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SHORT COMMUNICATION

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Janus particles with a functional gold surface for control of surface plasmon resonance

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Abstract We report in this study the presence of Janus particles, which are candidates for use with electronic color papers. We used negatively charged polystyrene particles (370 nm) as the core particles, and gold was then sputtered onto their packed monolayer under several conditions. The sputtered particles were next redispersed into the aqueous medium by gentle sonication. Gold nanoparticles localized on one side of the cores could also serve as seeds for subsequent shell growth by electroless gold plating. Through these treatments, a series of well-dispersed Janus particles were obtained with gold nanostructures of different size and shape only on one side. Their dispersions showed different colors originating from the surface plasmon resonance absorption of gold nanoparticles localized on the hemisphere. The particles obtained by this approach have potential applications such as in sensors and electronic color paper.

Keywords Janus particle · Gold nanoparticle · Sputtering · Surface plasmon resonance

Introduction

Recently, there has been a growing interest in the preparation and application of anisotropic particles, which have a large potential for use in photonic [1] and electronic devices and as diagnosis reagents. After the pioneering research [2, 3] regarding these particles, several improved methods for preparing Janus particles (possessing two different faces at the front and back of each particle) have been formulated during the last 5 years [4–14]. Although several new methods for preparing the anisotropic particles have been investigated, there have been few reports, other than that of electrophoretic rotation by Takei and Shimizu [4], of effective phenomena occurring as a result of use of anisotropic particles. In addition to the remarkable phenomenon of Janus particles, the method of Takei and Shimizu [4] is excellent in its ability to obtain particles easily and quickly. The particles obtained by their method were chemically modified on only one side of polystyrene (PS) particles (=5–20 μm) by gold evaporation and chemisorption. Very recently, we developed thermosensitive Janus particles by gold sputtering only on one side, followed by living radical graft polymerization of thermosensitive polymer from the other side [14]. The obtained particles show anisotropic adsorption and spontaneously self-assemble into particle chains. The Janus particles whose hemispheres are covered with gold nanoparticles or films are expected to change their character with the addition of thiol derivatives. For example, dipolar particles, whose surface charges segregate onto separate poles with the addition of 2-aminoethanethiol onto the gold hemisphere, could show electrophoretic rotation [4]. In addition to dipolar particles, we would be able to obtain amphiphilic particles which have an hydrophilic face on one side and a hydrophobic face on the other side by the addition of hydroxyl groups onto the gold hemisphere.

We report in this study that Janus particles are candidates for use in electronic color papers. We used negatively charged PS particles (Dw 370 nm, Dw/Dn 1.02) as the core

particles, and gold was then sputtered onto their packed monolayer under several conditions. The sputtered particles were next redispersed into the aqueous medium by gentle sonication. Gold nanoparticles localized on one side of the cores could also serve as seeds for subsequent shell growth by electroless gold plating. Through these treatments, we obtained a series of well-dispersed Janus particles with gold nanostructures of different size and shape only on one side. Their dispersions showed different colors originating from the surface plasmon resonance absorption of gold nanoparticles localized on the hemisphere. Figure 1 shows the scheme of this study.

Experimental section

Materials

Styrene (St) was purchased from Wako Pure Chemicals Industries and purified by distillation under reduced pressure to remove inhibitors. Divinylbenzene (DVB) was purchased from Tokyo Kasei Kogyo and used as received. Potassium persulfate (KPS) was purchased from Wako Pure Chemicals Industries and purified by recrystallization from water. Hydrogen tetrachloroaurate(III) tetrahydrate ($HAuCl_4 \cdot 4H_2O$) was purchased from Wako Pure Chemicals Industries and used as received. Hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) was purchased from Junsei Chemical and used as received.

Preparation of the PS particles

A mixture of 10.0 g of St, 0.1 g of DVB, and 100 g of water was put into a 300-ml, three-necked round-bottom flask equipped with a stirrer, a nitrogen gas inlet, and a condenser. Nitrogen gas was bubbled into the mixture to purge oxygen. The system was kept at 70 °C in a water bath. A total of 10 g water containing 0.1 g of KPS was added to the flask to initiate the polymerization, and the polymerization was continued for 24 h. The obtained particles (PS particles) were purified by centrifugation and then washed with water four times.

Preparation of the Janus particles

PS particles were arranged to a monolayer on a PS substrate by a spin coater. Next, the gold was sputtered onto the particle monolayer at a discharge current of 20 mA for 2–200 s at 4 Pa (E-1030 Ion Sputter, Hitachi). The sputtered particles were then redispersed in an aqueous medium by gentle sonication for 10 s.

Electroless plating of the Janus particles and the gold-patterned substrate

Two milligrams of Janus particles (PSAu-30) was diluted to 5 ml of water, and 5–100 μl of 1 wt% $HAuCl_4$ and 25–500 μl of 40 mM $NH_2OH \cdot HCl$ were added under stirring. The reaction continued for 15 min. After the reactions, the particles were purified by centrifugation and then washed four times with water. For the patterned gold film, the film was immersed into a solution of 10 μl of 1 wt% $HAuCl_4$ and 50 μl of 40 mM $NH_2OH \cdot HCl$, and 1 ml of water. After 15 min of the reaction, the substrate was repeatedly rinsed with water.

Characterization

Approximately 2 μl of the diluted particle suspension was dried on a collodion film on copper grid and observed by field emission transmission electron microscopy (TEM, TECNAI F20, Philips Electron Optics) operated at 200 kV. Scanning electron microscopy (SEM) images were recorded with a Hitachi (S-4700) instrument operated at 5 kV. X-ray photoelectron spectroscopy (XPS) spectra were obtained on a spectrometer with a Mg Kα X-ray (JPS-

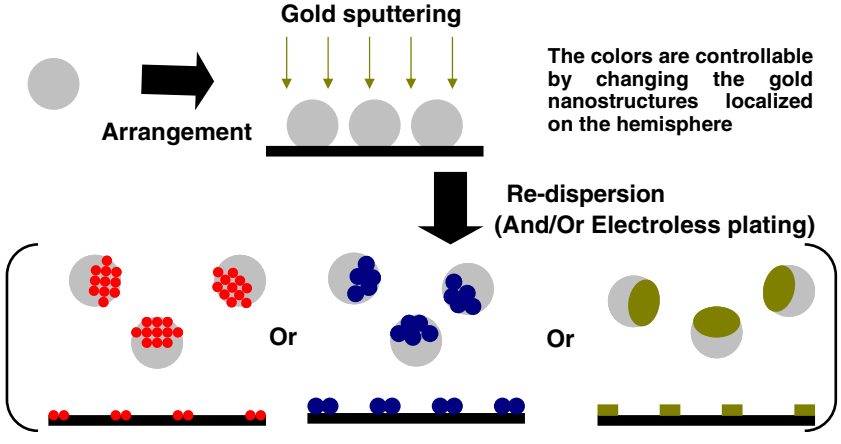

Fig. 1 Schematic representation of the preparation of Janus particles by gold sputtering. The *colors* are controllable by changing the gold nanostructures localized on the hemisphere

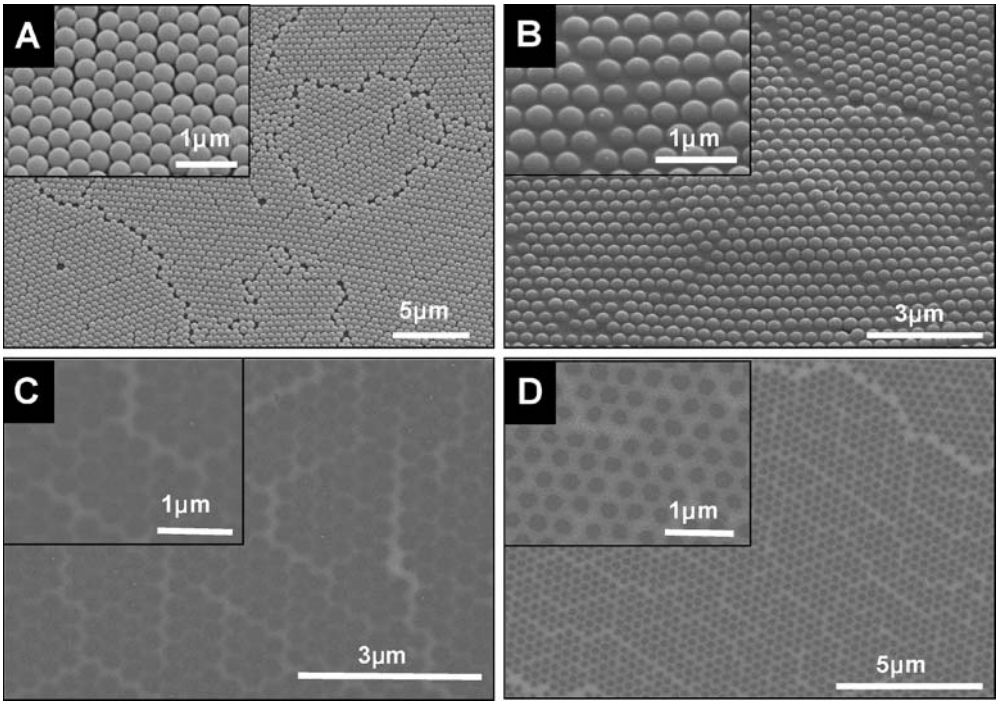

Fig. 2 **a** SEM view of a 370-nm PS particle monolayer after gold sputtering for 200 s at the discharged current of 20 mA at 4 Pa. **b** SEM view of the converted PS monolayer of (**a**) attached to carbon tape. **c** SEM view of the substrate of (**a**) after redispersal of sputtered particles by gentle sonication. **d** SEM view of the substrate of (**c**) treated with electroless gold plating. (**a**–**d**) *Insets* are close-up images

9000MX, Nippon Electronics). The atomic ratio ($Au_{4f7/2}$/C_{1s}) was calculated from the area of $Au_{4f7/2}$ and C_{1s} peaks in the spectra. Relative sensitivity factors of 40.850829 and 4.079042 were used for $Au_{4f7/2}$ and C_{1s}, respectively.

Results and discussion

Preparation of gold-localized Janus particles

Figure 2a provides an SEM view of a monolayer of 370-nm PS particles on a PS substrate after sputtering gold for 200 s at a discharge current of 20 mA at 4 Pa. Such close-packed monolayer can be easily, quickly, and reproducibly obtained with a spin coater. The introduction of gold on only one side of the particles was confirmed by XPS analysis of the top and bottom sides of the sputtered monolayer. The XPS samples for the bottom side were prepared by transferring the sputtered monolayers onto the carbon tape. Figure 2b provides an SEM view of a transferred monolayer attached to the carbon tape. The particle monolayer could be transferred onto the carbon tape in a monolayer. But the particles seemed to be slightly far apart from each other due to the stretch of the carbon tape during sample preparation, which caused an increase in the intensity of C_{1s} originating from the carbon tape by XPS analysis for the bottom side samples. Figure 3a shows the wide-range XPS spectra of the gold-sputtered monolayer for the top and bottom sides shown in Fig. 2a,b respectively, as one example. In the top-side spectrum, the peaks of gold can be easily confirmed; for example, the $Au_{4f7/2}$ peak at 84.0 eV is the characteristic peak of gold. On the other hand, no peak of elemental gold was detected from the bottom-side spectrum. Although XPS data are

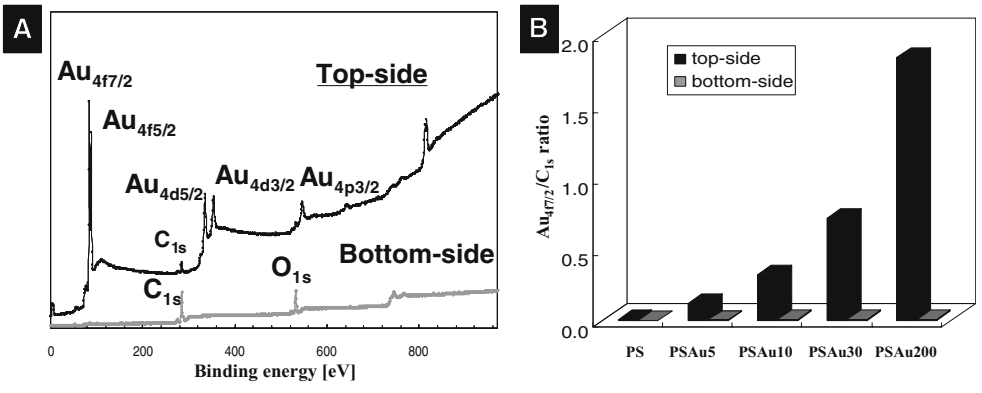

Fig. 3 **a** Wide-range XPS spectra of top and bottom sides of the gold-sputtered monolayer shown in parts **a** and **b** of Fig. 2 **b** $Au_{4f7/2}$/C_{1s} ratios for gold-sputtered PS particle monolayers for both the (left) and (*right*)

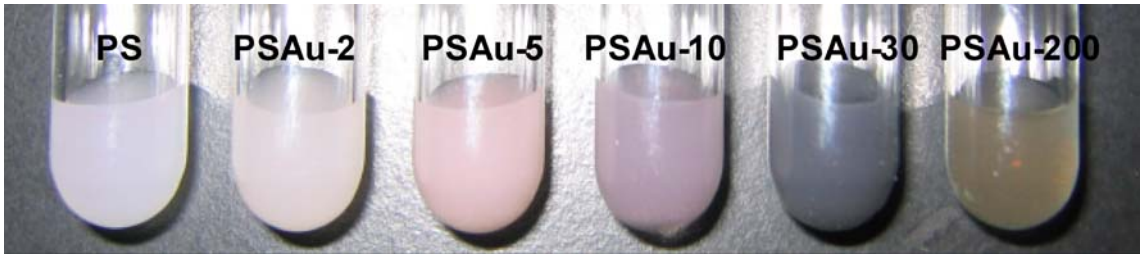

Fig. 4 Observation of the dispersions of Janus particles in aqueous medium. The concentrations of all dispersions are 1 wt%

influenced by surface topology and lateral heterogeneity [15], these data suggest that sputtered gold was localized on one hemisphere even though submicron particles were used as the cores. Figure 3b shows the $Au_{4f7/2}/C_{1s}$ ratio for the top and bottom sides of the particle monolayer sputtered under different conditions. Gold was sputtered for 2–200 s keeping other conditions unchanged, and the obtained particles were coded as PSAu-5, PSAu-10, PSAu-30, and PSAu-200. From these data, we could confirm that sputtered gold under different conditions was localized on one hemisphere, and that the thickness of the gold layer increased depending on the sputtering time. Note that not only the thickness but also the size and shape of the gold nanostructures could be controlled just by changing the sputtering time (shown in Fig. 5). The sputtered gold was no longer in nanoparticle form when the sputtering was carried out for 200 s (see Fig. 6d). After redispersion of the sputtered particles by sonication, the deposited gold still adhered to the PS substrate (Fig. 2c). These findings indicate that the obtained dispersions included sole Janus particles and no more gold agglomerates, which would be important for further applications. In addition to the nonexistence of gold agglomerates in the dispersion, the resultant two-dimensional ordering structure was very attractive. These nanostructures have been found in previous works [16, 17], but in this case, we found that the area of patterned gold film was controllable by subsequential electroless gold plating (Fig. 2d).

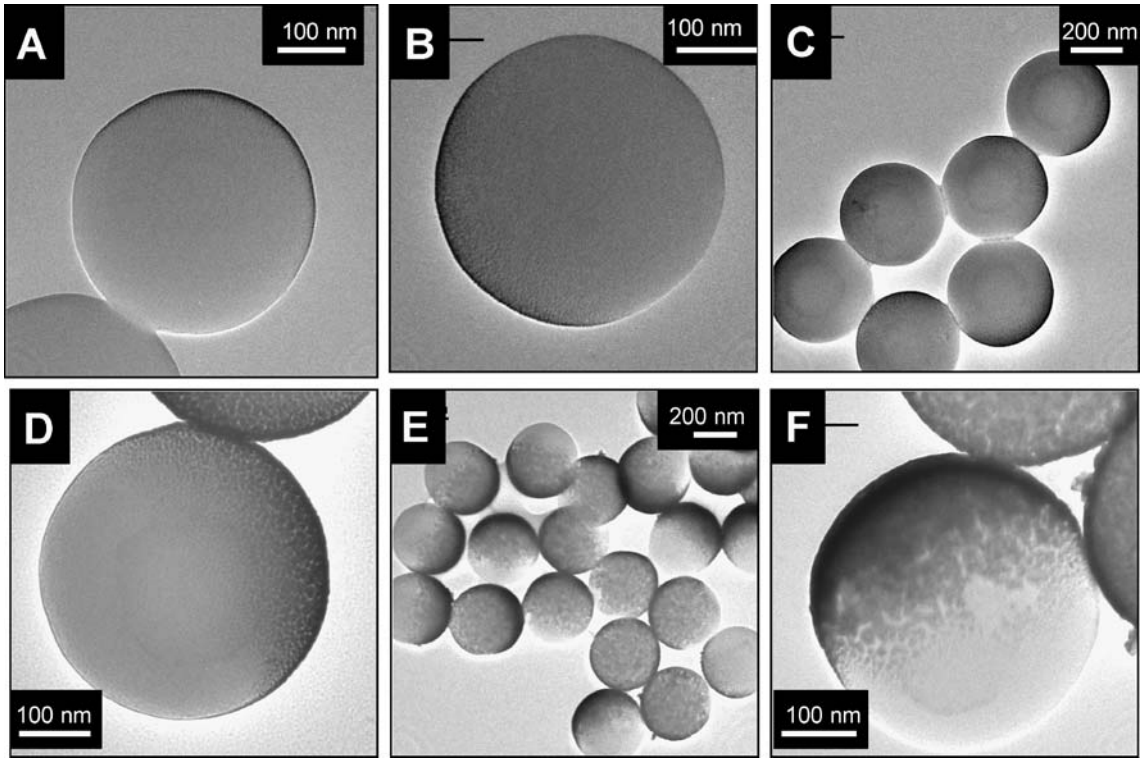

Fig. 5 TEM views of Janus particles. Sputtered times: (**a**) 5 s. (**b**) 10 s. (**c**, **d**) 30 s. (**e**, **f**) 200 s. (**d**) and (**f**) are close up images of (**c**) and (**e**), respectively

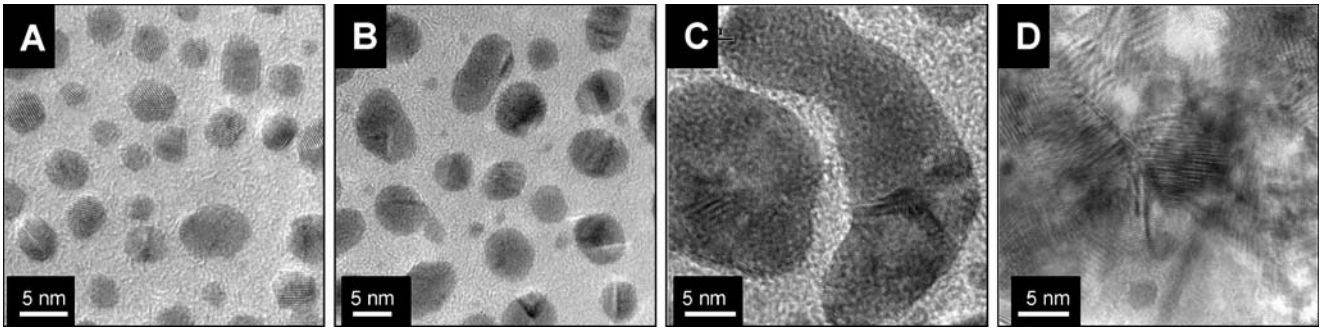

Fig. 6 TEM views of gold nanostructures formed by sputtering onto a collodion film on copper grid. Sputtered times: (**a**) 5 s. (**b**) 10 s. (**c**) 30 s. (**d**) 200 s

Observation of a series of Janus particles

A series of dispersions containing Janus particles are shown in Fig. 4. The dispersions show several colors depending on the sputtering time for each particle. TEM views of each Janus particle are shown in Fig. 5. The dispersions of Janus particles were monodispersed, as confirmed by TEM observations and dynamic light-scattering measurements. Although it is difficult to distinguish the borders on the particles between the gold-sputtered side and the PS side from these pictures, especially from Fig. 5a,b, we have already confirmed from XPS analysis that these particles were Janus-shaped particles (shown in Fig. 3a,b). We could not focus on all the gold nanostructures on the PS particles, perhaps due to the big difference in size between the polymer particles and the gold nanostructures on the particles. We then utilized another method to confirm the presence of the sputtered gold nanostructures. Figure 6 provides TEM views of gold nanostructures that were generated by gold sputtering onto a collodion film on copper grid. The sputtering conditions for the samples shown in Fig. 6 corresponded to those for the Janus particles shown in Fig. 5, respectively. When sputtered for 5 s (Fig. 6a), the sputtered gold was shaped as spherical nanoparticles (mean diameter, 4.5±0.3 nm). On the other hand, in the case of 10-s sputtering (Fig. 6b), the

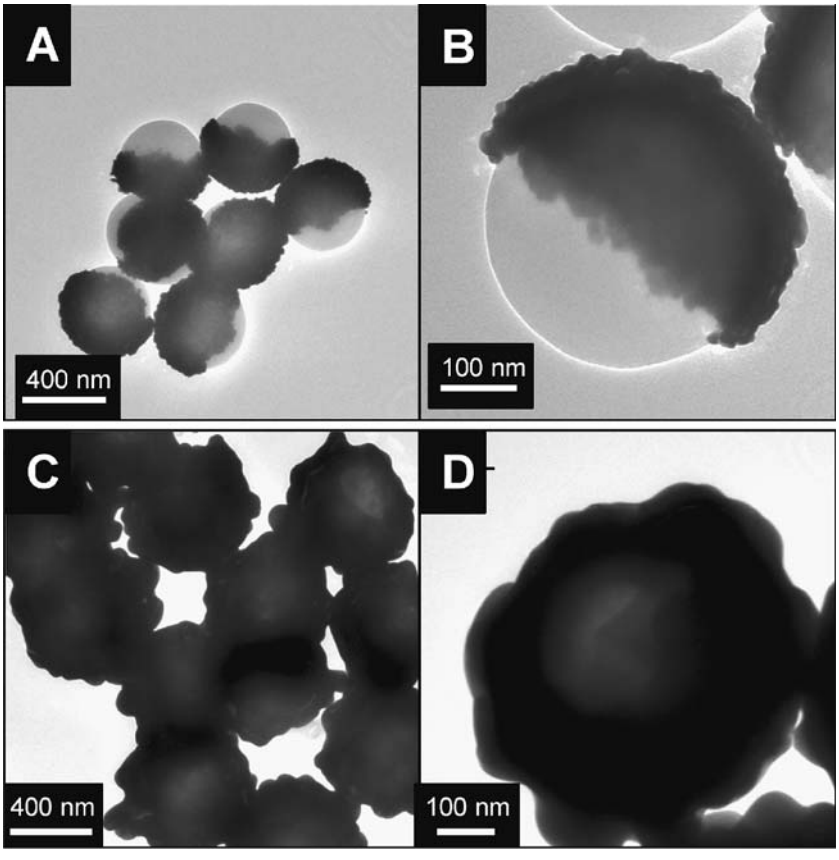

Fig. 7 TEM views of PSAu-30 particles treated with electroless gold plating. Conditions of electroless plating: (**a**, **b**) 10 μl of 1 wt% $HAuCl_4$ and 50 μl of 40 mM $NH_2OH{\cdot}HCl$, (**c**, **d**) 100 μl of 1 wt% $HAuCl_4$ and 500 μl of 40 mM $NH_2OH{\cdot}HCl$. Each couple was taken at different magnification

sputtered gold was also in the form of nanoparticles but seemed to be slightly ellipsoidal (mean diameter, 7.0± 0.6 nm). These nanostructures affected the colors of the dispersions. The difference between them originated from the surface plasmon resonance absorption of the gold nanoparticles. In general, gold nanoparticles in aqueous medium show a red color due to the strong absorption around 520 nm. The resonance frequency is dependent on the size, shape, and state of aggregation of the nanoparticles [18, 19]. The dispersion of PSAu-5 shows a red opaque color, while that of PSAu-10 shows a purple opaque color (shown in Fig. 4). For the Janus particles sputtered for 10 s, the size and shape of the gold nanoparticles on the PS particles differed from the particles sputtered for 5 s, and consequently, the absorption peak was red-shifted. It is known that the wavelength of a gold nanorod's longitudinal surface plasmon can be accurately controlled from 600 to 1,300 nm by altering the aspect ratio [20]. By increasing the sputtering time, gold nanostructures grew to islands (Fig. 6c) and finally to a film (Fig. 6d). The dispersions containing these Janus particles showed black and gold colors, respectively, due to each of the gold nanostructures shown in Fig. 4. As a result, we obtained several colored dispersions containing Janus particles. These Janus particles are monodispersed and reproducible. We are still investigating further the application of these Janus particles to electronic color paper.

In addition, the gold nanostructures localized on one side of the cores were also controllable by electroless gold plating. Gold nanoparticles can serve as seeds for subsequent shell growth by electroless plating [21]. Such treatment results in a uniform increase in gold coverage. Figure 7 shows TEM views of Janus particles (PSAu-30) treated by electroless gold plating. We were able to control the formation of gold nanostructures to only one side (Fig. 4a,b); a gold shell covering the whole PS surface was also found under certain conditions (Fig. 4c,d). The obtained particles shown in Fig. 7b look like cap-wearing particles. These structure-controlled Janus particles would be useful for applications such as in sensors, and as anisotropic building blocks for photonic and electronic devices.

Conclusions

Janus particles with a functional gold surface were prepared by sputtering or by subsequent electroless plating. The Janus particles were characterized by electron microscopy and XPS. Obtained Janus particles were monodispersed and reproducible. By changing the sputtering conditions, we could obtain red-, purple-, black-, and gold-colored dispersions containing Janus particles with gold nanostructure localized on one side of the cores. Cap-wearing particles were also obtained by electroless gold plating using preformed Janus particles as cores.

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