



Original Research Paper

Flow microreactor synthesis of gold nanoshells and patchy particles



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ABSTRACT

Silica@Au core-shell type composite particles are promising for biomedical applications due to their unique optical and chemical characteristics, although the problem lies in the synthetic processes. They are typically synthesized via batch type reactions including multiple steps, and the complexity in the synthetic process is an obstacle to practical applications. A robust and facile process is thus required. In the present study, we developed a flow synthetic process by applying a microreactor with a high mixing performance to silica@Au nanoshells and patchy particles. Following a concept of selective nucleation and subsequent growth of the gold on the core surface, we mixed a suspension of surface-modified silica particles containing gold ions with a reducing agent solution in the microreactor, and investigated the effects of the core particle size and the type of reducing agents on the composite particle synthesis. Through the investigation, we found that the ratio of the gold ion amount to the surface area of core particles is a key factor for obtaining uniform core-shell particles. In addition, the morphology of gold formed on the core surface was demonstrated to change from spherical nanoparticles to dendritic patches depending on the reducing ability of reducing agents.

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1. Introduction

Dielectric core/metallic shell type composite particles include nanoshells in which core particles are coated with continuous shells [1], core-shell clusters (CSCs) in which core particles are uniformly covered with nanoparticles [2], and patchy particles in which core particles have discrete sites of varying chemical and/or physical properties [3,4], schematics of which are shown in Fig. 1. They are promising for biomedical applications such as imaging, sensing, and photothermal therapy as well as steam generation by solar illumination because of their unique optical property to absorb visible and near-infrared lights due to the plasmon resonance [5–8]. Because the absorption peaks can be tuned by the morphology of the shell, the control in the shell structure is of crucial importance. However, typical synthetic processes of metallic nanoshells are batch-type reaction and require a long reaction period with multiple steps [9–11], although some modified methods have been reported [12–15]. As for the patchy particle synthesis, typical approaches use templates because of the complexity in the particle structure [16–19], which can lead to lower throughput and are accordingly not suitable for mass

production. A template-free solution process of patchy particles has been reported [20–23], but the process is still batch-type. Although flow synthesis of metallic shell particles has been proposed [24–26], the number is still very few and, in addition, the shell structure control has not yet achieved. A robust, facile, and flow process to enable the shell structure control is thus strongly required.

An intrinsic problem in the batch-type reaction is the non-uniform reaction field provided by weak mixing intensity, which inevitably makes the process complicated. A uniform reaction field would enable one-step synthesis of core-shell type particles through preferential nucleation and growth on the core particle surface. One promising reaction device is a microreactor with excellent mixing performance [27], which can instantaneously provide the appropriate reaction conditions of the concentration with which the heterogeneous nucleation at the interface is promoted while self-nucleation in the bulk phase is suppressed. In addition, the use of microreactors can realize a flow synthetic process of core-shell type particles with high throughput. Following the concept, in our previous study, we established a continuous flow process using a microreactor and successfully synthesized CSCs and gold nanoshells [28]. Our technique was demonstrated to dramatically shorten the synthetic period compared with a batch-type process. However, the morphology of the shell was limited to spherical shape with a fixed core particle size of

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Nomenclature

d	diameter of core particles (m)	σ	surface area of particles per unit volume of suspension ($\text{m}^2\text{-particles}/\text{m}^3\text{-suspension}$)
ϕ	volume fraction of particles ($\text{m}^3\text{-particles}/\text{m}^3\text{-suspension}$)		
γ	gold ion amount per unit surface area of core particles ($\text{mol}/\text{m}^2\text{-particles}$)		

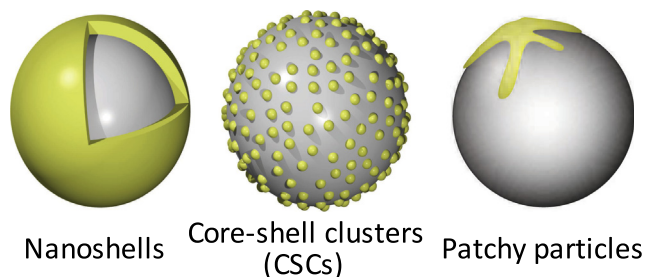


Fig. 1. Core-shell type composite particles.

120 nm. How the core particle size affects the synthetic process and what determines the shell morphology thus need to be investigated to further demonstrate the versatility of our technique.

In the present study, we synthesized silica@Au core-shell and patchy particles via our flow microreactor process. The key concept is selective nucleation and subsequent particle growth on core particle surfaces enabled by high mixing intensity of the microreactor, avoiding the nucleation in the bulk solution phase. We investigated the effects of the core particle size and the type of reducing agents on the shell morphology and uniformity of resultant particles to find out a critical factor that governs the shell and patch formation on core particles.

2. Experimental section

2.1. Materials

Aqueous suspensions of silica particles with diameters of 120 nm and 570 nm (Spherica Slurry) were purchased from Catalysts & Chemicals Ind. Co., Ltd. (Japan) and a suspension of 300 nm silica particles (Seahostar KE-W30) was purchased from Nippon Shokubai Co., Ltd. (Japan). The diameters were reported values by the manufacturer. 3-Aminopropyl trimethoxysilane (APTS, 97%), L-ascorbic acid ($\geq 99\%$), chloroauric acid (HAuCl_4 , 30 wt% solution), potassium carbonate (K_2CO_3 , 99.99%), and sodium borohydride (NaBH_4 , 99%) were purchased from Sigma-Aldrich Co. LLC. (USA). Ammonium hydroxide (28%), hydrochloric acid (HCl, 0.1 mol/L), and sodium hydroxide (NaOH, 0.1 mol/L) aqueous solutions and tri-sodium citrate (99%) were purchased from Kishida Chemical Co., Ltd. (Japan). All chemicals and silica particle suspensions were diluted to desired concentrations with ultrapure water with a resistivity of $18 \text{ M}\Omega \text{ cm}$ obtained from a Direct-Q3 UV water Purification System (Millipore Corp., USA).

2.2. Gold nanoshell synthesis

Silica@Au core-shell particles were synthesized with the seed-mediated growth method [9], in which gold nanoparticles (AuNPs) are seeded on surface-modified silica particles, followed by the growth of the gold seeds into a complete shell by reducing gold ions. We applied a microreactor to both gold seeding and shell growth processes. As a pretreatment of core particles, the silica

particle surface was modified with APTS molecules to make the surface positively charged. In the case of 120 nm silica particles, we added 0.1 mL of a 28% ammonium hydroxide solution to a 1 mg/mL silica suspension under magnetic stirring, to which 0.5 mL of a 10 vol% APTS aqueous solution was then added, followed by stirring for 24 h at 1500 rpm. The silica particles in the reaction suspension was repeatedly centrifuged and redispersed in 10 mL of ultrapure water. The pH value of the suspension was then adjusted to be approximately 3 by adding 50 μL of 0.1 mol/L HCl. When modifying silica particles with different diameters, we adjusted the concentration of silica particle suspensions so that the surface area is the same as the case of 120 nm silica particles. We measured zeta potentials of silica particles at $\text{pH} \sim 6$ before and after the modification step and confirmed that they turned into positive (approximately +40 mV) from a negative one of bare silica particles (approximately -40 mV), suggesting successful surface modification of silica particles with APTS (referred to as APTS-SiO₂). These APTS-SiO₂ particles were used as core particles.

AuNP seeding on the surface of APTS-SiO₂ were conducted by *in-situ* reducing HAuCl_4 with a strong reducing agent in the presence of core particles. A schematic of the experimental setup is shown in Fig. 2a. We mixed an APTS-SiO₂ suspension containing HAuCl_4 put in syringe A with a NaBH_4 solution in syringe B by pumping the two syringes into a microreactor with a two-channel syringe pump at a flow rate of 10 mL/min for each syringe (a total flow rate of 20 mL/min from the outlet). A typical concentration set after mixing was 0.25 mg/mL APTS-SiO₂ (120 nm), 0.075 mmol/L HAuCl_4 , and 1.5 mmol/L NaBH_4 . The microreactor we used is a central collision-type, which is composed of three plates as shown in Fig. 2b [29]. Each of the two inlet fluids is separated into seven channels in the inlet plate and flows through

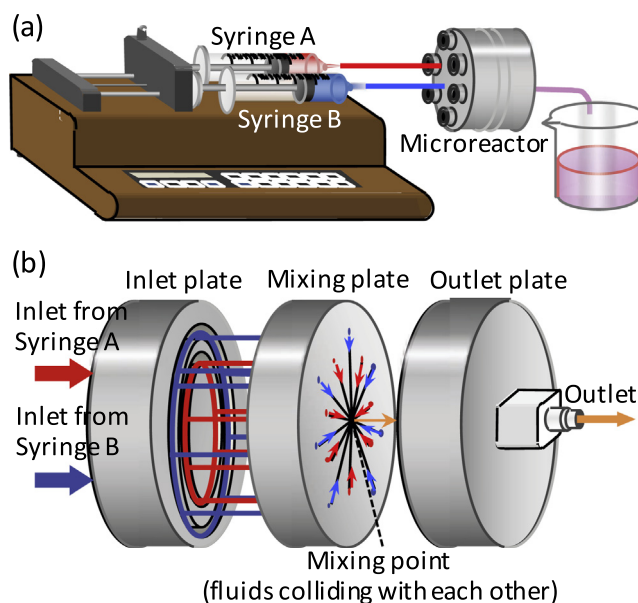


Fig. 2. Schematic illustrations of the experimental set-up. (a) Synthetic process of core-shell clusters, gold nanoshells, and patchy particles in the microreactor and (b) the central collision-type microreactor.

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