

# Synthesis and Characterization of metallic Indium embedded SiO<sub>2</sub> composite nanoparticles by reverse micelle and sol-gel processing

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**Abstract**— Metallic In nanoclusters were embedded into SiO<sub>2</sub> matrix that were synthesized within reverse micelle via a solution reduction of In(NO<sub>3</sub>)<sub>3</sub> by hydrazine hydrate. The size of the particles can be controlled by manipulating the relative rates of the hydrolysis and condensation reaction of tetraethoxysilane within the microemulsion. The spherical equivalent size for the In clusters formed in SiO<sub>2</sub> matrix was estimated to be around (3±1) nm. The presence of In in the matrix was confirmed by EDS spectroscopy. The effects of synthesis parameters, such as the molar ratio of water to surfactant and the mechanism of composite formation are discussed.

**Index Terms**— Nanoparticles, Micelle, Sol-gel processes, SiO<sub>2</sub> matrix, microemulsion, nanoclusters, Transmission electron microscopy

## 1 INTRODUCTION

Nanoparticle composites have been given importance because the connection of two semiconductor nanocrystals will lead to a series of novel optical and electronic properties [1, 2]. Oxides, such as silica, are particularly interesting as host matrices for metal and semiconductor nanoparticles, because they can be used as catalytic supports, as insulating and protective coatings, and also as carriers in biological applications [3]. The general principle of nanocomposite preparation involves the intimate mixing of nanocrystals with a processable matrix such as micelles [4] and [5]. The preparation of nanoparticles in a reverse micelle system has attracted great attention because of its possibility to obtain monodispersed particles in nm size [6]. In addition, the water pool in the reverse micelle cage can be expected as hydrolysis and polymerization reaction field of the silica [7]. Recently a number of attempts have been made to use this technique to prepare nanoparticles as Pd embedded TiO<sub>2</sub> [8] and Ag/Pd doped SiO<sub>2</sub> [6]. The nanometer-sized composite particles were synthesized in reverse micelles through two steps [9]. First, spherical nanometer-sized clusters of a metal such as In having various diameters were prepared in reverse micelles. Second, after the formation of nanometer-sized clusters, the fabrication of nanometer-sized composite particles of In/SiO<sub>2</sub> was fabricated by hydrolysis and condensation of the organometallic precursors such as tetraethoxysilane (TEOS) in the microemulsion matrix. The object of this study is to prepare In nanoclusters that were embedded into silica matrix by a combined reverse micelle and sol-gel technique.

## 2 EXPERIMENTAL PROCEDURE

Reverse micelles were prepared from non-ionic surfactants using the procedures as reported elsewhere [9]. The non-ionic surfactant Igepal CO-520, poly (oxyethylene) nonylphenyl ether, was also from Aldrich Chemical Company. Surfactants were used without further purification. Other chemicals, such as tetraethoxysilane (TEOS, Aldrich Chemical Co.), cyclohexane (TEOS, Aldrich Chemical Co.), ammonium hydroxide (28% Dae Jung Chemicals), Indium (III) nitrate (Aldrich Sigma Aldrich Chemical Co), hydrazine hydrate (9M N<sub>2</sub>H<sub>4</sub>X·H<sub>2</sub>O, Aldrich Chemical Co.) were used as received.

The microemulsion reaction matrix was prepared using Igepal. A typical recipe was 20 ml of a microemulsion prepared at ambient temperature in a 30 ml vial with rapid stirring. The microreaction reactant compositions were 4 g surfactant, 10 ml Cyclohexane and 0.65-1.3 ml of 0.04 M aqueous solution of Indium (III) nitrate. The amount of aqueous solution was added in accordance with the different molar ratio of water to surfactant,  $R = [\text{water}] / [\text{surfactant}]$ . The microemulsion was mixed rapidly, and after 5 min of equilibration, one drop (~0.05 mL) of hydrazine hydrate (9M N<sub>2</sub>H<sub>4</sub>X·H<sub>2</sub>O, Aldrich Chemical Co.) was added as a reducing agent. After nanosize water droplets formed while stirring, TEOS was added into the stirred microemulsion. The ratio of water to TEOS  $H = [\text{water}] / [\text{TEOS}]$  was maintained at 100, which is the most important factor dictating the size of the nanoparticle. NH<sub>4</sub>OH was injected into the microemulsion to accelerate the condensation reaction of metal alkoxide precursors. The amount of base added was maintained through another ratio:  $X = 1 / [\text{NH}_4\text{OH}] / [\text{TEOS}]$ . The size of the nanoparticles was observed by Transmission electron microscopy (JEOL-3010). EDS spectrum of the composite nanoparticles was obtained by

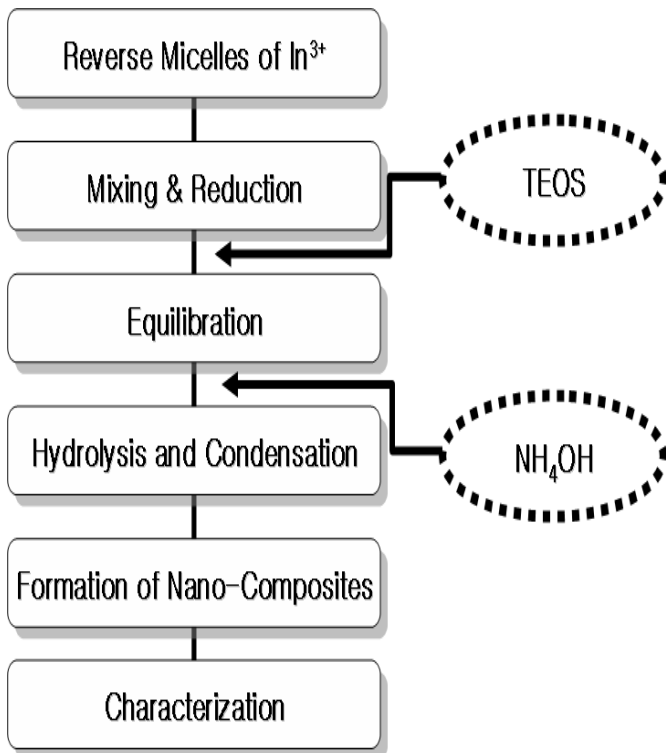


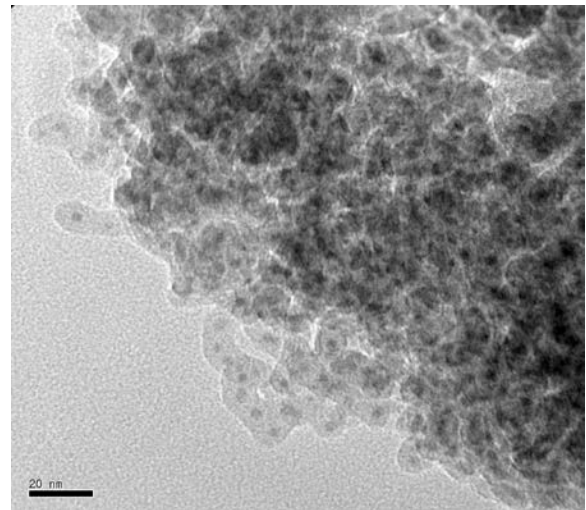
Fig. 1 Flow chart for the preparation In/SiO<sub>2</sub> core shell particles by reverse micelle and sol-gel processing

### 3 RESULTS AND DISCUSSION

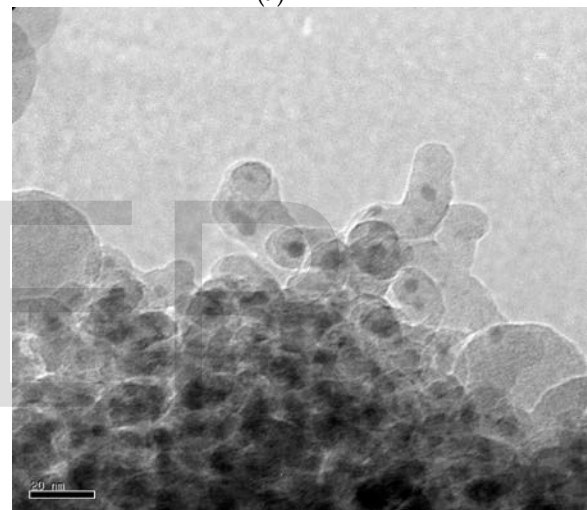
Ternary systems of cyclohexane/Igepal CO 520/water offer certain advantages: they are spheroidal and monodisperse aggregates where water is readily solubilized in the polar core, forming a “water pool” characterized by the molar ratio of water to surfactant concentration (R). Another important property of reverse micelle is their dynamic character; the “water pool” can exchange their contents by collision process. The aggregation and self-assembly of the oil/surfactant/water species is complex and very little is known about the cluster growth and final nanostructure as a function of synthesis condition. The molar ratio of water to surfactant can determine the size of the micro-emulsion water core [10]. Therefore, the R-value can control the diameter of the nanoparticles in the micro-emulsion.

In/SiO<sub>2</sub> nanometer size composite particles were obtained by reduction of In in reverse micelles followed by in-situ hydrolysis and condensation in the microemulsion. While the core particles are formed by homogeneous nucleation and growth, the shells are most likely formed through heterogeneous nucleation and growth. Because the two steps are different in mechanism, controlling the formation of nanocomposites is very sensitive to modest processing changes [11]. The nanosize particle formation process in reverse micelles has been based on a two-step model [12]. The first step is rapid, complete reduction of the metal to the zero valence state. The se-

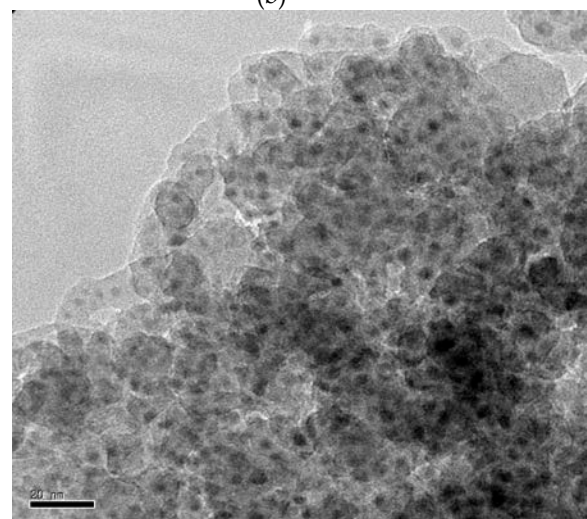
cond step is growth via reagent exchanges between micelles.



(a)



(b)



(c)

Fig. 2 TEM images of In/SiO<sub>2</sub> nanoparticles synthesized as a function of R: (a) 4, (b) 6, and (c) 8 at H=100, X=1.

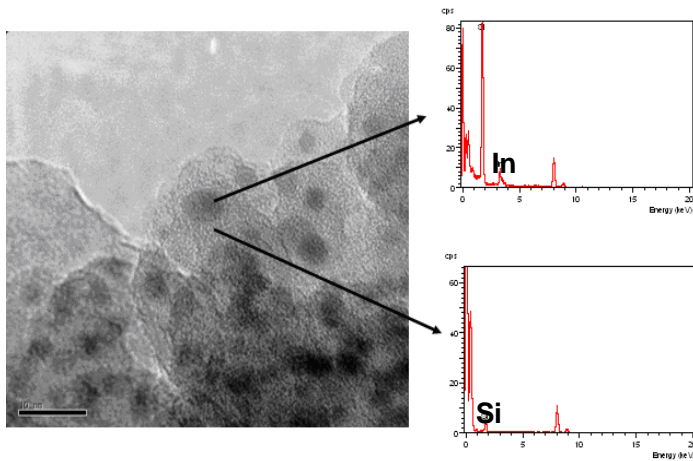
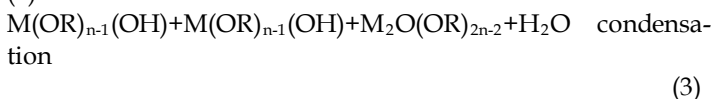
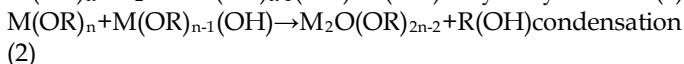
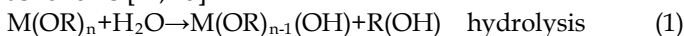


Fig. 3 EDS of In/SiO<sub>2</sub> core shell particles at R=8; H=100; X=1

The nucleation and growth of In nanoclusters is likely to be diffusion controlled process through interaction between micelles, but it can be influenced by many other factors such as phase behavior and solubility, average occupancy of reacting species in the aqueous pool, and the dynamic behavior of the microemulsion [13]. Fig. 2 shows that In/SiO<sub>2</sub> composite nanoparticles synthesized at R = 4–8, H=100, X = 1. The distinct contrast change under bright field mode indicates insertion of In species. The dark areas in particle aggregates reflect a In-SiO<sub>2</sub> particulate matrix while the gray areas are more similar to pure SiO<sub>2</sub> aggregates (Fig. 3). The average size of the core shell In-SiO<sub>2</sub> nanoparticles synthesized with increasing water to cannot be determined due to cluster formation. The spherical equivalent size for the In nanoparticles formed in SiO<sub>2</sub> matrix is estimated to be around (3±1) nm. The chemical composition analysis performed by EDS revealed In is successfully embedded in SiO<sub>2</sub> (Fig. 3).

#### 4. Mechanism of In/SiO<sub>2</sub> Composite particle formation

Metal-organic derivatives within the microemulsion reaction matrix are undergoing a hydrolysis reaction and the two possible condensation reactions, which can be represented as follows [14, 15]



As a first approximation, it is assumed that the reverse micellar aggregates present in the solution are not affected by the addition of TEOS molecules nor by the subsequent reactions, and in particular that the aggregation numbers (micellar concentration) remain unchanged. The TEOS alkoxide molecules would then interact rapidly with the water molecules inside the reverse micellar aggregates, forming partially hydrolyzed species. These hydrolyzed species remain bound to the micellar aggregates due to their enhanced amphiphilic character

brought about by the formation of silanol groups. All further reactions are restricted to the micelle region, and thus the overall mechanisms of oxide layer formation and growth involve both intra- and inter-micellar events [14]. It is likely that hydrolysis occurs within each reverse micelle, whereas condensation (particle growth) may occur within a given micelle or by inter-micellar contacts. Therefore, formation and size of the composite particles depends on the relative rates of the hydrolysis and condensation reactions [9, 11]. There are several factors, which may affect the rate of hydrolysis in reverse micelles; the rate of the hydrolysis decreases as the R ratio decreases. With low water content (small R ratio), most of the water molecules are bound to the polar head of the surfactant molecules. Thus, the hydrolysis rate is slow. With increasing water content (R ratio), more free water is available to participate in the hydrolysis reaction. Thus, the hydrolysis reaction can be expected to be enhanced when more free water is present [9, 11].

#### 4 CONCLUSION

Metallic In nanoclusters were embedded into a SiO<sub>2</sub> nanoparticles that were synthesized within reverse micelle via a solution reduction of In(NO<sub>3</sub>)<sub>2</sub> by hydrazine hydrate. The spherical equivalent size for the In clusters formed in SiO<sub>2</sub> matrix was estimated to be around (3±1) nm. The chemical composition analysis performed by EDS revealed In is successfully embedded in SiO<sub>2</sub> matrix.

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