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Synthesis and microstructure of Pd/SiO$_2$ nanosized particles by reverse micelle and sol–gel processing

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Pd/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 reaction of tetraethyl orthosilicate (TEOS) within the microemulsion. The average size of synthesized Pd/SiO$_2$ particles was in the size range 20–40 nm and Pd particles were 1–5 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.

I 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.[1–10] The effect of particle size on the electronic and optical properties of these nanosized particles during the growth of the crystallite from the molecular level to the bulk material is an area of fundamental interest.[1] Numerous approaches have been explored for the preparation of spherical nanosized particles, including the use of colloids, polymers, glasses, and micelles to successfully control aggregation.[2–4] Many new and unusual physical and chemical properties also arise as particles attain nanosized dimensions.[5,6] Compared with conventional solid-state reaction methods, solution-based synthesis results in higher levels of chemical homogeneity. Also, mixing of the starting materials at the molecular level is achieved in solution-based systems; this is especially important when multi-component oxides are being prepared. In addition, surface coating or surface modification of nanometer semiconductor and metal particles offers a new challenge to synthesis. Not only metal/silica nanocomposites, but also semiconductor/oxide and even semiconductor/insulator/metal multiple-layer heterostructures can be prepared using this method.[9]

The object of this study was to prepare silica (SiO$_2$) particles containing nanometer-size palladium particles by a combined reverse micelle and sol–gel technique.

II Experimental procedure

The experimental procedure used to prepare Pd/SiO$_2$ nanosize composites 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 4 mL of Igepal (Igepal CO-520, Aldrich Chemical Co.), 10 mL of cyclohexane, 0.65–1.32 mL of 10^{-2}–3×10^{-2} M Pd(NO$_3$)$_2$·6H$_2$O solution, and deionized water. The average size of the resulting particles was controlled by varying the water/surfactant ratio (R). The microemulsion was mixed rapidly, and after 5 min of equilibration, one drop ($\sim$0.05 mL) of hydrazine hydrate (9 M $N_2H_4 \cdot xH_2O$, Aldrich Chemical Co.) was added as a reducing agent. Tetraethyl orthosilicate (TEOS) was added to the microemulsion after nanosized palladium aqueous droplets formed with stirring. The amount of TEOS was varied according to give different molar ratios of water to TEOS, H = [water]/[TEOS]. This is the most important factor dictating the size of the nanosize particles. NH_4OH was injected into the microemulsion to accelerate the condensation reaction of metal alkoxide precursors. The amount of NH_4OH

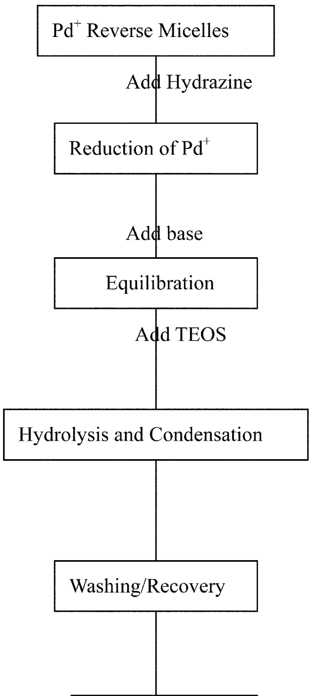

Fig. 1 Flow chart for synthesis of Pd/SiO$_2$ particles by reverse micelle and sol–gel processing.

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was fixed according to the molar ratio of TEOS to NH_4OH, x = [TEOS]/[NH_4OH]. New reverse micelles were prepared from the nonionic surfactant poly(oxyethylene) nonylphenyl ether (Igepal CO-520, Aldrich Chemical Co.). The surfactant was used without further purification. Other chemicals, such as TEOS, cyclohexane, and NH_4OH (29%) (all from Aldrich Chemical Co.) were used as received. The structure, size and morphology of the resulting particles were examined by transmission electron microscope (TEM). For the TEM studies, the samples were prepared by placing drops of freshly prepared cluster solution on a carbon film supported on a Cu grid.

III Results and discussion

Spherical Pd/SiO_2 nanometer-sized composite particles were obtained in reverse micelles followed by *in situ* hydrolysis and condensation in the microemulsion. The average size of the cluster was found to depend on the micelle size, the nature of the solvent, and the concentration of reagent. Fig. 2 shows that

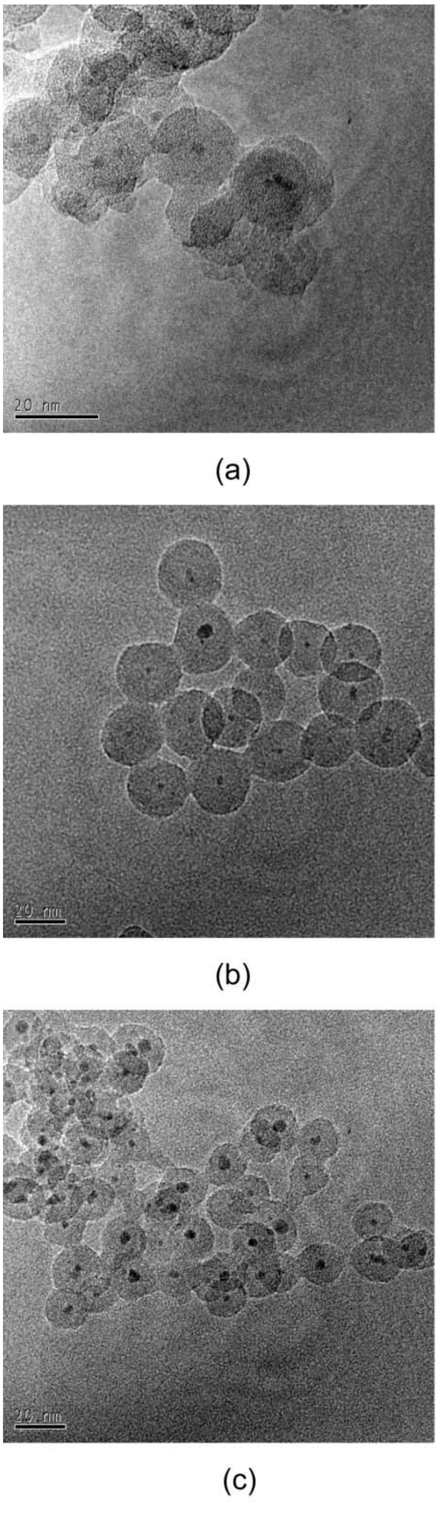

Fig. 2 TEM micrographs of the synthesized Pd/SiO_2 particles by reverse micelle and sol–gel processing as a function of R; $R = 4$ (a), 6 (b), and 8 (c) at $x = 1$ and $H = 100$.

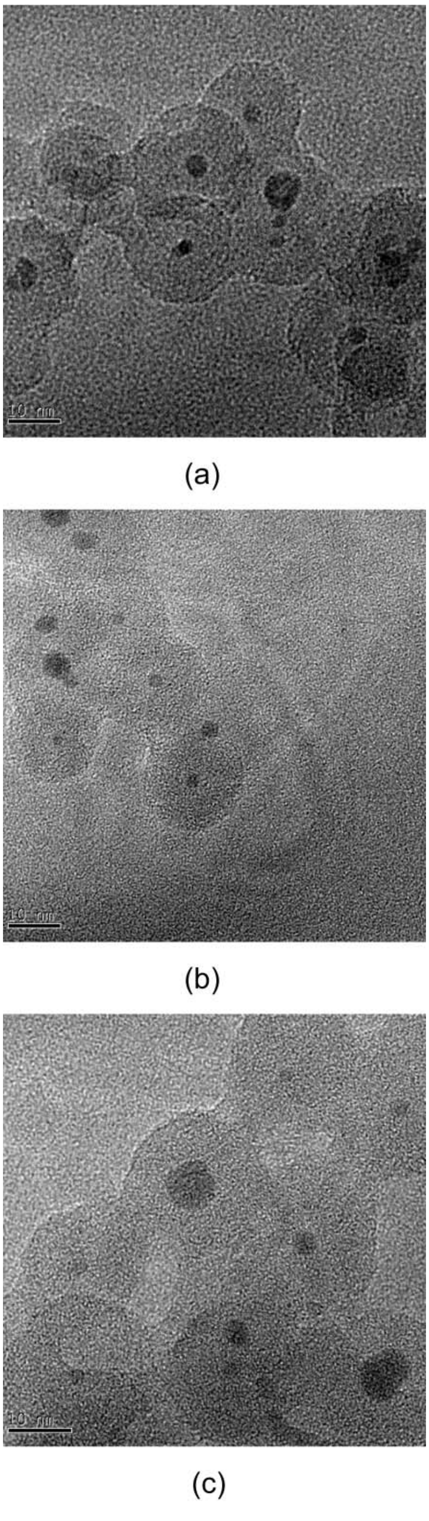

Fig. 3 TEM micrographs of the synthesized Pd/SiO_2 particles by reverse micelle and sol–gel processing as a function of H; $H = 50$ (a), 100 (b), and 200 (c) at $R = 8$.

the water/surfactant molar ratio (R) influenced the particle size and distribution of the synthesized Pd/SiO_2. The average size of the synthesized Pd/SiO_2 particles changed slightly with increasing water/surfactant molar ratio. However, the average size of the palladium increased with increasing R. The core particles are formed by a homogeneous nucleation and growth process; the shells are most likely formed through heterogeneous nucleation and growth. The nucleation and growth of palladium particles is likely to be a 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 the reacting species, the aqueous pool, and the dynamic behavior of the microemulsion.

Fig. 3 shows that the water/TEOS molar ratio (H) influences the particle size and distribution of the synthesized Pd/SiO_2. The average size of the synthesized Pd/SiO_2 particles changed slightly with increasing H at $R = 8$. The median particle size was determined by counting the number of particles of a given grain size in a given area. The median diameter of the Pd/SiO_2 nanocomposite particles was determined to vary from 15 to 35 nm as H varied from 50 to 200, at $R = 8$, with a standard deviation of 10 nm. The palladium phase is crystalline because the micrograph of the palladium is a fringe image (Fig. 4). EDS of the synthesized particles was carried out in order to analyze the type of metal. Fig. 5 shows that a peak in the element spectrum represents palladium metal.

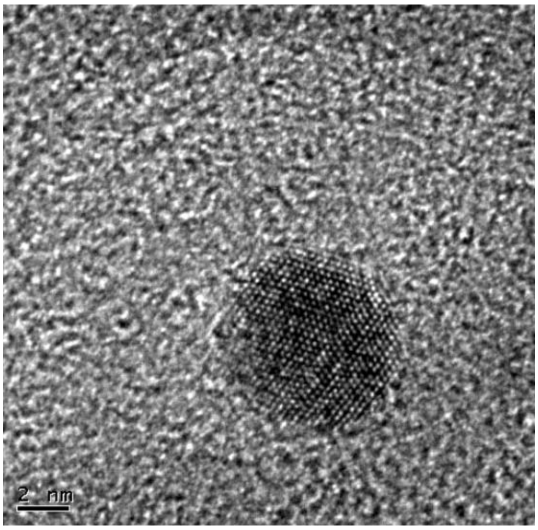

Fig. 4 HRTEM micrograph of a synthesized Pd/SiO_2 particle by reverse micelle and sol–gel processing at $R = 8$, $H = 50$, and $x = 1$.

IV Conclusions

Spherical nanosize Pd/SiO_2 nanometer-sized particles with 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 Pd/SiO_2 particles changed slightly with an increasing water/surfactant molar ratio. The phase and type of synthesized core metal particle was crystalline and palladium. TEM studies of the particle formation indicated that the reaction process in the complex system, which contained reverse micelles and TEOS, is governed by a diffusion-controlled process. By controlling the water/surfactant ratio and the water/TEOS ratio, the particle size can be adjusted.

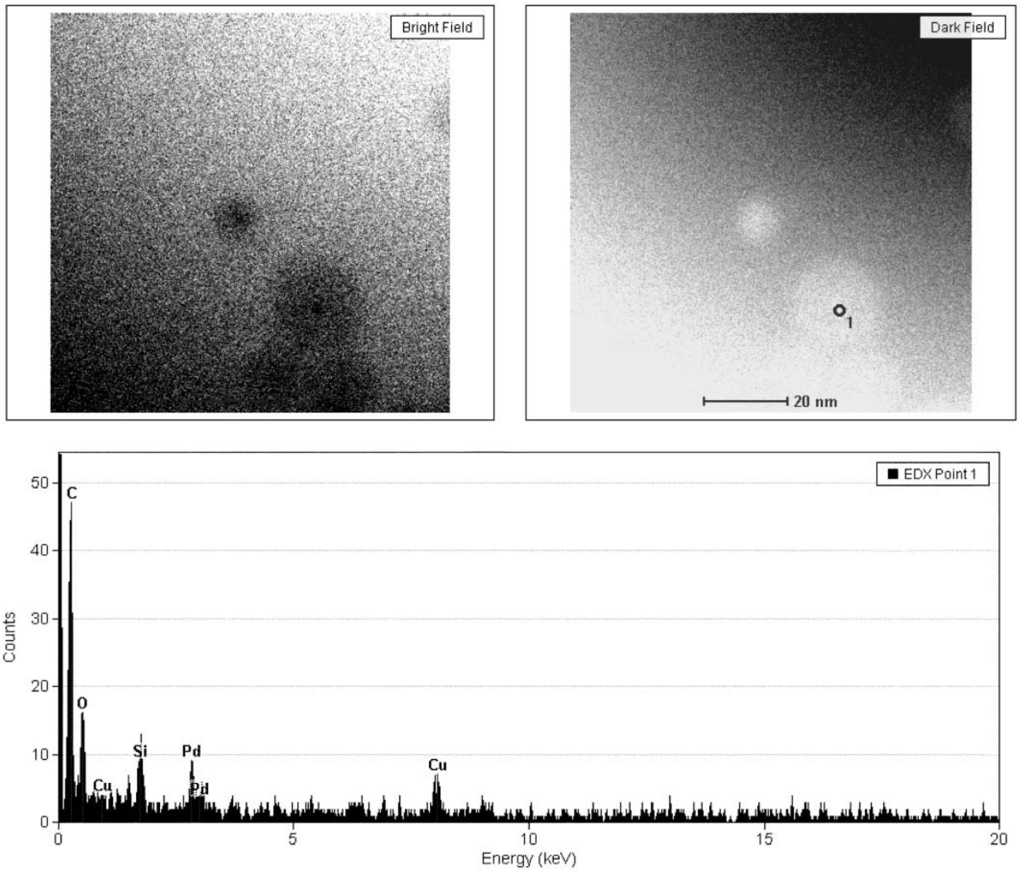

Fig. 5 TEM micrographs and EDS of a synthesized Pd/SiO_2 particle by reverse micelle and sol–gel processing at $R = 4$, $H = 50$, and $x = 1$.

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