Facile synthesis of core–shell and Janus particles via 2-D dendritic growth of gold film

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Abstract

We report a facile method for the electroless deposition (ELD) of gold film via two-dimensional (2-D) dendritic growth. Our scheme employs protonated amine groups, which electrostatically attract both the negatively charged reducing agent and gold-precursor. This electrostatic interaction increases the local concentrations of gold-precursor and reducing agent near the silica surface to levels high enough for gold films with a 2-D fractal morphology to form directly on the surfaces of the amine-functionalized silica nanospheres by diffusion-limited aggregation. Our one-pot reaction avoids the need for seed attachment, which is typically employed for the growth of metallic shells on nanospheres. Therefore, the proposed method significantly reduces the number of processing steps required for the production of core–shell nanospheres. The gold morphologies were systematically investigated in terms of various synthesis variables, including solution pH, reducing agent concentration, and gold precursor injection speed. In addition, we synthesized gold-capped silica nanospheres via ELD of gold on a patterned array of silica nanospheres embedded in polystyrene (PS) film followed by dissolution of the PS matrix, thus demonstrating the potential utility of the proposed method in emerging fields of materials science such as patterning of noble metals and studies of nanometer-scale optics.

Keywords: Core–shell; Electroless deposition; Surface plasmon resonance; Nanopatterning; Diffusion-limited aggregation

1. Introduction

Colloidal gold nanoparticles with various shapes have attracted considerable interest over several decades because of their shape-dependent optical properties such as surface plasmon resonance (SPR) and light scattering [1]. As part of these efforts, methods for the solution-based synthesis of core–shell and anisotropic nanoparticles such as rods and polygons have been intensively studied [2–4]. In general, the anisotropic growth of metal nanoparticles requires weak reduction conditions and selective binding of a capping agent onto a specific crystal plane [5]. Recently, star-shaped Au nanoparticles with multiple plasmon resonance have been synthesized using surfactant molecules as capping agents [6]. In addition, 2-D anisotropic fractal growth of noble metals such as Ag and Au has been achieved by electro- or electroless deposition (ED or ELD) of the metals under a surfactant monolayer assembled at an air/water interface [7,8]. Complexation between a metal precursor and an oppositely charged surfactant was found to be a key factor in the formation of a fractal thin metal film at the interface. Typically, the fractal or dendritic growth of metals is mediated by diffusion-limited aggregation (DLA) [9]. In DLA systems, reduced metal nuclei diffuse and attach to islands of pre-deposited metal. When sufficient time is available for the active nuclei to reach the most energetically favorable sites before inactivation, well-organized 3-D crystalline metal particles can be obtained; otherwise, metal nanoparticles with fractal structures are formed. Previously, Au nanoparticles and Au dendrites were produced on thermally evaporated fatty amines and on zinc plates, respectively [10,11]. On the other hand, thin films of dendritic metals are usually formed at an air/water interface because the diffusivity of the metal nuclei is higher at the interface than in other environments. The dendritic growth of noble metals on an arbitrary surface is an emerging issue in theoretical studies of DLA as well as for practical applications of such deposits in the coating industry. Furthermore, 2-D deposits of noble metals on structured materials such as anisotropic inorganic particles are expected to exhibit promising optical properties.

Core–shell nanospheres composed of a nanosphere-core and a noble-metal-shell have been intensively studied in the field of nano-optics, especially in regard to their SPR characteristics [4,12]. The SPR of core–shell nanospheres can be tuned from visible to infrared by varying the ratio of the outer and inner radii of the metal shell [13]. To investigate the material-dependent optical properties of core–shell nanospheres, core–shell nanospheres with various cores and shells have been synthesized [14–17]. In particular, silica-core/gold-shell nanospheres with finely tunable
near-infrared absorption can be utilized in biomedical and bioimaging devices for cancer therapy [18–21].

Here, we report a facile and simple method for synthesizing gold-shell and gold-capped silica nanospheres via a one-pot ELD method using 2-D dendritic growth of gold film on an amine-functionalized surface. In the proposed method, ascorbic acid (ASA) is used as a reducing agent and polyvinylpyrrolidone (PVP) as a complexing agent for the gold precursor (HAuCl₄·3H₂O) [22,23]. Notably, the use of 2-D dendritic growth of gold film on nanospheres is a significantly simpler approach than previously reported multi-step synthetic procedures for preparing core–shell nanospheres [14–21]. Our single-step method affords complete core–shell nanospheres on a timescale as short as several minutes, without the need for repetitive washing or purification steps. Silica-core/gold-shell structures with a wide range of core-sizes and shell thicknesses can be readily synthesized in a controlled manner. The morphological characteristics of the reduced gold were examined systematically to elucidate the effects of various factors including pH, ASA concentration and speed of gold precursor injection. As another demonstrative purpose of our ELD method, we created hexagonal arrays of nanoscopic gold–caps and gold–capped Janus particles [24] by combining the ELD with a method for embedding silica spheres into polymer film [25–29]. The ELD method developed in the present work is applicable not only to the synthesis of functional nanospheres but also to recently emerging fields of materials science such as patterning of noble metals, nano-optics, biomolecular diagnosis and theoretical studies on the growth of metals via processes such as DLA.

2. Experimental

2.1. Materials used

Tetraethylorthosilicate (TEOS, 99.999%), aminopropyltrimethoxysilane (APMTMS, 97%), L-ascorbic acid (99%, A.C.S. reagent), polyvinylpyrrolidone (Mw ~ 55,000 g/mol), hydrogen tetrachloroaurate (III) trihydrate (99.99%), polyethylene glycol (212 kg/mol PDI = 1.05), toluene (anhydrous) were purchased from sigma–aldrich and stored in a desiccator. NH₄OH (30%) was purchased from Merck. Colloidal silica beads with a diameter of 900 nm and 1.6 μm were purchased from Merck and stored in a desiccator. NH₄OH (30%) was purchased from Nalgene. Then, the solution color was turned to deep blue gradually from green. The resulting silica beads with gold-shell were centrifuged and washed three times with deionized water to remove unreacted reagents.

2.2. Synthesis of silica beads and functionalization of amine groups

Colloidal silica beads with diameters ranging from 80 nm to 340 nm were synthesized by the well-known Stöber method [30]. Colloidal silica beads with a diameter of 900 nm and 1.6 μm were synthesized by a modified seeded-growth method as described in elsewhere [31]. Silica beads were functionalized with amine groups by self-assembled layers of aminopropyltrimethoxysilane (APMTMS). In detail, 0.23 g of dry silica beads with a diameter of 340 nm were dispersed in 40 mL ethanol and stirred in a plastic bottle (Nalgene) with Teflon coated magnetic bar. Then, 4 mL ammonia solution (0.727 M in EtOH) was poured into the dispersion with 100 μL APMTMS (0.013 M in EtOH) and the reaction bottle was kept at 25 °C. The required amount of APMTMS for the formation of a monolayer on the whole silica surface was calculated as about 1 μL by considering the total surface area of silica beads (2.2 m² for 0.23 g of silica) and the area occupied by each APMTMS molecule on the surface of silica (0.6 nm²/molecule) [32]. After 12 h, the suspension was washed with a mixture of methanol and ethanol more than five times by centrifugation to completely remove unreacted APMTMS molecules because APMTMS molecules unbound on silica can reduce gold precursors and drive the formation of gold nanoparticles in suspension rather than on the silica beads. After washing, the silica beads were dispersed in acidic water (pH 3.0, by HCl) with 2 wt.%. Other silica beads with various diameters were coated with APMTMS by following the same procedure mentioned above. The amount of APMTMS was retained to be less than 100 times relative to the one required to cover the whole surface area of silica beads.

2.3. Synthesis of core–shell nanospheres

Six milliliters of fresh aqueous solution containing ascorbic acid (0.1 M) and polyvinylpyrrolidone (0.01 g/mL) were prepared in a 20 mL glass vial with a 0.5-in.-long Teflon coated magnetic bar. The solution was stirred at 800 rpm. Thirty microliters of amine-functionalized silica dispersion (340 nm in diameter) was injected immediately using a micropipette. After 30 s, aqueous solution of gold precursor (hydrogen tetrachloroaurate (III) trihydrate (HAuCl₄·3H₂O), 0.2 M in DI water) was injected drop by drop with an injection speed of about 2 μL/s. Due to the formation of gold–shell, the solution color was turned to green from transparent. The injection of 20 μL of 0.2 M gold precursor afforded the formation of complete gold–shell when the total surface area of silica beads in the reactant solution was calculated as 5.4 × 10⁻³ m² (the amount of silica dispersion injected to the reactant solution was adjusted by considering the total surface area of silica beads to be remained as about 5.4 × 10⁻³ m² when silica dispersions with various diameters from 80 nm to 900 nm were used for the synthesis). Then, the thickness of shell was increased by adding more amount of gold precursors. As a result, the solution color was turned to deep blue gradually from green. The resulting silica beads with gold-shell were centrifuged and washed three times with deionized water to remove unreacted reagents.

2.4. Embedding of silica spheres into polystyrene (PS) film

PS film was spun-cast on silicon wafer with toluene solution of PS. The thicknesses of the film were about 480 nm and 1.6 μm in diameter, respectively. After brief oxygen plasma treatment of the PS film for better wetting of colloidal solution, a monolayer of silica spheres was spun-cast onto the PS film using colloidal silica dispersion (10 wt.% in a mixture of ethanol and methanol (50:50 v/v)). The silica beads were embedded into the PS film by heating the wafer with a conventional hot-plate heated at 150 °C for 3 min and 4 h for 250 nm and 1.6 μm silica spheres, respectively. After the heat treatment, the samples were cooled down immediately on aluminum plate.

2.5. Synthesis of gold-capped particles

Four centimeter square silicon wafer with partially embedded silica spheres were soaked in 100 mL of ethanol solution containing 10 μL APMTMS and 5 mL of ammonia for 12 h. The sample was washed with ethanol and dried under nitrogen blowing. Then, 6 mL of fresh aqueous solution containing ascorbic acid (0.1 M) and polyvinylpyrrolidone (0.01 g/mL) was poured on a plastic petri dish (5 cm in diameter). The sample was gently shaken for 30 s. Aqueous solution of HAuCl₄·3H₂O (0.2 M in DI water) was injected consecutively with an injection volume of 5 μl in every 30 s. Total amounts of 30 μL and 40 μL were used to create the gold-caps for 250 nm and 1.6 μm silica spheres, respectively. After deposition of gold on the exposed surface of embedded silica beads, the samples were sonicated in DI water for 10 s followed by drying with nitrogen blowing. Then, the gold-capped silica spheres were dispersed by sonication in toluene. After drying, the solvent was exchanged with ethanol.
2.6. Characterizations

For scanning electron microscopy (SEM) and transmission electron microscopy (TEM) characterizations, 3 μL of aqueous dispersion containing core–shell nanospheres was dropped and dried on a piece of Si wafer and a Formvar/carbon coated TEM grid, respectively. SEM images were taken by FE-SEM (Philips-XL20SFEG) without coating of conductive metal on the sample. TEM images were taken by TEM (CM20, Philips, 200 kV). Zeta-potential of APTMS-coated silica beads was measured using Particle Size Analyzer (Zetasizer nano zs, Malvern). The thickness of APTMS on silicon wafer was measured by Spectroscopic Ellipsometer (M2000D, Woollam). The pH was measured by dipping electrode into the solution using pH meter (Model 520, Thermo Orion). Absorption spectrums of core–shell nanospheres were characterized by UV/VIS–NIR spectrometer (Jasco V-570, Jasco). For the measurement, the dispersion of core–shell nanospheres was diluted with DI water and 1 mL of diluted dispersion was poured in a quartz cuvette. The cuvette was placed in the spectrometer and the extinction of core–shell nanospheres was recorded.

3. Results and discussion

3.1. Gold-shells via the direct reduction of gold on amine-functionalized surfaces

The method proposed here uses the single-step ELD of gold on silica nanospheres, as shown in Fig. 1a and b. The silica beads are first functionalized with layers of aminopropyltrimethoxysilane (APTMS) (Fig. 1a), and then, thin gold films are deposited directly on the amine-functionalized silica beads via 2-D dendritic growth (Fig. 1b). The reactant solution is composed of ASA and PVP dissolved in deionized water. ASA has been widely used in the synthesis of anisotropic metal nanoparticles because of its characteristic slow reduction of metal precursors. When ASA is dissolved in deionized water, the solution becomes acidic due to the dissociation of anisotropic metal nanoparticles because of its characteristic slow reduction of metal precursors. When ASA is dissolved in deionized water, the solution becomes acidic due to the dissociation of anisotropic metal nanoparticles because of its characteristic slow reduction of metal precursors. When ASA is dissolved in deionized water, the solution becomes acidic due to the dissociation of protons from ASA: 

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\text{ASA} + \text{H}_2\text{O} \rightarrow \text{ASA}^- + \text{H}_2\text{O} + \text{H}^+. \]

This protonate the amine groups on the silica beads, and the ASA− anions in aqueous solution are attracted to the protonated amine groups. PVP has been extensively used to stabilize colloidal spheres in various solvents because the amphiphilic PVP chains adsorb on various surfaces, including organic, inorganic, and metallic materials [33]. The ion–dipole interaction between the carbonyl group of PVP and protonated amine groups has recently been investigated [22]. Furthermore, the carbonyl groups of PVP are known to form complexes with metal ions and bind onto hydrophobic metal surfaces [34]. Fig. 1c shows a schematic illustration of the binding of reagents around a silica sphere covered with protonated amine groups. The dissociation constant (pKₐ) of the aminopropyl group is about 10, and the pH of a 0.1 M ASA solution is about 2.7 [22]. Hence, the amine groups on the silica beads are predominantly protonated, and thus attract negatively-charged reagents such as the gold precursor, \(\text{ASA}^-\), and PVP. As a result, such reagents will be concentrated near the surfaces of the silica beads. This local concentration of reagents is important for the direct deposition of gold on the silica beads because the reduction of gold occurs more favorably near the silica beads than in the reaction solution. Furthermore, the reduced gold nuclei near the silica beads are trapped by the PVP chains surrounding the silica beads in a manner similar to that observed during metal nanoparticle capping by PVP [34]. Thus, the presence of amine groups on the silica beads and their protonation are crucial factors in the proposed ELD method.

The surface charge on a nanosphere can be estimated by measuring the zeta-potential. Fig. 2 shows the variation in zeta-potential according to the solution pH, where the pH was varied by adding HCl or \(\text{NH}_4\text{OH}\) to the solution. The zeta-potential was found to range from 71.6 mV at pH 2.7 to −58.1 mV at pH 11. In the present work, silica beads were functionalized with APTMS via a silane-coupling reaction in a mixture of ammonia and ethanol. The presence of water in the reactant solution is significant for the formation of complete self-assembled layers on silica. However, the presence of excess water induces the polymerization of the self-assembled molecules and leads to the formation of multilayered self-assembled layers [35,36]. In the present experiments, the silica beads were expected to be coated by APTMS multilayers because a significant amount of aqueous ammonia solution was used in the APTMS reactant solution. To confirm this multilayer formation, we coated an oxidized silicon wafer with APTMS layers under the same reaction conditions as used in the functionalization of the silica beads because direct measurement of the thickness of APTMS layers on silica beads was not feasible. The amount of APTMS was 100 times greater than the amount of APTMS required to completely cover the silicon wafer. The thickness of the APTMS coating was found to be about 2.63 nm by spectroscopic ellipsometry. Given that the thickness of a monolayer of aminopropyltriethoxysilane (APTES), which has a chemical structure similar to that of APTMS, is between 0.5 and 0.9 nm [37]. We expect that multilayers of APTMS formed on the silica beads in the present work.

3.2. Dendritic growth of the gold films on the silica beads

Fig. 3 shows representative SEM and TEM images of silica beads covered with thin gold films formed via dendritic growth. Fig. 3a, b, and e show the dendritic growth of the gold films and the gradual...
formation of complete gold-shells via lateral growth of the fractal gold films. The gold films were grown as follows. First, 6 mL of fresh aqueous solution containing 0.1 M ascorbic acid and 0.01 g/mL polyvinyl-pyrrolidone was poured into the 20 mL glass vial with agitation. Then, 30 L of 2 wt.% dispersion of 340 nm amine-functionalized silica beads was injected into the vial with a micropipette. After agitation for 30 s, various amounts of 0.2 M aqueous hydrogen tetrachloroaurate (III) trihydrate solution were injected at an injection speed of 2 L/s. The reduction of gold on the silica surfaces was completed within several minutes (see Movie clip S1 in Supplementary information). Interestingly, when 5 L of gold precursor (10^-6 mol) was injected, the reduced gold grew laterally on the silica surfaces with a dendritic morphology, without forming gold nanoparticles in the reactant solution (Fig. 3a and inset TEM image). The injection of 15 L gold precursor (3 × 10^-6 mol) resulted in the growth of dendrites (Fig. 3b), while the injection of 20 L (4 × 10^-6 mol) afforded a complete gold-shell (data not shown). Fig. 3c and d are the TEM images of the core–shell nanospheres in Fig. 3b. In Fig. 3d, the lattice fringe of the gold-shell is clearly observed with the lattice spacing of ~0.24 nm, corresponding to the [1 1 1] lattice plane of gold.

3-D thickening of the gold-shell was observed after shell formation was completed as shown in Fig. 3e. The total amount of gold precursor injected was 40 L (8 × 10^-6 mol). The thickness of the final gold-shell, as determined by TEM analysis, was found to be 30 ± 3 nm (see inset of Fig. 3c). Additional injections of gold precursor caused the formation of small gold nanoparticles in the reactant solution as well as thickening of the gold-shells (data not shown).

Zhao and Fendler [7] and Saliba et al. [8] examined the dendritic growth of gold during the electrodeposition of gold precursor under an organized monolayer of surfactant molecules formed at an air/liquid interface. In particular, Saliba et al. showed that a monolayer of dimethyldioctadecylammonium (DODA) at an air/liquid interface immobilized a negatively-charged gold precursor. Further, the authors found that when the density of the surfactant molecules at the interface was increased by compressing the DODA monolayer, lateral growth of a uniform 2-D gold film with a dendritic morphology occurred rather than 3-D thickening. Although we employed ELD instead of electrodeposition, our system of positively-charged protonated amine groups and negatively-charged gold precursor ions showed behavior similar to that observed by Saliba et al. In our method, the protonated amine groups on the silica surface attract the negatively-charged gold precursor ions as well as the other reagents involved in the reduction process. As a result, the trapped gold precursors are reduced by ASA, and the

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Fig. 3. SEM and TEM images of the gold dendrites grown on the silica beads (340 nm in diameter). (a) and (b) Silica beads partially covered by the gold dendrites. (c) and (d) TEM and HRTEM images of core–shell nanospheres in SEM image b. (e) Complete core–shell nanospheres with the shell thickness of 30 ± 3 nm. Inset is a TEM image of the core–shell nanospheres. (f) Anisotropically grown gold rods formed when an excess amount of gold precursor is injected at once. Scale bars in (a), (b), and (e) are 200 nm. Scale bars in the inset TEM images in (a) and (e) are 100 nm. Scale bars in (c) and (d) are 100 nm and 5 nm, respectively. Scale bar in (f) is 500 nm.
reduced gold nuclei diffuse on the surfaces of the amine-functionalized silica beads due to the weak binding between the amine groups and the gold adatoms. Finally, the diffusing nuclei rapidly stick to and relax on the facets of the pre-deposited gold without forming well-organized crystals, thus forming fractal gold aggregates on the silica surfaces. This phenomenon is known as DLA. In DLA, the active, diffusing nuclei are usually deactivated within a short time. Therefore, the nuclei rarely reach the most energetically favorable sites on the surfaces of the pre-deposited metal [7–9].

The dendritic growth of gold film in our system shown in Fig. 3a–e is quite different from the seeded-growth of gold nanoparticles. In seeded growth [18–20], tiny gold nanoparticles with diameters of several nanometers initially bind to the surface of amine-functionalized silica, and the bound nanoparticles are then grown to form a complete gold-shell. In this type of growth, the density of seed particles on the silica surface is an important factor determining complete shell formation. In growth of a gold film via DLA, by contrast, active nuclei generated on the amine-functional-

![Fig. 4. SEM images of reduced gold on silica beads at pH values of: (a) 2.7, (b) 5, (c) 8 and (d) 10. Insets are the magnified SEM images of each sample. Scale bars are 500 nm.](image1)

![Fig. 5. SEM images of silica beads covered by gold-nanoparticles or -shell reduced in various concentrations of ASA: (a) 0.001 M (b) 0.05 M (c) 0.1 M (d) 1 M. Scale bars are 200 nm.](image2)
ized silica surface grow and extend laterally to cover the entire surface of silica spheres. Therefore, using the DLA-based approach, complete gold-shells can be easily obtained within a few minutes without concerns regarding the attachment and density of gold-seed particles.

Fig. 3f shows the anisotropic growth of gold that occurs when an excess amount of gold precursor is injected at once. In this case, 40 μL of 0.2 M gold precursor solution was injected immediately. In the systems that exhibited dendritic growth (Fig. 3a–e), the concentration of the gold precursor in the solution remained as low as 10^{-4} M because the precursor supplied at an injection speed of 2 μL/s was consumed quickly on the silica surfaces. However, when 40 μL of the gold precursor was injected at once, the concentration of the precursor increased suddenly up to 10^{-3} M. This rapid increase in precursor concentration resulted in the formation of a significant number of gold nanoparticles in the reactant solution as well as on the silica beads. Furthermore, the reduced gold on the silica beads grew anisotropically. A large concentration gradient is induced between the silica surfaces and the reactant solution because the gold precursor is consumed rapidly near the surfaces of the silica beads. This concentration gradient accelerates the mass transport of gold precursor from the solution to the silica surfaces, causing greater amounts of precursor to be delivered. This enhanced transport of gold precursor results in the formation of a large population of reduced gold nuclei near the silica surfaces, leading to 3-D growth of gold [8]. Therefore, 3-D thickening becomes the dominant process rather than 2-D dendritic growth. This example demonstrates that the injection speed of the gold precursor into the reactant solution is an important factor in the synthesis.

3.3. Effects of solution pH and concentration of ASA on the morphology of the deposited gold

The protonation state of the amine groups on the silica surfaces is dependent on the solution pH and is one of the important factors in our method. ASA molecules provide the protons: the pH of the solution reaches 2.7 when 0.1 M of ASA is dissolved in deionized water. When a base was added to the reactant solution, the zeta-potential was decreased, as shown in Fig. 2. The SEM images in Fig. 4a–d show the morphologies of gold reduced on silica beads at pH values of 2.7, 5, 8, and 10, respectively, where the solution pH was adjusted by the adding of sodium hydroxide (NaOH). A complete core–shell was found to be synthesized when the...
reaction was carried out in the absence of NaOH (Fig. 4a), whereas gold nanoparticles were observed on the silica beads at pH 5 (Fig. 4b). The formation of nanoparticles instead of a gold film can be attributed to the decrease in electrostatic attraction between the protonated amine groups and the reactants as a result of the reduced zeta-potential of amine-functionalized silica beads at higher pH. Further increase of solution pH to 8 resulted in the formation of nanoparticle aggregates in the solution rather than on the silica beads (Fig. 4c). Finally, free gold nanoparticles with a spherical shape were synthesized at pH 10 (Fig. 4d). The direct deposition of gold onto the silica beads cannot be achieved at this pH because of the reduced concentrations of the reactants near the silica beads.

Since ASA acts as a reducing agent, the concentration of ASA in the reactant solution also affects the morphology of the reduced gold. Fig. 5 shows the reduced gold synthesized on silica beads in solutions with various concentrations of ASA. When the gold precursor was reduced in 0.001 M ASA solution, gold nanoparticles formed on silica beads (Fig. 5a). There are two possible reasons for this phenomenon. First, the growth of gold nanoparticles may be due to the higher solution pH that arises at low concentrations of ASA. The pH of the 0.001 M ASA solution was found to be 3.9. Although the amine groups on the silica beads are expected to be predominantly protonated at this pH, the higher pH reduces the magnitude of the zeta-potential of the beads and the charge interactions, as discussed above. Second, gold nanoparticles may form because of the slow reduction of gold near the silica beads at low ASA concentrations. The number of ASA molecules near the beads and the rate of reduction of gold are significantly diminished due to the low concentration of ASA around the beads. It is well-known that slow reduction conditions are usually give rise to anisotropic growth of metal nanoparticles such as nanorods or polygons because mild reducing conditions provide enough time for the metal nuclei to crystallize [2,3]. The observation of triangular and hexagonal gold nanoplates (indicated by the arrows in Fig. 5a) provides strong evidence of the anisotropic growth of gold. In contrast, a complete gold-shell was obtained when the ASA concentration was 0.05 M (pH 2.9) or 0.1 M (pH 2.7), as shown in Fig. 5b and c, respectively. Although these conditions were found to be suitable for the formation of complete gold-shells, the surfaces of the gold-shells formed in the 0.1 M solution were smoother than those formed in the 0.05 M solution. Further, higher concentrations of ASA resulted in the formation of small gold nanoparticles in the reactant solution, as shown in Fig. 5d. When the concentration of ASA is suitable for shell growth, the reduction is much faster near the surface of the silica beads than in the reactant solution because ASA is a slow reduction agent and the concentration of ASA molecules is enriched around the silica beads.

3.4. Surface plasmon resonances of core–shell nanospheres

Using conditions identical to those described above, core–shell nanospheres with diameters ranging from 100 to 900 nm were synthesized (see Supporting information S2 and Fig. S2). There were no significant variations in film quality according to the size of the silica beads. Also, SPR tuning from visible to near-infrared was achieved by manipulating the shell thickness relative to the core-radius as shown in Fig. 6, which showed the same performance as the core–shell nanoparticles synthesized by multi-step seeded-growth method. The core–shell nanospheres in Fig. 6a–d were obtained by injecting 1 μL, 2 μL, 4 μL, and 8 μL of 0.2 M gold precursor, respectively. The average thicknesses of the gold-shells, measured by TEM from more than 20 core–shell nanospheres for each sample, were gradually increased as shown in Fig. 6a–d, respectively. The optical absorptions induced by surface plasmon resonance from the core–shell nanospheres in Fig. 6a–d were plotted in Fig. 6e. For spectrum (a) for which the ratio of the core-radius to the shell thickness of the sphere (R/L) is about 7.27, the absorption maximum is observed at 888 nm. The absorption maximum blue shift gradually to 782 nm for R ~ 5.40 (spectrum (b)) and 732 nm for R ~ 3.70 (spectrum (c)). Finally, the extinction wavelength in spectrum (d) arise at 669 nm when R is about 2.83. To support our experimental

Fig. 7. SEM images of the hexagonally-ordered gold-caps deposited on the partially embedded silica spheres into the PS matrix and the gold-capped particles obtained after removal of the PS film matrix: (a) hexagonally arranged gold-caps deposited on the embedded silica spheres. The average diameters of the gold-caps and the silica spheres are 228 ± 5 nm and 250 nm, respectively, (b) a tilted SEM image of the array of gold-caps. The average diameters of the gold-caps and the silica spheres were 1.09 ± 0.01 μm and 1.60 μm, respectively, (c) and (d) are gold-capped Janus particles obtained from the samples in (a) and (b) after dissolving of PS matrix, respectively. Scale bars are 200 nm in (a) and (c) and 2 μm in (b) and (d).
plasmonic responses, we performed full three-dimensional numerical calculation using the Finite Difference Time Domain (FDTD) method [38]. In the simulation, we assumed that the core–shell nanoparticles are comprised of silica-core of 40 nm in radius and uniform thickness of gold-shell. The simulated extinction coefficients were compared with experimentally observed results in Fig. 6f. The experimentally observed extinction coefficients were slightly red shifted compared to the simulated results by a factor of ca. 50 nm in wavelength. This slight discrepancy might be due to the surface roughness of the gold-shell [39] and the adsorption of PVP, which were not considered in our FDTD simulation. Overall, our core–shell nanoparticles created by the simple one-pot reaction showed the same performance to those synthesized by the multi-step method using seeded-growth of gold on silica surface.

3.5. Nanopatterning of gold-caps and synthesis of gold-capped particles

We created gold-capped silica particles from nanoscopic arrays of gold-caps on a polymer substrate. The ELD method was applied to a monolayer of silica spheres that was partially embedded in a PS film matrix [25]. The embedding of the silica particles was induced by wetting of the viscous liquid-like PS at a temperature above the glass transition temperature of PS ($T_g \sim 100^\circ C$). The embedding depth of the silica spheres was precisely controlled by adjusting the heating time. After the embedding of silica spheres to a depth of more than a particle radius, hexagonally-ordered silica islands partially exposed to air on the PS film matrix were created. Next, APTMS was coated on the silica islands by soaking the sample in an ethanol solution of APTMS. Finally, ELD of gold film onto the APTMS-coated islands gave rise to an array of gold-caps (Fig. 7a and b). The average diameters of the silica spheres in Fig. 7a and b were about 250 nm and 1.60 µm, respectively. Notably, a smooth boundary between each gold island and the embedding matrix was observed even on silica islands with diameters of about 200 nm, as shown in Fig. 7a. This method for creating a nanoscopic array of gold-caps provides a simple and versatile protocol for nano-patterning of gold islands. Furthermore, a dispersion of gold-capped silica particles could be created from the array of embedded gold-capped particles by dissolving the PS matrix with toluene under sonication. The dispersion of gold-capped particles in toluene showed low stability due to the hydrophilic surface property of silica; however, after removal of the PS matrix, a more stable dispersion was obtained by redispersing the gold-capped particles in ethanol. Fig. 7c and d show SEM images of gold-capped Janus particles obtained from the arrays shown in Fig. 7a and b, respectively. The average sizes of the gold-caps in Fig. 7c and d were 228 ± 5 nm and 1.09 ± 0.01 µm in diameter, respectively. Thus, the combination of the PS matrix as a protection layer and ELD only on the exposed silica surface enables the creation of the gold-capped Janus particles with well-defined boundaries. Furthermore, the size of the gold-caps on the silica spheres could be easily controlled by adjusting the embedding depth of the silica spheres [25].

4. Conclusions

In this paper, we have demonstrated a simple and straightforward ELD method using two-dimensional (2-D) dendritic growth of gold film. In the proposed system, the amine groups on the silica surfaces are protonated, and hence attract the negatively-charged ascorbate ions and the gold precursor via electrostatic. As a result, gold films are reduced directly on the amine groups with a 2-D fractal morphology induced by the DLA of gold nuclei. A systematic investigation of the synthesis of silica-core/gold-shell particles using the proposed ELD method was conducted, in which the effects of various parameters were studied, specifically, the zeta-potential of the silica beads, the solution pH, the ASA concentration, the speed of injection of the gold precursor, and the size of the silica beads. In addition, silica beads with various sizes and different shell thicknesses were synthesized via a one-pot reaction. Finally, we synthesized gold-capped silica particles via ELD of gold on a patterned array of silica nanoparticles embedded in PS followed by dissolution of the PS matrix, thus demonstrating the potential utility of the proposed method in emerging fields of materials science such as patterning of noble metals and studies of nanometer-scale optics [40].

Acknowledgments

This work was supported by a grant from the Creative Research Initiative Program of the Ministry of Education, Science & Technology for “Complementary Hybridization of Optical and Fluidic Devices for Integrated Optofluidic Systems.” This research was supported by WCU (World Class University) program through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology (R32-2008-000-10142-0). The authors also appreciate partial support from the Brain Korea 21 Program.

Appendix A. Supplementary material

Movie clip S1: procedures for the synthesis of silica-core/gold-shell nanospheres; discussion about synthesis of silica-core/gold-shell nanoparticles with various size of silica and following SEM images of Fig. S2. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcis.2010.07.007.

References