Palladium-Catalyzed Electroless Plating of Gold on Latex Particle Surfaces

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ABSTRACT: Gold can be deposited onto a latex particle surface via the growth of metal islands with the electroless plating method. A new method is proposed for the electroless plating of gold on the surface of poly(styrene-*co*-vinylimidazole) latex particles, which is catalyzed by palladium present on the latex particle surfaces. The palladium ions are anchored to the latex particle surfaces by the formation of a palladium–imidazole complex, and palladium nanoparticles are nucleated by a reductant. These palladium islands act as catalytic sites, so gold is preferentially deposited onto the latex particle surfaces. Transmission electron microscopy, X-ray photoelectron spectroscopy, and sucrose density gradient column results indicate that the palladium is associated with the imidazole-functionalized latex particles. Different gold loading levels and reductant types were explored. Latex particles were partially encapsulated by finely dispersed gold nanoparticles less than 2 nm in diameter or by gold islands with sizes ranging from 10 to 100 nm up to a gold loading level of 3.1 mg of Au/m^2 of latex. However, using higher gold loading levels led to uncontrollable electroless plating of gold because gold reduction in the water phase became very dominant even in the presence of catalytic palladium on the latex particle surface. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 843–849, 2009

Key words: catalysts; emulsion polymerization; ESCA/XPS; latices; metal-polymer complexes

INTRODUCTION

Metal-encapsulated polymer particles have been employed to take advantage of the properties of metal particles because colloidal metal particles have been shown to exhibit size-selective optical properties and have been demonstrated as optical sensing materials.[1–3] For instance, the preparation of metal-encapsulated polymer particles has been carried out by the simple adsorption of preformed fine metal particles onto latex particle surfaces.[4–7] Electroless plating, that is, the *in situ* reduction of metal ions, has been investigated in the presence of latex particles. However, the formed metals are not only unevenly distributed on the latex particle surfaces but also exist separately in the aqueous water phase.[8,9] Such metal particles produced in the continuous phase could serve as new catalytic surfaces, resulting in a poorly controlled electroless plating process.

For electroless plating to occur, the surface of the polymeric microspheres must be chemically treated to achieve a high metal loading on the polymer surfaces. This process is called sensitization and is normally carried out with $SnCl_2$ on various latex particle surfaces.[10–13] Sensitization via $SnCl_2$ is dependent on the concentration of oxygen dissolved in the water and the hydrolysis of metal halides, which is very difficult to control.[14] It has been reported that metal ions can be anchored to the functionalized surfaces of latex particles by complex formation.[15–17]

The binding of catalytic amounts of noble metals such as palladium onto latex particle surfaces may allow a controlled means of introducing metal atom populations at preselected sites on the latex particle surfaces because the electroless plating of the metal would occur primarily by autocatalysis of palladium present on the particle surfaces. These metal particles initially do not fully cover the particle surface. However, small metal particles can also grow and coalesce with one another as electroless plating proceeds, eliminating the metallic island boundaries and thus resulting in high coverage of the polymer surface by the metal. The introduction of specific functional groups into latex particles can capture the catalytic palladium via metal–ligand complex formation.

Our previous work[18] showed that gold particles were nucleated from gold–imidazole complex formation followed by *in situ* gold reduction, and the amount of gold ions complexed on imidazole-functionalized latex could depend on the surface

imidazole density. More importantly, gold particles could be desorbed and re-aggregated into different morphologies during the reduction process. The interaction between the ligand and the metal ion and its reduced atom should be strong enough to prevent metal dissociation, which can lead to the desorption of metals from the surface when the metal ions are reduced, and thus, to the subsequent uncontrolled formation of metal seeds and clusters in the solution phase. Palladium (in both ionic and zerovalent states) has been reported to be well associated with nitrogen atoms present in a ligand.[19,20] In this work, palladium as the precursor element was used for further metal deposition. Different reductants and concentrations of metal ions to be deposited were explored to obtain different and preferably high gold loading levels on latex particles.

EXPERIMENTAL

Materials

Styrene monomer (99%; Fisher Scientific Co., Pittsburgh, PA) was distilled in the presence of cuprous chloride (>97%; Sigma–Aldrich, Milwaukee, WI) at a reduced pressure of 35 mmHg at 50°C to eliminate inhibitors. 2,2′-Azobis(2-methylpropionamidine) dihydrochloride (V-50, Wako, Richmond, VA) was used as received. 1-Vinylimidazole (Sigma–Aldrich) was used after cleaning with inhibitor-removing columns.[21] Sodium borohydride (NaBH$_4$; 99.995%), dimethylamine borane [DMAB or (CH$_3$)$_2$NHBH$_3$; 97%], ascorbic acid, hydroxyl amine (NH$_2$OH; 50 wt % solution in water), sodium tetracholoropalladate (Na$_2$PdCl$_4$; 99.999%), hydrogen tetrachloroaurate hydrate (HAuCl$_4$·nH$_2$O; 99.999%), and sucrose were used as received (all from Sigma–Aldrich).

Characterization

The formation of metal on the surface of latex particles was investigated by transmission electron microscopy (TEM) with a Philips (Eindhoven, The Netherlands) 420T instrument operated at an accelerating voltage of 100 kV and with a JEOL (Peabody, MA) 2000FX instrument at an accelerating voltage of 200 kV.

Binding energies of the N1s core level and Pd3d core level were investigated previously after the application of the palladium electroless plating process to latex particles with a Scienta ESCA 3000 instrument (Scienta Instrument AB, Uppsala, Sweden). The reference binding energy to shift the obtained spectra was 284.82 eV because polystyrene was the main component of the model latex system in this work and the C1s core levels in polystyrene have been well reported as 284.76 (75%) and 285 eV (25%).[22]

The metal-encapsulated latex particles were separated by ultracentrifugation of sucrose density gradient columns (DGCs)[23,24] at 30,000 rpm and 5°C for 1 h. The DGC columns were prepared with 15, 20, 25, 30, and 35 wt % aqueous sucrose solutions. The corresponding densities were 1.059, 1.087, 1.103, 1.127, and 1.151 g/cm^3. For a clearer imaging analysis, sucrose-contaminated particles were washed and redispersed in deionized water with ultracentrifugation at 10,000 rpm and 5°C for 30 min before TEM imaging.

Ultraviolet–visible (UV–vis) absorbances at 430 nm were measured to determine the concentration of ionic palladium species with a Spectronic Genesys 2 UV–vis instrument (Thermo Electron Corp., Waltham, MA). The chemistry of palladium halides in aqueous solutions is dominated by hydrolysis, which results in the formation of water-insoluble hydroxo- or chloro-bridged palladium(II) oligomer precipitates.[25–31] In this work, the pH was maintained at 2 because hydrolysis could be thermodynamically suppressed by the pH being kept low or by external chloride ions being added.[32]

Model latex synthesis

Imidazole-functionalized latex particles were prepared as a model system for nitrogen-containing ligands with an emulsifier-free batch emulsion copolymerization process with styrene and 1-vinylimidazole (30 mol % with respect to styrene), as described in our previous work.[33] The number-average diameter (D_n) of the resulting particles was 257.8 nm, the weight-average diameter (D_w) was 258.5 nm, and the polydispersity index (D_w/D_n) was 1.003, as determined by TEM.

Preparation of palladium-catalyzed latex particles

An aqueous Na$_2$PdCl$_4$ stock solution (68.1 g, 0.4 g/L, pH 2) was slowly added to 11.9 g of an imidazole-functionalized latex particle dispersion (solids content = 2.28 wt %) under stirring at room temperature. The amount of added palladium was 1.56 mg of Pd/m^2 of latex. After 24 h, the latex particles were cleaned and separated by centrifugation at 10,000 rpm for 30 min. The amount of adsorbed palladium was 1.16 mg of Pd/m^2 of latex, as determined from the UV–vis spectral analysis of the supernatant solution. The theoretical density of this composite particle ($\rho_{Pd–Latex}$) can be calculated as follows:

$$\begin{aligned}\rho_{Pd-Latex} &= M_{Pd-Latex}/V_{Pd-Latex} \cong M_{Pd-Latex}/V_{Latex} \\ &= \rho_{Latex}(1 + M_{Pd}/M_{Latex}) \\ &= \rho_{Latex}(1 + W_{Pd} \times 6\rho_{Latex}^{-1}D^{-1})(g/cm^3) \end{aligned} \quad (1)$$

where ρ_{Latex} is the density of the latex (1.05 g/cm^3; polystyrene), W_{Pd} is the weight of palladium

TABLE I
Recipes for Electroless Plating of Gold on Latex Particles with Various Amounts of Added Gold

Gold loading level (mg of added Au/m^2 of latex)	0.6	1.6	3.1	12.5
Palladium-catalyzed latex (g; 0.34 wt %)	1.0	1.0	1.0	1.0
$HAuCl_4$ (mL; 0.4 g/L)	0.2	0.5	1.0	4.0
Reductant (mL; 0.1177M)	0.02	0.05	0.1	0.4
Deionized water (mL)	6.78	6.45	5.9	2.6

adsorbed on the latex surface (1.16 mg of Pd/m^2), and D is the latex diameter (257.8 nm). The theoretical density was calculated to be 1.077 g/cm^3. The sedimented latex particles were redispersed in a sonication bath (Aquasonic model 50T, VWR Scientific Products, Bridgeport, NJ) at room temperature for 10 min. The pH of the water used in the redispersion process was also 2. The cleaning process by centrifugation was repeated two more times. Subsequently, cleaning by serum replacement was carried out with fresh deionized water, and the volume was adjusted to the initial total volume of 80 mL.

Seven milliliters of a 0.1177M DMAB solution (ca. 20 times the excess molar amount of the palladium) was added to 49 mL of a previously prepared palladium-associated latex particle dispersion to reduce the palladium ions associated with imidazole groups. After 24 h of stirring at room temperature, the resulting palladium-nucleated latex particles were cleaned by three centrifugation (10,000 rpm for 30 min)/redispersion cycles followed by serum replacement.[34] The solids content of the resulting palladium-nucleated latex particles was 0.34 wt %.

Gold electroless plating on palladium-catalyzed latex particles

As shown in Table I, the electroless plating of gold was carried out with the variation of the gold loading level per unit of surface area of palladium-nucleated latex particles previously prepared with different types of reductants, such as $NaBH_4$, DMAB, ascorbic acid, and NH_2OH. The surface area of the palladium-catalyzed latex could be calculated from the density and diameter of the composite particles ($\rho_{Pd-Latex}$ and $D_{Pd-Latex}$, respectively). The surface area of palladium-catalyzed latex (m^2) was calculated $[(6000/\rho_{Pd-Latex}D_{Pd-Latex}) \times$ solids weight percentage, where the solids weight percentage was 0.34%, $D_{Pd-Latex}$ was assumed to be the same as the diameter of the latex (nm), and $\rho_{Pd-Latex}$ was 1.077 g/cm^3]. The calculated surface area was 0.0734 (m^2). Gold loading levels were calculated from the amount of added gold per surface area of the palladium-catalyzed latex [volume (mL) of the $HAuCl_4$ solution (0.4 g/L) $\times$ 0.4 $\times$ (196.96/339.70)/0.0734 mg of added Au/m^2 of latex; Table I], and the gold loading levels used in this work were 0.6, 1.6, 3.1,

and 12.5 mg of added Au/m^2 of latex. The reductant/gold concentration ratio was 10.0.

RESULTS AND DISCUSSION

### Palladium-catalyzed (palladium-reduced) latex particles

Figure 1 shows TEM micrographs of palladium-catalyzed latex particles. Extremely small palladium particles (<1 nm) were formed by DMAB reduction, so it was difficult to determine the size of the metal particles, even with TEM. According to the sucrose DGC analysis, the particles were located between two layers (1.059 and 1.087 g/cm^3). The theoretical density of these composite particles, calculated earlier to be 1.077 g/cm^3, was the average value of the densities of the two sucrose density layers, 1.059 and 1.087 g/cm^3. This implies that palladium was reduced and then located on the surface of the latex particles; otherwise, the separate metal particles would have precipitated to the bottom of the DGC.

The binding energy of $Pd3d_{5/2}$ in a phosphinated polystyrene polymer-bound Pd(0) chloride complex has been reported to be 337.5 eV.[35] When the zero-valent palladium is free of ligands, the binding energy of $Pd3d_{5/2}$ becomes close to one from metallic palladium, 335.7 eV.[36] As shown in Figure 2, the
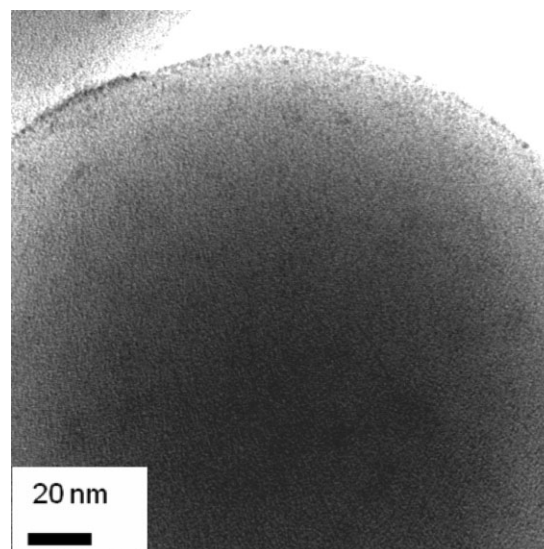
Figure 1 TEM micrograph of a palladium-nucleated latex particle.
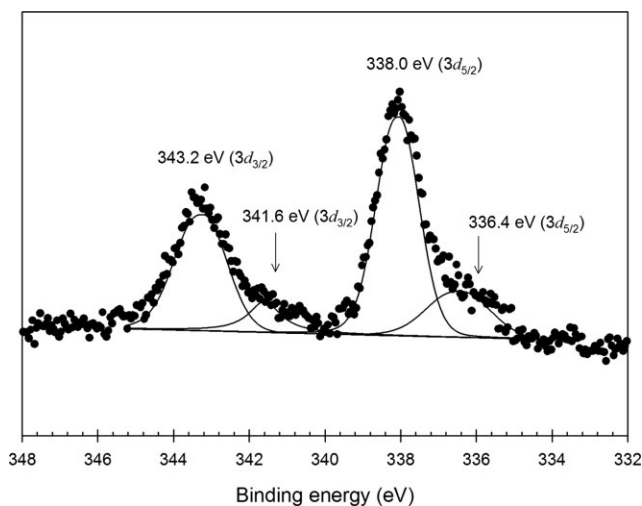
Figure 2 X-ray photoelectron spectra of the Pd3d core line of palladium-nucleated latex particles.

Pd3d spectra have main peaks present at 338.0 eV for Pd3d$_{5/2}$ and at 343.2 eV for Pd3d$_{3/2}$, and these peaks represent imidazole polymer-bound palladium chloride. Two minor peaks can also be observed at 336.4 eV for Pd3d$_{5/2}$ and at 341.6 eV for Pd3d$_{3/2}$, and they can be attributed to metallic palladium(0) surrounded by imidazole ligands. However, the identification of the reduced palladium bound with imidazole groups was not clear only from the binding energies of palladium; however, the change in the binding energy of nitrogen would support the proposed formation of reduced palladium complexed with imidazoles.

As shown in Table II, the N1s core level signal of the imidazole-functionalized latex particles contained two peak components at binding energies of 398.9 and 400.9 eV corresponding to the nitrogens of imine and amine positions, respectively.[37] The higher binding energy, 400.9 eV, for the nitrogen in the amine position, as observed in this work, might be caused by the positively charged nitrogen obtained from protonation in water and resonance

TABLE II
X-Ray Photoelectron Spectroscopy Binding Energy Positions of the N1s Core Level

|	Binding energy (eV)	
Particle	N at the imine position	N at the amine position
Imidazole-functionalized latex	398.9	400.9
Palladium-associated latex particle	399.5	400.9
Palladium-catalyzed (reduced) latex particle	399.5	400.3

stabilization of the imidazole ring.[38] When DMAB was added, this peak was slightly shifted to the reported value of the nitrogen in the tertiary amine, 400.3 eV, indicating that DMAB is a reductant as well as a deprotonating agent. The binding energy for the nitrogen in the imine position of the imidazole ring, 398.9 eV, was shifted to a higher binding energy during the palladium association and the palladium reduction stage, indicating charge transfer between the ligand and the metal atom through the existence of metal–ligand coordination bonding.

Electroless plating of gold on palladium-catalyzed latex surfaces

The electroless plating of gold on the latex particle surfaces was carried out by the reduction of the gold ions in the presence of palladium-nucleated latex particles with NaBH$_4$, DMAB, ascorbic acid, and NH$_2$OH as reductants. In Figure 3, the morphologies of the particles obtained from the different reduction processes are compared at different gold loading levels ranging from 0.6 to 12.5 mg of applied Au/m^2 of latex. The utilization of strong reductants such as NaBH$_4$ and DMAB led to the formation of relatively well distributed and small gold particles that were present on latex particle surfaces at a low gold loading level. For example, in the case of NaBH$_4$ reduction, very small gold particles, less than 2 nm in diameter, were quite evenly distributed over the surface of the latex particles up to a medium loading level of gold (i.e., 3.1 mg of applied Au/m^2).
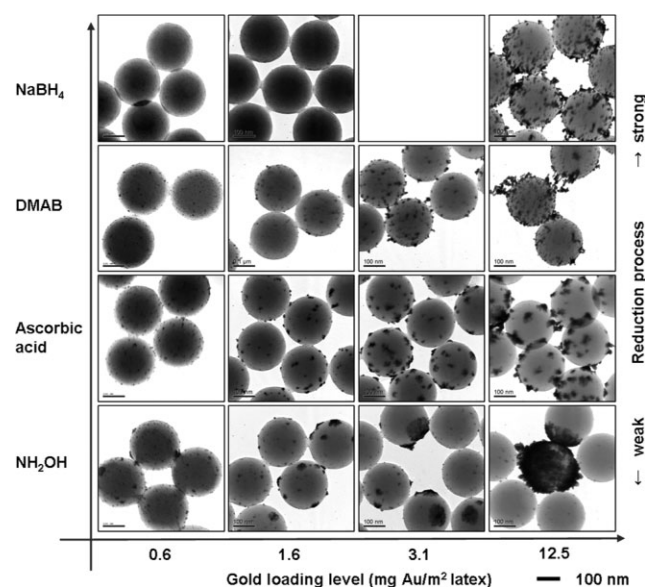
Figure 3 TEM micrographs showing the electroless plating of gold on palladium-catalyzed latex particles as a function of the gold loading level and reductant type.
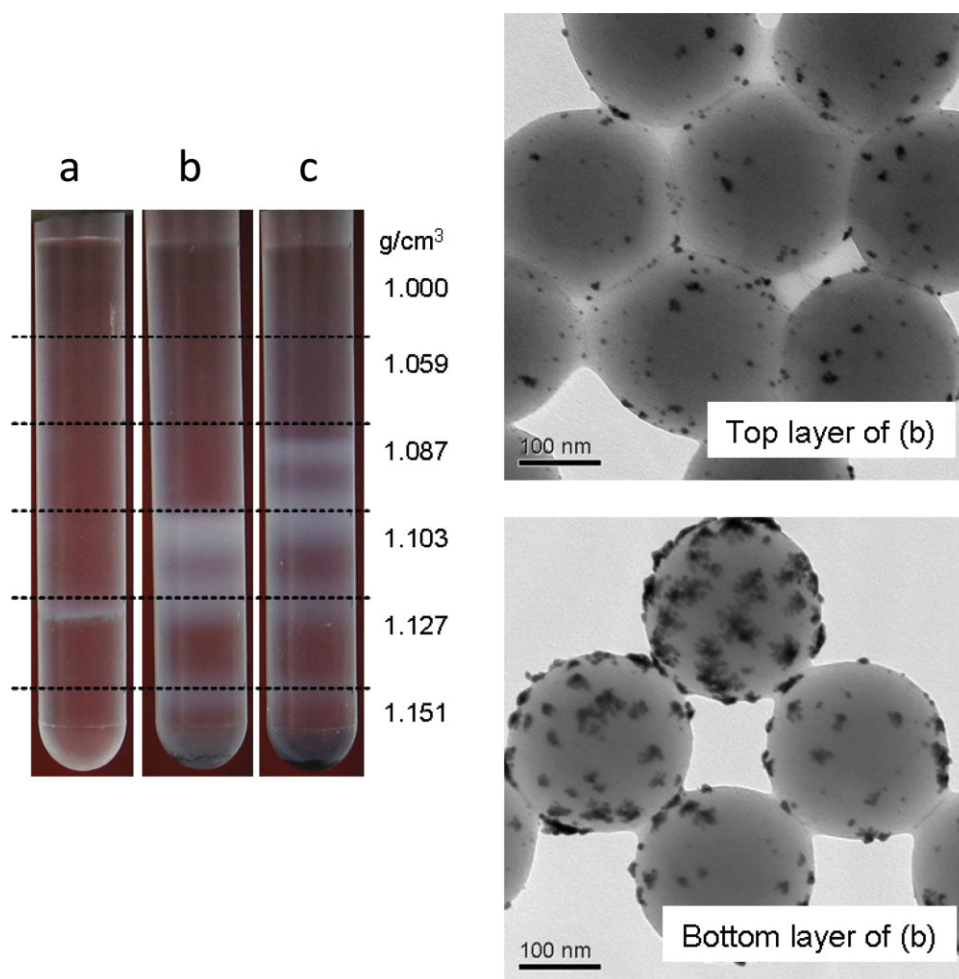
Figure 4 Sucrose DGCs of latex particles. Gold was deposited onto the latex particle surfaces via electroless plating in the presence of palladium at different gold loading levels: (a) 1.6, (b) 3.1, and (c) 12.5 mg of Au/m^2 ([ascorbic acid]/[Au] = 10). TEM imaging analysis was carried out with the particles in the top and bottom layers as separated by DGC (part b). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Gold aggregates were also observed in the form of a thin layer on the latex particle surfaces or as metallic bridges between latex particles, instead of becoming evenly distributed gold islands on the particle surfaces. This localization of gold aggregates became obvious as the amount of gold was increased. The utilization of weak reductants such as ascorbic acid and NH_2OH primarily led to the formation of localized metal aggregates on the latex particle surfaces, regardless of the gold loading levels. As shown from the micrograph for NH_2OH reduction at the highest gold loading level (12.5 mg of applied Au/m^2) in Figure 3, one of the latex particles was almost entirely covered by a thin layer of metal aggregates, but there were no recognizable metal particles in the other latex particles.

The model latex particles used in this work were prepared by a simple emulsifier-free emulsion copolymerization of styrene and a large amount of a hydrophilic comonomer, 1-vinylimidazole (30 mol % based on styrene), and its hydrophilic nature

resulted in the imidazole groups preferably being located near the surface of the latex particles. The palladium was supposed to be evenly distributed on the palladium-nucleated latex particle surface because the palladium would have been associated with the imidazole groups present on the particle surface. Conductometric titration results showed that the surface imidazole density of the model latex particles was 2.1 µequiv of imidazole/m^2 of latex, and the resulting packing area of the imidazole molecule was 80.3 $Å^2$/imidazole, as determined by surface titration.[33] However, it was observed that gold aggregates were unevenly distributed on the palladium-nucleated latex particle surface, and this could be attributed to two possibilities.

The first possibility is that the catalytic palladium was locally aggregated via surface migration or desorption from the latex particle surfaces, which was followed by the aggregation of ligand-associated palladium atoms after palladium ions were reduced. The locally distributed palladium from surface

migration or desorption and re-adsorption would have exhibited similar morphologies of gold aggregates, regardless of the reductant type, but gold aggregates were distinctly observed when a weak reductant was used at all gold loading levels in the experimental range. Therefore, palladium was believed to be evenly distributed on the latex particle surface.

The other possibility is that the reduction of gold ions in water is so dominant that gold particles are nucleated in the aqueous phase, even in the presence of palladium-catalyzed latex particles. The reduction of gold ions could also be catalyzed by palladium present on the surface of the latex particles. The reduced primary metal particles are able to react with many radicals or electrons, leading to the accumulation of electrons.[39] As a result, the metal ion reduction would rather occur at the surface of the cathodically polarized (negatively polarized) existing metal particles than in the continuous aqueous medium, and the generation of free metal particles separate from the surface can be avoided. However, if the reduction of gold in the continuous water medium is comparable to that on the existing palladium metal surface on the latex surface, both reductions can compete and nucleate metal particles either on the surface of existing metal islands on the latex particle surfaces or as free metal particles in the continuous medium.

Gold reduction was intended to occur primarily on the particle surface via the autocatalytic electroless plating process resulting from the presence of palladium on the latex particle surface, resulting in the formation of evenly distributed gold islands. However, localized gold aggregates became obvious when the gold loading level was increased, leading to a very broad distribution of densities resulting from nonuniform morphologies. This can be experimentally supported by the TEM analysis of the resulting particles separated by the sucrose DGC, as shown in Figure 4. The existence of localized gold aggregates might not be desirable, particularly for the design of metal-encapsulated latex particles with well-defined gold plasmon absorption. The aggregation of gold would exhibit a broad plasmon absorption.[40]

The use of reductants with different reducing abilities can vary the rate of gold reduction. The utilization of a strong reductant led to the fast nucleation of gold particles in the aqueous medium and on the latex particle surfaces where catalytic palladium was present. The gold particles that nucleated in the aqueous phase were not stable, and so they aggregated with one another when more nuclei were created. When large surface areas of latex particles were provided at a low gold loading level per unit of latex surface area, such aggregative deposition

onto the latex particle surfaces was favored because gold was also reduced at catalyzed palladium sites on the latex particle surface. This aggregation process finally resulted in the formation of recognizable gold islands strongly bound to the latex particle surface. When the latex surface areas were not large enough for the adsorption of gold that was nucleated in the aqueous phase, the addition of further excess amounts of gold ions facilitated their aggregation in water. These gold aggregates then adsorbed onto the surface of the latex particles, resulting in the formation of localized metal aggregates on the latex particle surfaces.

A weak reductant, such as ascorbic acid or NH_2OH, could lead to a lower population of gold nuclei in the water phase and thus a low number density of gold nuclei. However, once the particles were nucleated, they could serve as catalytic surfaces for further electroless plating, resulting in the formation of larger metal particles. They could be adsorbed onto the latex particle surface in the form of larger aggregates. When the gold aggregates were adsorbed onto the latex particle surface, the electroless plating of gold could be catalyzed to form much bigger gold clusters from the adsorbed gold aggregates. As a result, highly localized thin layers or gold aggregates could be formed on specific areas of the latex particle surface.

CONCLUSIONS

Palladium-catalyzed latex particles were prepared, and the subsequent electroless plating of gold was carried out to obtain latex particles with high gold loading levels. Latex particles were partially well encapsulated with either finely dispersed gold nanoparticles or relatively large gold islands, depending on the reductant type, up to the gold loading level of 3.1 mg of Au/m^2 of latex. The reduction of gold ions in the continuous aqueous phase was very competitive with the reduction of gold ions at catalytic sites on the latex particle surfaces, and so the use of very high gold loading levels led to uncontrollable electroless plating of gold, regardless of the type of reductant. As a result, gold aggregates can act as metallic bridges between latex particles or as localized metallic thin layers.

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