to cause sedimentation of indium−tin hydroxide particles. The sedimented indium−tin hydroxide particles were washed with acetone and pure water successively to remove surfactant molecules and sodium ions from the particle surfaces. Indium hydroxide particles doped with tin hydroxide were converted into indium−tin oxide particles by calcination at 700 °C for 2 h.

Cryo-SEM (Topology of Reaction Medium). A drop of the sample (reaction medium) was placed into a copper holder and then rapidly quenched in a liquid-nitrogen chamber. The frozen sample was fractured at 93 K and 10 Pa with a liquid-nitrogen-cooled knife in a cryo-chamber (BIO-RAD, E7450). The etching was done to sublime ice from the specimen surface at 203 K for 15−20 min, and then, the specimen was coated with gold by sputtering at 93 K for 195 s in a sputtering module (BIO-RAD, E7400). Photographs were obtained using a scanning electron microscope (JEOL, JSM-840A) operating at 20 kV and a stage temperature of 93 K at 3000−8000 magnification.

Morphology of Particles (FE-SEM). The morphology of particles formed in spherulites was studied with FE-SEM (JEOL model JSM-6340F). Spherulites containing indium−tin hydroxide particles were coated with gold by sputtering for 10 s before observation. However, in the case of ITO, coating was not needed because of its high electrical conductivity. Photomicrographs were obtained by operating at 15 kV, with a working distance of 6−8 mm at 6000−100 000 magnification.

EDS (Chemical Composition of Particles). The chemical composition of the particles was investigated with a EDS component attached to FE-SEM.

Results and Discussion

Chemical Reaction for the Formation of Indium−Tin Oxide Particles. Indium nitrate and tin chloride in aqueous solution react with ammonium hydroxide to produce indium−tin hydroxide particles by the following overall reaction mechanism:[22]

$$In(NO_3)_3 + 3NH_4OH \rightarrow In(OH)_3 + 3NH_4^+ + 3NO_3^-$$

and

$$SnCl_4 + 4NH_4OH \rightarrow Sn(OH)_4 + 4NH_4^+ + 4Cl^-$$

Because indium and tin salts are present in the same aqueous phase, a simultaneous doping reaction takes place between indium hydroxide and tin hydroxide proportional to their compositions:

$$In(OH)_3{:}Sn(OH)_4 + 7NH_4^+ + 3NO_3^- + 4Cl^-$$

Indium hydroxide particles doped with tin hydroxide are converted into indium−tin oxide particles by calcination at 700 °C for 2 h by following reaction mechanism:

$$In(OH)_3{:}Sn(OH)_4 \rightarrow In_2O_3{:}SnO_2$$

The partial substitution of In^{3+} ions into crystalline indium oxide by Sn^{4+} ions yields the electron holes in the indium−tin oxide crystal. When electrical potential is applied to this material, electron holes act as electron

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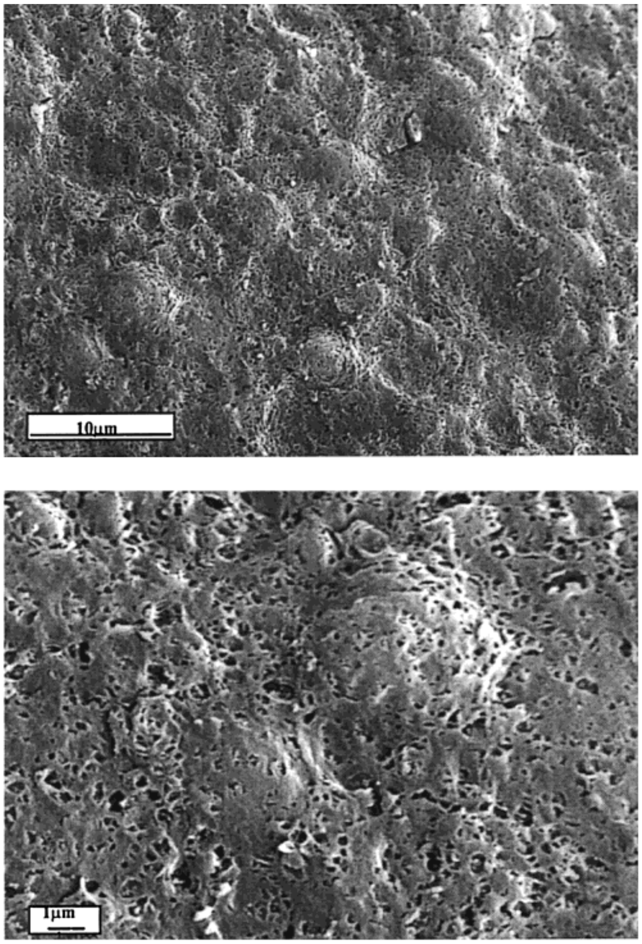

Figure 4. Cryo-SEM pictures of perforated spherulites containing indium−tin hydroxide particles (before calcination).

carriers. The electrical conductivity of ITO depends on the carrier concentration and the carrier mobility.[23]

Spherulites Containing Indium−Tin Hydroxide. The views of freeze-fractured pictures of spherulites after mixing two lamellar phases under strong shear force are shown in Figure 4. In these pictures, the spherelike structure that is highly perforated can be observed. The size distribution of the spherelike structure was about 1.7−4.8 μm in diameter. This result implies that the applied shear forces changed the lamellar structure into spherulites. Similar transition behavior has been observed by many authors.[13,15−17,24−26] For a more detailed observation, completely packed spherulites were diluted with acetone, and a small amount of dispersion of spherulites was placed on the FE-SEM mount. The sample surface was observed using FE-SEM. Figure 5 shows more apparently the spherulites structure.

In addition, one can observe the perforated structure (the so-called passages, mesh structure (L_α^H)). The transition between the sponge (L_3) and lamellar (L_α) phase has been induced by varying the temperature,[27−29] the salt concentration,[30,31] or in the case when a cosurfactant is present, the cosurfactant/surfactant ratio.[32−34] These transitions take place during equilibrium between the thermodynamically stable systems.[35]

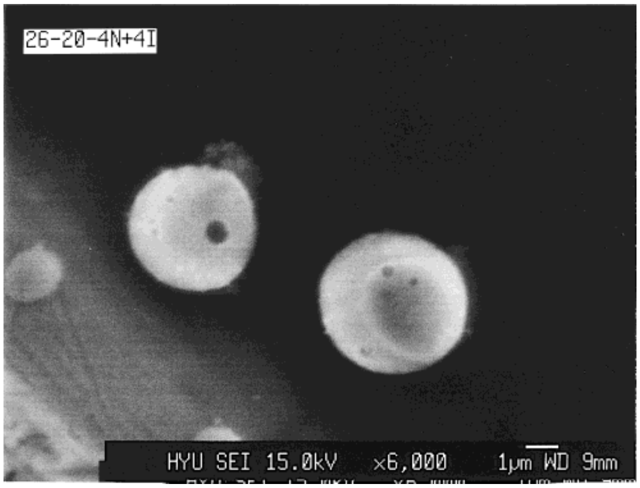

Figure 5. FE-SEM pictures of perforated spherulites containing indium−tin hydroxide particles after dilution with acetone (before calcination).

Lamellar structure was formed below 140 °C in the binary system of AOT and water mixtures[36] when the weight percent of AOT is 40%. No defective (mesh or passage) structure was observed. Strey et al. found the passages between the layers in AOT/brine system and reported that from a theoretical point of view, they are expected[37,38] to be the precursors of the transformation from L_α to L_3.[39] From the above-mentioned facts, we can see that perforated spherulites were induced from the perforated lamellar structure by shear force.

Despite their relatively large and wide size distribution, the closely packed spherulites containing indium−tin hydroxide particles were transparent. The closely packed spherulites were essentially transparent since the refractive indexes of the spherulite and its surroundings are not different from one another. Spherulites can only be distinguished from their surroundings by curvature because curvature of their outer bilayer is different from the average curvature of their surroundings. Therefore, it can be inferred that the reaction for the formation of particles takes place at hydrophilic layers of spherulites with dimension of nanometer size. The size of prepared particle is in the nanometer level

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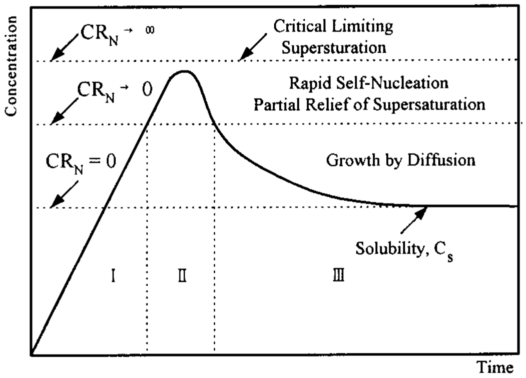

Figure 6. Schematic representation of the concentration of molecularly dissolved sulfur before and after nucleation as a function of time (from Tricot and Fendler[19]).

because of the nanometer level size of reaction field and prepared particles have no flocculation and agglomeration due to the stabilizing and protecting effects by surfactant bilayers.

Reaction for Particle Formation in Spherulites. The reaction medium in this study consisted of closely packed spherulites systems of AOT. There is no outer water phase, and spherulites are distinguished from surroundings by their curvatures. Thus, leakage of cations is not important as it is in unilamellar system in aqueous solution. However, bilayers of vesicle wall are selectively permeable to small anions, and cations are bound at hydrophilic headgroups of anion surfactant molecules (AOT).

Nuclei can be formed from clusters of a few molecules or ion pairs of components of the precipitate. The formation of nuclei from ions is an energy-consuming process because an organized structure with well-defined surfaces is created from a random arrangement of solution constituents. Because of this energy requirement, it is necessary for the solution to be supersaturated or to have concentrations greater than that predicted by equilibrium with the precipitate, before the precipitates are formed from a homogeneous solution.

Vesicle walls are permeable to small anions but allow no cation-transport. Only OH^- ions diffuse down their chemical potential gradient into the vesicular space of other hydrophilic layers of vesicular space and react with available In^{3+} and Sn^{4+} ions to form intravesicular indium−tin hydroxide particles. Hydrolysis reaction occurred by diffusion of hydroxyl ions at the inside of hydrophilic headgroups of bilayers. In 1950, La Mer and Dinegar proposed a nucleation and growth model for the sulfur sol.[40] This model was generally used to explain the nucleation and growth of colloidal particles. In addition, the nucleation and growth of indium−tin hydroxide particles in spherulites can be explained by the La Mer and Dinegar model.

When the concentration of hydrolyzed species reached supersaturation concentrations, nucleation occurred (stage II in Figure 6). Actually, the hydrolysis reaction occurred at the hydrophilic headgroup site, and hydrolyzed species existed in very thin hydrophilic layers of spherulites. As a result, restriction of the hydrolysis reaction site and mobility cause the decrease in the probability of nucleation at a moderate supersaturation level. Therefore, the nucleation occurred simultaneously at many sites at high supersaturation concentrations. After nucleation, the low levels of supersaturation were maintained by the slow rate of hydroxyl ion influx. Only this level of supersaturation can bring the controlled growth of well-defined crystallites (stage III in Figure 6).

In the coprecipitation process, the initial concentrations are moderately high, and there is no restriction of the hydroxyl ion concentration and reaction field. So, the rate of production of hydrolyzed species by reaction will become so rapid that the concentration of hydrolyzed species continuously exceeds the concentration that can bring nucleation. Thus, nucleation and growth of the particle happen simultaneously. Obviously, the size of the particle will depend on when it was formed. As a result, nonuniform growth occurred. Nonuniform growth of particle caused the irregular shape and wide size distribution for the prepared particles. This result was observed by many authors and was also reported in our previous paper.[3]

When the cations that were contained in hydrophilic layers were entirely consumed, the reaction for particle growth would be ended. Residual hydroxyl ions diffuse into other hydrophilic layers containing available cations, and same particle formation process would be repeated.

In the microemulsion method, ultimate particle size was controlled by the geometrical restriction of the water pool (film rigidity, water pool size, and so on) and the concentrations of reactants in microemulsion droplet.[3] However, in the case of spherulite method, the final particle size can be controlled by mainly nucleation and particle growth mechanism due to selective permeability of bilayers.

Particles produced in spherulites were stabilized by steric hindrance of bilayers as well as friction between bilayers and particles. Ostwald ripening did not occur because of low solubility of indium−tin hydroxide and relatively uniform particle size distribution due to controlled particle growth.

Size of Nanoparticle Prepared in Spherulites. Indium−tin hydroxide nanoparticles was obtained by destroying the spherulites. Figure 7, shows three pictures of ITO particles that were obtained after calcination. These pictures are very interesting. The material for Figure 7a was obtained by calcination of spherulites themselves after reaction involving indium−tin hydroxide. One can observe very densely packed spherulite agglomerates. During the calcination process, defective spherulites form agglomerates with distorted individual boundaries. However, the defectiveness of spherulites was maintained throughout the calcination process and could be observed clearly in the SEM picture. In this picture, nanoparticles are not observed. However, In, Sn, O, Na, and S components were detected in EDS analysis as shown in Figure 8a.The spherulites containing indium−tin hydroxide particles with defective structure were collapsed partially during the washing process. The sample was obtained during the middle of the washing process and calcinated. Figure 7b shows the SEM for calcinated ITO particles of this sample, and one can observe the nanosize particle at the point of partly collapsed spherulites.

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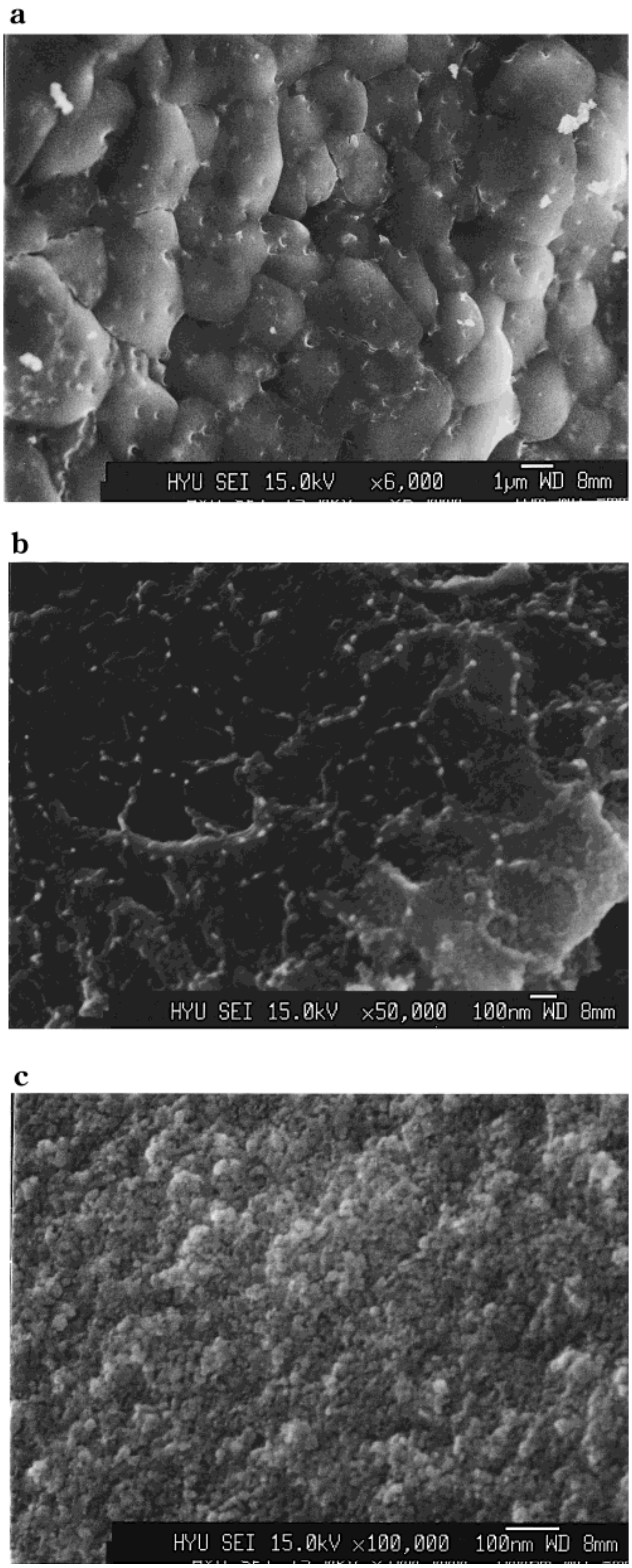

Figure 7. FE-SEM pictures after calcination of (a) intact spherulites containing indium−tin hydroxide just after reaction, (b) partially collapsed spherulite during washing process, and (c) indium−tin hydroxide particles prepared in spherulites after complete washing.

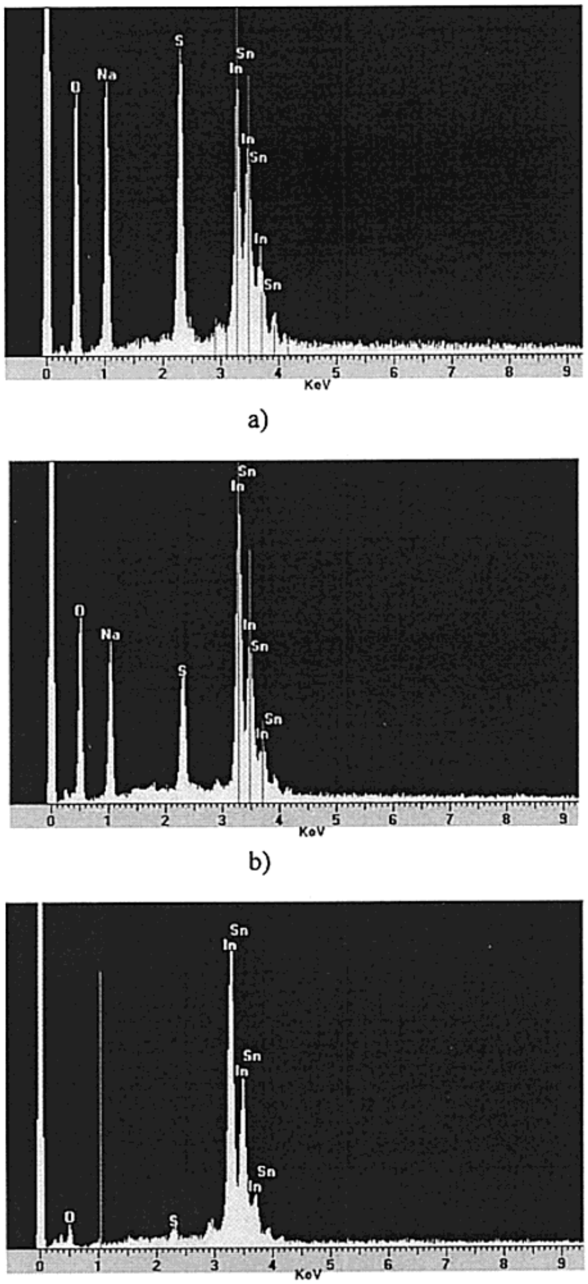

Figure 8. Chemical compositions after calcination of (a) intact spherulites containing indium−tin hydroxide just after reaction (b) partially collapsed spherulite during washing process, and (c) indium−tin hydroxide particles prepared in spherulites after complete washing.

Finally, the structure of spherulites containing indium−tin hydroxides with defects was completely collapsed after the washing process. The calcinated ITO particles were reformed into agglomerates consisting of nanosized ITO particles that range from about 10 to 30 nm by the complete destruction of spherulites, as shown in Figure 7c.

When the chemical compositions of each state were analyzed by EDS, it was found that the atomic percent of tin was approximately 9.0%. The peaks for oxygen, sulfur, and sodium from AOT were strongly detected at spherulites agglomerates that were composed of defective spherulites with distorted individual particle boundaries, but in the case of ITO particle agglomerates, no sodium peak was detected, and sulfur was detected at only 1.9 atom % as is shown in Figure 8c. These facts imply that indium−tin hydroxides were prepared in hydrophilic layers of spherulites structures and that the prepared particles possessed a size of 10−30 nm.

Conclusion

Bilayers of spherulites are permeable to small anions but allow no cation transport. Only OH^- ions diffuse down their chemical potential gradient into the other vesicular spaces of other hydrophilic layers of the vesicles and react with available In^{3+} and Sn^{4+} ions to form intravesicular indium−tin hydroxide particles. The indium−tin hydroxide particles formed in spherulites structure were not sedimented due to the strong stabilization effect by steric hindrance and low mobility due to the high viscosity of the reaction medium. After reaction, the ultrafine indium−tin hydroxide particles were obtained by destroying the spherulite structures, and indium−tin hydroxide was reformed into dense agglomerates of ITO particles whose diameters were about 10−30 nm by calcination.

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