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Facile and Continuous Synthesis of $Ag@SiO_2$ Core–Shell Nanoparticles by a Flow Reactor System Assisted with Homogeneous Microwave Heating

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$Ag@SiO_2$ core–shell nanoparticles were synthesized by integration of a series of flow processes including microwave (MW)-assisted Ag nanoparticle formation followed by coating with SiO_2 shell. TEM monitoring of the reaction intermediates revealed that two reaction pathways take place concurrently during the SiO_2 shell coating. MW heating (70 °C, 1 s) remarkably reduced the SiO_2 shell-formation reaction time.

The physical and chemical properties of metal nanoparticles change dramatically by homogeneous encapsulation with metal oxides.[1] $Ag@SiO_2$ core–shell nanoparticles are a noteworthy example.[2–6] Primarily, the presence of the SiO_2 shell suppresses particle aggregation and inhibits Ag surface oxidation, leading to improved stability and handling flexibility of Ag nanoparticles. Furthermore, the dielectric environment around Ag nanoparticles and their optical properties, particularly surface plasmon resonance and Raman scattering, are tunable by control of the SiO_2 layer thickness.[7] The Stöber process based on sol–gel reaction of alkoxysilanes is a popular method applied to the coating of Ag nanoparticles with a SiO_2 shell.[2,4–6,8] Tetraethoxysilane (TEOS) is widely used as a typical SiO_2 precursor combined with water, alcohol, and ammonia/amines as base-hydrolysis catalysts. Control of the shell thickness has been examined by changing the amount and molar ratio of these reactants and other reaction parameters.[5,6] A recent study demonstrated that MW irradiation remarkably facilitated the SiO_2 coating reaction more than conventional heating and that single core $Ag@SiO_2$ nanoparticles of uniform size were obtained within a short reaction time.[6] However, earlier studies generally involve multiple steps of batch procedures such as synthesis of metal core nanoparticles, isolation and pretreatment of the core nanoparticle dispersion, and subsequent coating of Ag nanoparticles with a SiO_2 shell.

In contrast to batch reactions, a flow-type process generally presents better methodology with respect to continuous material production. We have demonstrated the continuous synthesis of Ag (and Pt) nanoparticles of uniform particle size using an originally designed MW reactor system that can control reaction temperatures precisely and homogeneously.[9,10] In this work, we attempted to conduct a series of reactions coherently in a flow reactor system, i.e., MW-assisted flow synthesis of Ag nanoparticles followed by direct SiO_2 coating either with or without MW heating. The reaction conditions in terms of concentrations and ratios of reactants and the choice of solvents were optimized for integration of two reactions into a series of flow processes as well as to control the shell thickness.

The MW reactor system consists of a variable-frequency MW generator (2.5 GHz ± 200 MHz, 100 W) and an aluminum cylindrical single-mode cavity, as depicted in Figure 1.[11] A poly(tetrafluoroethylene) (PTFE) tube (ϕ 1 × 100 mm) was mounted coaxially in the center of the TM_{010} single-mode cavity for use as the flow-type reactor. The oscillation frequency for matching with the resonance frequency was monitored, and the applied power was controlled using the temperature feedback module.

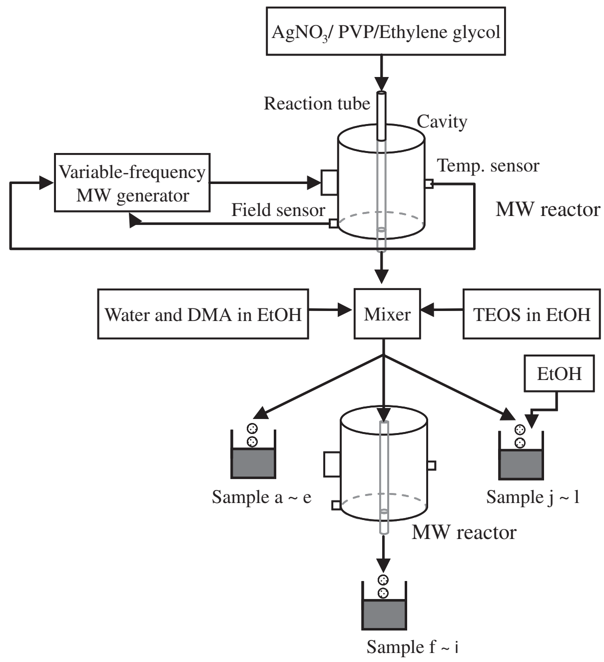

Figure 1. Schematic view of the continuous process of the Ag nanoparticles synthesis by MW heating and the SiO_2 shell formation. The Ag nanoparticle dispersion was transferred directly to the mixing unit for SiO_2 shell coating. It was then either heated by MW or left standing at room temperature.

The synthetic process of $Ag@SiO_2$ involves preparation of Ag nanoparticle dispersion, subsequent base-catalyzed hydrolysis of TEOS, and condensation of SiO_2 onto the surface of the Ag particle core. Ag nanoparticles were synthesized using the polyol process according to the procedure described previously.[9] Typically, ethylene glycol solution containing $AgNO_3$ (10 mM) and poly(vinylpyrrolidone) (PVP) (3 wt %) as the stabilizer was introduced continuously into the PTFE tube reactor. The MW heating temperature and flow rate were fixed, respectively, at 160 °C and 6 mL h^{-1} throughout this work. The size of thus obtained Ag nanoparticles was 16.5 ± 3.3 nm. The thus prepared Ag nanoparticle dispersion was transferred directly to the mixer for SiO_2 shell coating process without particle isolation or pretreatment.

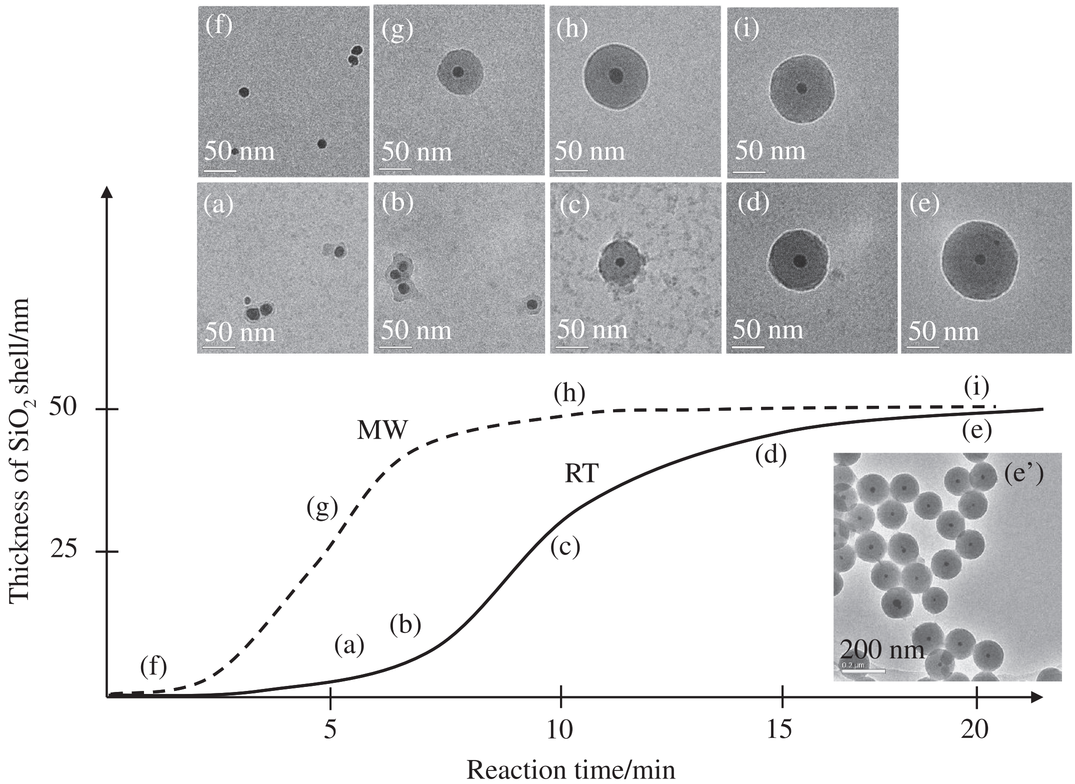

Figure 2. Time course of SiO_2 shell growth and the TEM images of the intermediate nanoparticles. Ag nanoparticle dispersion was transferred directly to the mixing unit for SiO_2 shell coating and then either heated by MW (broken line) or left standing at room temperature (straight line). Reaction times: (a) 6, (b) 7, (c) 10, (d) 15, (e) and (e′) 20, (f) 1, (g) 5, (h) 10, and (i) 20 min.

The Ag nanoparticle dispersion was mixed with an ethanol solution of TEOS (1.3×10^{-2} M) and ethanol solution of aqueous dimethylamine (DMA 0.4 M; water 11.1 M). The total flow rate was 320 mL h^{-1}. Shell coating was difficult for TEOS concentrations lower than 5×10^{-3} M, where aggregation of Ag nanoparticles tends to occur rather than core–shell particle formation. The addition of ethanol is necessary for the formation of homogeneous SiO_2 shells because TEOS is less soluble in ethylene glycol. Additionally, it was assumed that hydrolysis of TEOS and compatibility of SiO_2 nuclei with Ag nanoparticles is much more favorable by replacement of ethylene glycol by ethanol. We used DMA as the sol–gel catalyst because it does not dissolve out the Ag nanoparticles by Ag(I) complex formation as ammonia or monomethylamine do.[5] The DMA concentration was fixed to 0.4 M because the formation of core-free SiO_2 was reduced in the concentration range of 0.3 to 0.8 M.[6]

Coating of Ag nanoparticles with SiO_2 shell starts upon mixing of ethanol solutions of TEOS and aqueous DMA. Then the reaction mixture out of the mixer was let to stand at room temperature for shell growth. The SiO_2 shell-formation process was monitored using TEM images of samples taken at appropriate time intervals. The silica shell thickness increased rapidly within the initial 6 min and saturated in ca. 20 min (TEM images in Figures 2a–2e). Hydrolysis of TEOS and nucleation of SiO_2 occurred not only at the surface of Ag nanoparticles but also in the bulk solution. As portrayed in TEM images of (b) and (c), the SiO_2 aggregates generated were observed in the outer solution at the initial stage of the SiO_2 shell formation. However such aggregates were not found at the final stage of reaction (TEM images in (d) and (e)), where the SiO_2 shell grows by adsorption of SiO_2 aggregates onto Ag nanoparticles. This observation suggests that two reaction steps contribute concurrently to SiO_2 shell formation: one is the direct growth of SiO_2 nuclei on the Ag nanoparticles surface. The other is accumulation of outer SiO_2 aggregates onto the Ag nanoparticles. The final thickness of SiO_2 shell depends on the TEOS concentration as observed for 6×10^{-3} and 1.3×10^{-2} M cases (see Supporting Information[12]). When the TEOS concentration is lower than 5×10^{-3} M, the population of SiO_2 aggregates generated in the bulk solution is small. As a result, mutual aggregation of Ag nanoparticles tends to occur. Most of the products were single Ag core–shell particles; core-free particles are very few, as shown in the TEM image of (e′). We assumed DMA coordinates to the Ag surface where the catalytic base hydrolysis of TEOS occurs preferentially. Then, the thus formed hydrophilic surface might attract the hydrophilic SiO_2 aggregates generated in the bulk solution.

MW heating during the SiO_2 shell-formation process was examined to reduce the reaction time. The Ag nanoparticle dispersion was mixed with the ethanol solution of TEOS, H_2O, and DMA; then it was introduced into the MW reactor tube (ϕ 1 × 100 mm) kept at 70 °C. The flow rate of reaction solution was adjusted to attain 1 s of residence time in the reactor tube. The reaction solution out of the reactor was left to cool down to room temperature (ca. 5 min). During this time, the SiO_2 shell

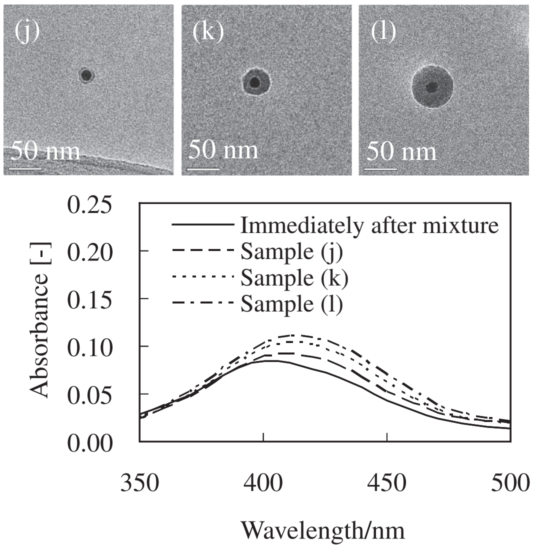

Figure 3. UV–vis absorption spectra of the Ag@SiO_2 dispersions and the TEM images of corresponding nanoparticles. Samples were taken at (j) 7, (k) 8, and (l) 10 min, and shell growth reaction was quenched.

thickness grew to ca. 25 nm and saturated to 50 nm within 10 min (Figure 2). Despite the very short time (1 s), MW heating remarkably reduced the reaction time of the SiO_2 shell formation. Such reaction enhancement by MW heating in the hydrolysis and condensation of TEOS has been observed in batch experiments.[6,13] For example, the reaction time of the SiO_2 nanoparticle formation and the time required for coating of SiO_2 shell over CeO_2 and ZnO core particles have been remarkably reduced compared to conventional heating. This rate enhancement can be primarily attributed to the thermal effect of MW heating. Because of the high dielectric loss constant, ethylene glycol and ethanol can convert MW energy into thermal energy efficiently.[14] In addition, direct energy transfer from MW to the core Ag metal through reasonance (and relaxation) is likely to contribute to the accerelation of the shell formation. Metal particles preferentially absorb MW energy and form localized high-temperature spots which induce the rate enhancement of TEOS hydrolysis.[15] Unlike Figures 2b and 2c, the formation of SiO_2 in the bulk solution was not observed for the MW heating process. This suggests that hydrolysis of TEOS preferentially occurred at the localized hot surface of core particles.

The SiO_2 shell growth can be quenched simply by high dilution of the reaction solution with ethanol (ten times). Monodispersed Ag@SiO_2 core–shell nanoparticles with the thinner shell such as less than 5 nm can be obtained. In this way, a series of Ag@SiO_2 core–shell nanoparticles with thickness of less than 20 nm was obtained (TEM (j)–(l)).

These Ag@SiO_2 nanoparticles were stable for standing more than 3 days. Figure 3 shows UV–vis absorption of Ag@SiO_2 dispersion of different SiO_2 shell thickness along with the TEM images of corresponding nanoparticles. The original Ag nanoparticles exhibited a typical absorption peak at around 400 nm associated with the surface plasmon resonance absorption. The peak shifted to longer wavelength by SiO_2 shell coating, and the intensity increases concomitantly with increased shell thickness. These phenomena are consistent with the previous observations and theoretical predictions.[5]

In conclusion, we demonstrated the continuous and facile synthesis of homogeneous Ag@SiO_2 nanoparticles by direct integration of MW-assisted Ag nanoparticle synthesis and the SiO_2 shell coating process.

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