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Synthesis and Characterization of Ga doped SiO_2 Nanoparticles by a Reverse Micelle and Sol–Gel Processing

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Abstract. Ga doped SiO_2 nanosized particles have been synthesized using a reverse micelle technique combined with metal alkoxide hydrolysis and condensation. The size of the particles and the thickness of the coating can be controlled by manipulating the relative rates of the hydrolysis and condensation reactions of tetraethyl orthosilicate(TEOS) within the micro-emulsion. The average size of synthesized Ga doped SiO_2 nanoparticles were about in the size range of 10-15 nm and Ga particles 2-5 nm. The effects of synthesis parameters, such as the molar ratio of water to TEOS, and the molar ratio of water to surfactant, are discussed.

Introduction

Recently, the synthesis of nanometer-sized particles of metals, semiconductors and metal oxides has been investigated extensively because of their novel electrical, optical, magnetic, and chemical properties. Composites formed by metal ions or nano-clusters embedded in ceramics or glasses have recently attracted much attention as promising materials for applications in optoelectronics[1], separation membranes [2]. The synthesis of nanoparticles and control of their properties are important in many critical areas of modern technology such as catalysis, ceramic processing, solar energy conversion, pharmaceutics, and photography. The effect of size on the electronic and optical properties of these nanosize particles is an area of fundamental interest during the growth of the crystallite from the molecular level to the bulk material [3]. Many approaches have been explored for the preparation of spherical ultrafine particles, including the use of colloids, polymers, glasses, and micelles to successfully control aggregation [4-6]. Many new and unusual physical and chemical properties also arise as particles attain nanosize dimensions [7,8]. There is increasing recognition that aqueous synthesis offers growth control capabilities that can be conveniently exploited in preparing these desirable fine particles [9]. Compared to conventional solid-state reaction methods, solution-based synthesis results in higher levels of chemical homogeneity. Also, in solution system, mixing of the starting materials at the molecular level is achieved in solution-based system; this is especially important when multi-component oxides are being prepared. In addition, surface coating or surface modification of a nanometer semiconductor and metal particles offers a new challenge to synthesis. Not only metal/silica nanocomposites, but also

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semiconductor/oxide and even semiconductor /insulator/metal multiple-layer can be prepared using this method [10]. The object of this study was to prepare silica (SiO_2) particles containing nanometer-size gallium particles by a combined reverse micelle and sol-gel processing.

Experimental Procedure

The experimental procedure used to prepare Ga doped SiO2 nanosize particles is illustrated in Fig. 1. Typically, microemulsions of total volume about 20 mL were prepared at ambient temperature in a 50 mL vial with rapid stirring, and they consisted of 4g of Igepal, 10 mL of cyclohexane, 0.65-1.30 mL of 0.02M $Ga(NO_3)_2$ solution. The average of the synthesized particles was controlled by varying the ratio R = [water]/[surfactant]. The microemulsion was mixed rapidly, and after 30 min of equilibration, one drop (~0.05 mL) of hydrazine hydrate (9M $N_2H_4X{\cdot}H_2O$, Aldrich Chemical Co.) was added as a reducing agent. After nanosize water droplets formed while stirring, tetraethyl orthosilicate (TEOS) was added into the stirred microemulsion. The amount of it was varied according to the different molar ratios of water to TEOS, H = [water]/[TEOS], which is the most important factor dictating the size of the nanoparticle. NH_4OH was injected into the microemulsion to accelerate the condensation reaction of metal alkoxide precursors. Reverse micelles were prepared from a nonionic surfactant, poly (oxyethylene) nonylphenly ether (Igepal CO-520, Aldrich Chemical Co.), which was used without further purification. Other chemicals, such as tetraethoxysilane (TEOS, Aldrich Chemical Co.), cyclohexane, isooctane, and NH_4OH(28%) were used as received. The structure, size and morphology of the resulting composite nanoparticles were examined by transmission electron microscope (TEM). For TEM studies, samples were prepared by adding drops of freshly prepared cluster solution on a carbon film supported on a Cu grid.

Results and Discussion

Spherical Ga doped SiO_2 nanometer-sized particles were obtained in reverse micelles followed by in situ hydrolysis and condensation in the microemulsion. The average size of the cluster was Fig. 2 shows spherical Ga/SiO_2 nanometer sized composite particles with a narrow size distribution were obtained in reverse micelles followd by in-situ hydrolysis and condensation in the micro -emulsion. Fig. 3 shows that the water/surfactant molar ratio (R) influenced the particle size and distribution of the synthesized Ga doped SiO_2 particle. The average size of the synthesized Ga doped SiO_2 particles changed slightly with increasing water/surfactant molar ratio. However, the average size of the gallium increased with increasing R. The median particles of a given grain size in a given area. The median diameter of the Ga doped SiO_2 nanocomposite particles was determined to vary from 10 to 15 nm R varied from 4 to 8, at H = 100, with a standard deviation of 5 nm. The core particles are formed by a homogeneous nucleation and growth processes, the shells are most likely formed through heterogeneous nucleation and growth. These two steps are different in mechanism, controlling the formation of the composite nanoparticles is very sensitive to modest processing changes. The first step is rapid, complete reduction of the metal to the zero valence state. The second step is growth via reagent exchanges between micelles [11]. Nucleation and growth of Ga

particles is likely to be a diffusion-controlled process through interaction between micelles, but it may be influence 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 micro-emulsion [11]. Metal-organic derivatives within the micro-emulsion reaction matrix undergo a hydrolysis reaction and two possible condensation reaction [12]. It may be assumed that the reverse micelle aggregates present in the solution are not affected by the addition of TEOS molecules or by subsequent reactions, and in particular that the aggregation numbers of the micelles remain unchanged. The TEOS alkoxide molecules would then interact rapidly with the water molecules inside the reverse micelles, forming partially hydrolyzed species. These hydrolyzed species remain bound to the micelles due to their enhanced amphiphilic character brought about by the formation of silanol groups. It is likely that hydrolysis occurs within each reverse micelle, whereas condensation (particle growth) may occur also by intermicellar contracts. Therefore, the size of the composite particles depends on the relative rates of the hydrolysis and condensation reactions. EDS of the synthesized particles was carried out in order to analyze the type of metal. Fig. 4 shows the spectrum of Ga doped SiO_2 composite nanoparticles by TEM - EDS analysis. The core particles appear Ga pattern peaks and the shells appear SiO_2 pattern peaks.

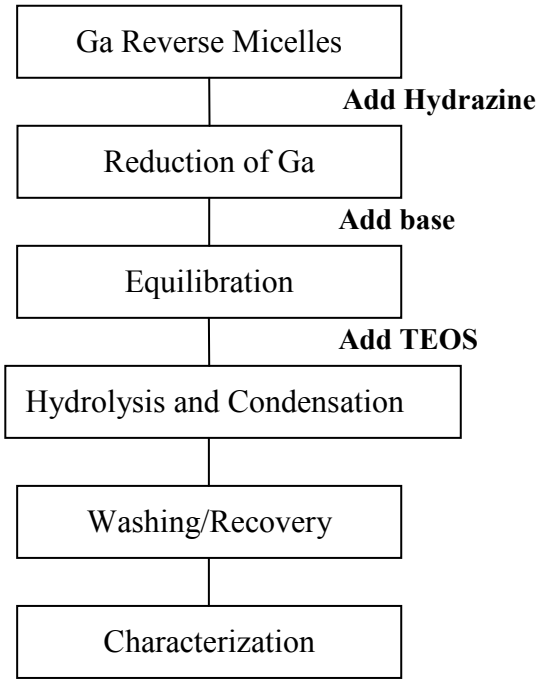


Figure 1. Flow chart for synthesis of Ga doped SiO_2 nanoparticles by reverse micelle and sol-gel processing.

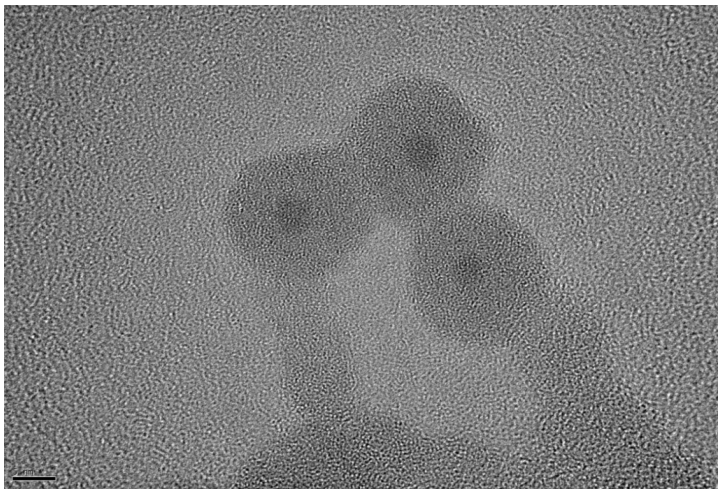
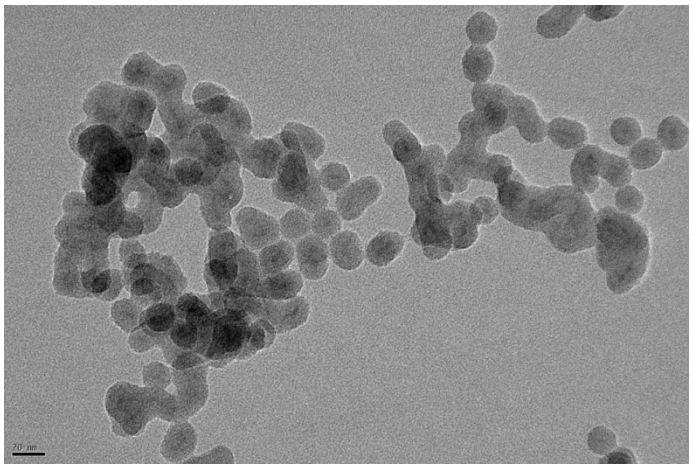
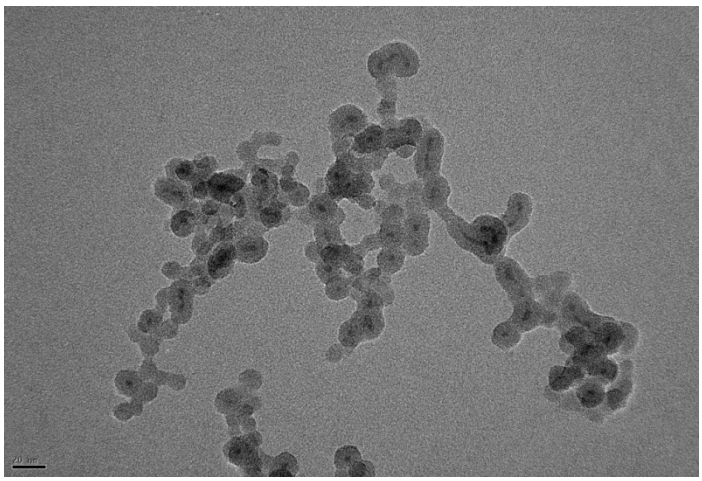


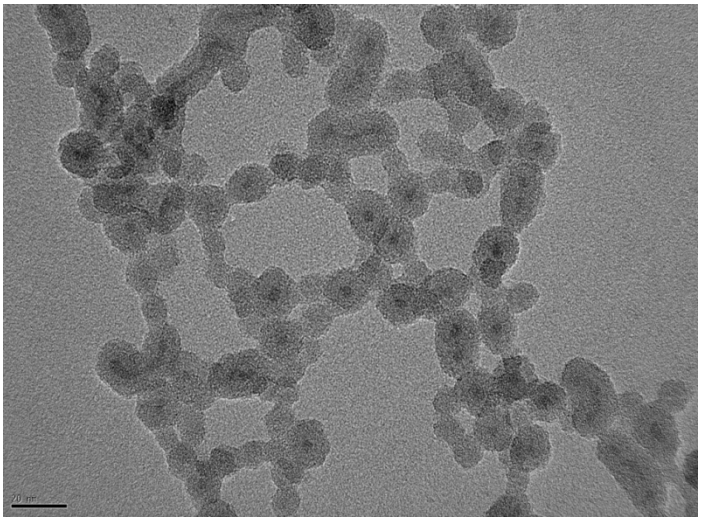
Figure 2. TEM micrographs of the synthesized Ga doped SiO_2 nanoparticles by a reverse micelle and sol-gel process (R = 6, H = 100, X = 1).



(a)

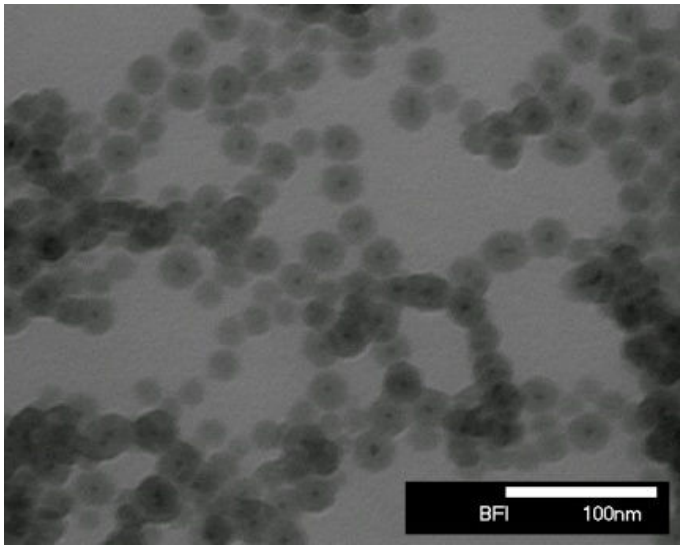


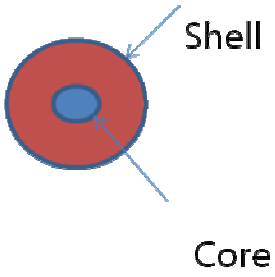
(b)

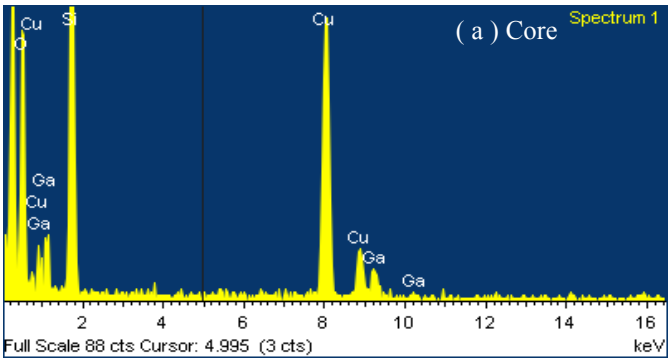


(c)

Figure 3. TEM micrographs of synthesized gallium doped SiO_2 nanopowders as a function of R value (H = 100, X = 1,C = 0.02 M); a) 4, b) 6, and c) 8.found to depend on the micelle size, the nature of the solvent, and the concentration of reagent.







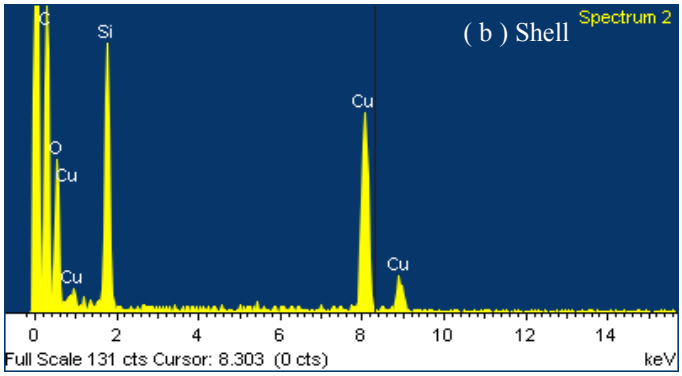


Figure 4. EDS spectrum of synthesized Ga doped SiO_2 nanoparticles by a reverse micelle and sol-gel processing; a) Core and b)Shell

Conclusion

Spherical Ga doped SiO_2 nanometer-sized particles with a uniform size distribution can be produced by a reverse micelle technique in conjunction with a sol-gel process, involving the hydrolysis and condensation of the organometallic precursors. The average size of the synthesized Ga doped SiO_2 nanometer particles changed slightly with an increasing water/surfactant molar ratio. The phase and type of the synthesized core metal particle was crystalline and gallium. TEM studies of the particles formation indicated that the reaction process in the complex system, which contained reverse micelle and TEOS, is governed by a diffusion-controlled process. By controlling the ratio of water to surfactant and the ratio of water to TEOS, the particle size can be adjusted.

Acknowledgment

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