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Facile preparation of gold nanoparticle with diarylethene polymers by disodium malate and its photoreversible optical properties

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ABSTRACT

We have developed a synthetic procedure of gold nanoparticle covered with polystyrene (Au-poly(St)) using organic acid salts, followed by a ligand exchange reaction. First, various chain lengths of polystyrenes (poly(St)s) bearing thiol-end group were used as the covering agent of gold nanoparticle prepared by reduction using trisodium citrate. The resulting nanoparticles with ca. 13 nm diameter were dispersed in toluene when the molecular weight of the ligand poly(St) is larger than 1200. Larger sized Au-poly(St) could be obtained using disodium malate instead of the citrate. The colloidal gold nanoparticle with ca. 40 nm diameter was easily prepared only by changing the reducing agent. Finally, we have demonstrated to prepare larger sized gold nanoparticle covered with a photochromic diarylethene polymer (Au-poly(DE)) that shows large change in local surface plasmon resonance absorption according to the photochromic reaction even in a solution.

1. Introduction

Nanometer-sized gold nanoparticle is characterized by local surface plasmon resonance (LSPR) absorption that exhibits deep red color and sensitivity to the particle size, interparticle distance, and ambient surrounding [1–3]. These features have been of great attraction in variety of research fields such as biology and sensing application [4,5]. Locally confined electric field in the vicinity of the gold nanoparticle upon photoirradiation is also one of the attractive features. The amplified electric field modifies photophysical and photochemical properties of materials in proximity to the particle, and enhances various signal intensities and reactions upon photoirradiation. For instance, surface enhanced Raman scattering (SERS) [6,7], quenching and enhancement of emission [8,9], and two-photon excitation [10,11] have been observed near the gold and silver nanoparticles or nanostructures. Thus, the preparation of the gold nanoparticle is of great importance to observe the specific properties based on LSPR. Citrate reduction pioneered by Turkevich et al. [12] and developed by Frens [13] is one of the promising synthetic procedures of colloidal gold nanoparticles in aqueous media. The procedure can result in spherical gold nanoparticles with narrow polydispersity and control the diameter by changing the amount of reagents. Larger sized colloidal gold nanoparticles can be prepared by a seeding growth method [14] and reduction with various reagents [15,16]. Although these synthetic procedures in aqueous media can yield relatively-monodispersed particles with controlled diameter, the resulting particles are irreversibly aggregated by the addition of electrolyte or nonpolar surfactant. Therefore, it is not easy to prepare gold nanoparticles covered with hydrophobic thiol using citrate reduction and other methods in aqueous media [15].

The preparation of gold nanoparticle with hydrophobic molecules such as alkanethiol has been developed by Brust et al. [17]. The resulting gold nanoparticles can reform a colloidal solution even after removal of the solvents. Although Brust's method is applicable to various hydrophobic molecules including macromolecules, the diameter of the particle is usually less than 10 nm. Larger sized gold nanoparticle (>10 nm) covered with hydrophobic molecules has also been reported. Kim et al. prepared various sized gold nanoparticle (16–170 nm) arrays covered with resorcinarene tetrathiol using citrate reduction [18]. However, in many case, larger sized particle could not be obtained as a colloidal solution but flocculation or aggregate [18,19], which indicates that it is difficult to disperse the larger sized particle in organic media. Meanwhile, we have prepared and characterized gold nanoparticle covered with a photochromic diarylethene polymer (Au-poly(DE)) [20]. Diarylethenes are one of the most attractive photochromic compounds because of their excellent properties such as thermal

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stability of both isomers, fatigue resistance, high sensitivity, and so forth [21–25]. Au-poly(DE) with 13 and 22 nm diameters could be obtained by preparation of core particle using citrate reduction or the seeding growth method, followed by a ligand exchange reaction with the diarylethene polymer (poly(DE)) bearing thiol-end group. The resulting Au-poly(DE) could be dispersed in a organic solvent to exhibit bright red color due to LSPR, which demonstrated that larger sized colloidal gold nanoparticles (13–22 nm) covered with hydrophobic macromolecules can be synthesized using core particles prepared by citrate reduction and the seeding growth method. However, detail and limitation of the synthetic method have not been reported and remain ambiguous.

In this study, we have investigated and developed the preparation of a colloidal gold nanoparticle covered with polystyrene (Au-poly(St)) and Au-poly(DE) using gold core synthesized by citrate and malate reduction, followed by the ligand exchange process. The dispersibility of Au-poly(St) in an organic solvent strongly depended on the chain length of the ligand poly(St). Malate reduction resulted in larger sized gold nanoparticle (ca. 40 nm) than citrate reduction (ca. 13 nm). Au-poly(DE) with ca. 40 nm diameter could be synthesized using malate reduction and exhibited large change in the LSPR band even in a solution upon photoirradiation.

2. Experimental section

2.1. Measurements

Gel-permeation chromatography (GPC) was performed using a Tosoh 8000 series GPC system equipped with TSK-gel columns at 40 °C in tetrahydrofuran (THF) as the eluent. Standard polystyrenes were used as the calibration standard. The transmission electron microscope (TEM) images were performed on a Hitachi H-7000 at 75 kV. The TEM samples were prepared by dropping a toluene or THF solution of Au-poly(St) or Au-poly(DE) on a carbon-coated copper grid to dry under air. The mean diameter of the core gold particle (*d*) and core size histogram were obtained by counting at least 150 particles on image analysis program package ImageJ (http://rsb.info.nih.gov/ij/index.html). Thermal gravimetric analyses (TGA) of Au-poly(St) and Au-poly(DE) were performed by weighing the samples before and after heating in a micro muffle furnace at more than 900 °C. The absorption spectra were measured by a JASCO V-560 spectrophotometer. Photoirradiation was carried out using a 200 W mercury–xenon lamp (Moritex MUV-202) or a 300 W xenon lamp (Asahi Spectra MAX-301) as the light source. Monochromic light was obtained by passing the light through a monochromator (JASCO CT-10) and glass filters.

2.2. Materials

All reagents, styrene (St), 2,2′-azobis(2,4,4-trimethylpentane) (ATMP), sodium borohydride, hydrogen tetrachloroaurate tetrahydrate, trisodium citrate, disodium DL-malate *n*-hydrate, and cetyltrimethylammonium bromide (CTAB) were commercially available from Wako Chemicals. St was purified by distillation under reduced pressure before use. ATMP was recrystallized from hexane. All other reagents were used without further purification. The *n* value of disodium DL-malate *n*-hydrate was determined to be 0.73 by TGA.

2.3. Synthesis of poly(St) and poly(DE) bearing thiol-end group

Polystyrene (poly(St)) was synthesized by RAFT polymerization using St, ATMP (1.0×10^{-3} mol dm^{-3}), and 1-phenylethyl dithiobenzoate (PEDB) [26] as the monomer, the initiator, and the RAFT agent, respectively, in toluene for 60 h at 100 °C. The polymer was obtained by precipitation in methanol. The experimental conditions and the molecular weight/conversion data for the resulting poly(St)s are shown in Table 1. The number- and weight-average molecular weights (M_n and M_w) of poly(St)s were determined by GPC. The degree of polymerization (*n*) of poly(St) was determined from the M_n value.

Poly(DE) was also synthesized by RAFT polymerization using styrene with a diarylethene pendant group (DE) [27] as the monomer. The *n* value of poly(DE) was determined by ^{1}H NMR spectroscopy and GPC [28]. The dithiobenzoate-end groups in poly(St) and poly(DE) were reduced to thiol-end group using sodium borohydride in THF and water [29].

2.4. Synthesis of Au-poly(St) using citrate reduction

Au-poly(St) with ca. 13 nm diameter was prepared according to our previous paper [20]. Standard synthetic procedure is described as follows. The core gold nanoparticle was prepared by the addition of an aqueous solution (50 mL) of trisodium citrate (120 mg; 0.46 mmol) to a boiling aqueous solution (100 mL) of hydrogen tetrachloroaurate tetrahydrate (40 mg; 0.097 mmol) with vigorous stirring and reflux for 30 min. After cooling to ambient temperature, to the aqueous solution of the core particle was added a THF solution of poly(St) with thiol-end group (ca. 0.04 mmol) and the mixture was stirred for several minutes to exchange citrate around the particle for poly(St). Toluene was added to the solution until the solution was separated into aqueous and organic phases. The red color derived from the core particle was completely transferred into the organic phase. The colored organic phase was collected and washed with distilled water several times. The organic solution was concentrated in a rotary evaporator and dried in a vacuum. The resulting solid was purified by centrifugation in diethyl ether as described in previous paper [28].

2.5. Synthesis of Au-poly(St) and Au-poly(DE) using malate reduction

Au-poly(St) and Au-poly(DE) with ca. 40 nm diameter were synthesized using disodium DL-malate *n*-hydrate instead of trisodium citrate. The core gold nanoparticle was prepared by the addition of an aqueous solution (50 mL) of disodium DL-malate *n*-hydrate (83 mg; 0.50 mmol) to a boiling solution (100 mL) of hydrogen tetrachloroaurate tetrahydrate (40 mg; 0.097 mmol) with vigorous stirring and reflux for 30 min. Au-poly(St) with ca. 40 nm diameter was obtained by the same procedure described above. For Au-poly(DE), to the aqueous solution of the core particle was added CTAB (1.0 g; 2.7 mmol). A THF solution (100 mL) of poly(DE) with thiol-end group (200 mg; 5.3×10^{-3} mmol) was added to the solution and the mixture was stirred until precipitate was generated. Toluene was added to dissolve the precipitate. The mixture

Table 1
RAFT polymerization of St or DE in toluene for 60 h at 100 °C.

Entry	Monomer	[Monomer] (*M*)	[PEDB] (*M*)	Conversion (%)	M_n	*n*	M_w/M_n
1	St	2.9	0.01	62	14,500	137	1.12
2	St	2.9	0.015	61	9700	91	1.10
3	St	2.9	0.02	50	6600	61	1.06
4	St	2.9	0.03	54	4800	44	1.06
5	St	2.9	0.045	50	3000	26	1.07
6	St	2.9	0.06	39	1900	16	1.07
7	St	2.9	0.08	24	1200	9	1.08
8	DE	2.9	0.025	77	62,200	38	1.10
9	DE	2.9	0.045	68	26,100	91	1.06

Table 2
Characterization of gold nanoparticle prepared using citrate reduction.

Polymer[a]	d^{b} (nm)	σ/d^{c} (%)	A^{d} (nm^2 molecule^{-1})	δ^{e} (g cm^{-3})
1	12.6	7	0.88	0.047
2	13.3	16	0.99	0.081
3	12.9	11	0.80	0.16
4	13.5	11	0.75	0.25
5	13.6	10	0.70	0.41
6	13.7	11	0.59	0.65
7	14.1	15	0.49	0.97
8	13.2	15	7.70	0.068
9	13.4	13	3.99	0.35

[a] The polymers shown in Table 1 were used as the covering agent.
[b] Mean diameter of the gold nanoparticle.
[c] σ: Standard deviation of the diameter of the gold nanoparticle.
[d] Occupied area of the polymer on the gold core.
[e] Grafting density of the polymer in the polymer shell.

was separated into aqueous and organic phases. The organic phase was treated by the similar procedure described above. The characterization of the resulting Au-poly(St) and Au-poly(DE) is shown in Table 2.

3. Results and discussion

3.1. Characterization of Au-poly(St) synthesized using citrate reduction

First, the gold nanoparticles covered with various chain lengths of poly(St) were synthesized by citrate reduction, followed by the ligand exchange reaction with poly(St) bearing thiol-end group as shown in Fig. 1. The aqueous solution of the core gold particle prepared by citrate reduction (ca. 10 mL) exhibited bright red color due to the LSPR absorption as shown in Fig. 1a. The solution was once clouded by the addition of the THF solution of poly(St) bearing thiol-end group (ca. 10 mL). The subsequent addition of toluene (ca. 5 mL) could transfer the red color substance in the aqueous phase into the separated organic phase as can be seen from Fig. 1c. Because the aqueous solution of the core particle was never transferred into the organic phase without poly(St) bearing thiol-end group, the diaphanous red organic phase indicates that the ligand exchange process was successfully completed. When the shorter poly(St) ($M_n \le 700$) was used, however, the insoluble precipitate was produced at the interface between the aqueous and the organic layers. Such a precipitate was also observed when stearyl mercaptan was used instead of poly(St). This result shows that there are two possibilities for a formation of the gold nanoparticles precipitated at the interface: (1) poly(St) with shorter chain length ($M_n \le 700$) and alkanethiol as the covering agents are not appropriate in the ligand exchange process so that they induce agglomeration of the particles, (2) the gold nanoparticle covered with the shorter organic molecules cannot be dispersed in the organic phase.

TEM images of Au-poly(St)s with various polymer chain lengths are shown in Fig. 2. The characterization of Au-poly(St)s is summarized in Table 2. The TEM samples were prepared using Au-poly(St) well-dispersed in toluene. Au-poly(St)s used are well-spread on the copper grid without agglomeration. The interparticle distance in the TEM images varies according to the length of the ligand poly(St). These results indicate that Au-poly(St) was successfully prepared by citrate reduction independent on the chain length of the ligand poly(St). In addition, each sample has similar mean diameter (d = 13–14 nm) and narrow polydispersity (σ/d = 7–16%, σ corresponds to standard deviation of the core diameter) of the core diameter as shown in Table 2. It means that the core size of Au-poly(St) is determined during the preparation of the core particle. This is considered to be versatile to fabricate hydrophobic gold nanoparticles with controlled diameter covered with various macromolecules because there are a number of reports to control the diameter of the gold nanoparticle in aqueous phase such as citrate reduction in various conditions. Interestingly, gold nanoparticle covered with stearyl mercaptan put onto the TEM grid was also spread well on the grid without fusion or agglomeration as shown in Fig. 2h though it was insoluble both in the aqueous and the organic phases. The result clearly indicates that the insolubility of the gold nanoparticle covered with stearyl mercaptan and Au-poly(St) having short chain length ($M_n \le 700$) is not due to drawback in the ligand exchange process but due to intrinsic property of the particles itself. On the other hand, it has been reported that the gold nanoparticle with less than 10 nm diameter covered with alkanethiol can be dispersed in an organic solvent [17]. Therefore, it is considered that the solubility of the particle is derived from both diameter of the core particle and the length of the covering agent.

3.2. Occupied area and grafting density of the ligand polymer around the gold core

In order to investigate the insolubility of Au-poly(St) with shorter polymer chain length in more detail, we estimated the occupied area per molecule and the grafting density of the ligand poly(St) around the gold core. The occupied area of the ligand poly(St) on the surface of the gold core was determined from TGA data of Au-poly(St), d of core particle, and M_n of poly(St). Assuming that all the core particles are regarded as perfect spheres whose radii corresponds to each d value, the occupied area per molecule (A) can be described as follows:

$$A = \frac{6M_n}{N_A \rho_{Au} d} \times \frac{W_{Au}}{W_{polymer}} \tag{1}$$

where W_{Au} and $W_{polymer}$ are the weights of the gold core and the polymer shell, respectively. The ratio of their weights ($W_{Au}/W_{polymer}$) can be determined by the weights of the residual ash (gold) and the reduction (polymer) in the TGA measurement of Au-poly(St). N_A is Avogadro constant and ρ_{Au} is density of bulk gold

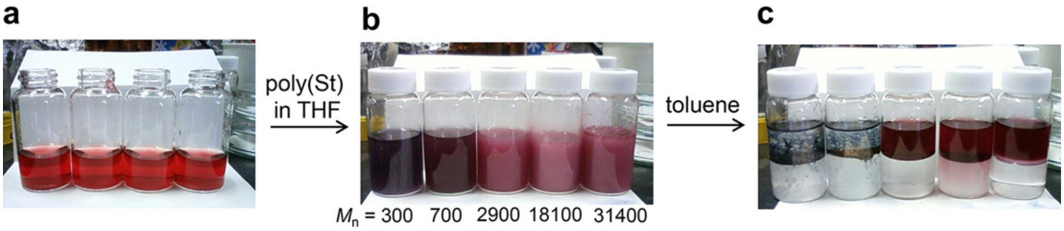

Fig. 1. Demonstration of preparation of Au-poly(St): (a) aqueous solutions of core gold nanoparticle prepared by citrate reduction, (b) (a) after addition of THF solution of poly(St) bearing thiol-end group, and (c) (b) after addition of toluene. Values under (b) correspond to M_n of poly(St) used.

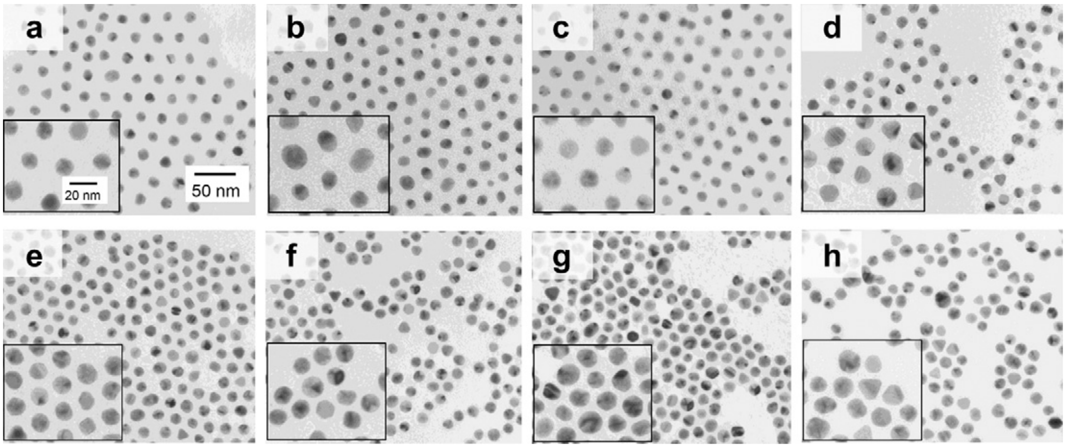

Fig. 2. TEM images of gold nanoparticle covered with (a) poly(St) (M_n = 14,500), (b) poly(St) (M_n = 9700), (c) poly(St) (M_n = 6600), (d) poly(St) (M_n = 4800), (e) poly(St) (M_n = 3000), (f) poly(St) (M_n = 1900), (g) poly(St) (M_n = 1200), and (h) stearyl mercaptan prepared using citrate reduction.

(19.3 g cm^{-3}). The *A* values for Au-poly(St)s with various polymer chain lengths are summarized in Fig. 3 and Table 2. When the molecular weight of poly(St) attached to the gold surface was increased, the occupied area per molecule became larger. These results lead to comprehensible conclusion that longer polymer chain is bulkier than shorter one so that longer polymer chain requires broader area on the gold surface. Fig. 3 and Table 2 also show the occupied area for Au-poly(DE) that coated with ligand bulkier than poly(St). As expected, poly(DE) required larger area to bond to the gold surface.

Assuming that poly(St) around the gold core fully stretches in the organic solution, the grafting density (δ) corresponding to the density of the polymer shell can be determined as follows:

$$\delta = \frac{\pi d^2 M_n}{N_A A (V_{\text{shell+core}} - V_{\text{core}})} \tag{2}$$

$$V_{\text{shell+core}} = \frac{4}{3}\pi\left(l + \frac{d}{2}\right)^3 \tag{3}$$

where $V_{\text{shell+core}}$ and V_{core} are volume of entire Au-poly(St) or Au-poly(DE) including the shell thickness and that of core particles, respectively. l is theoretically fully-stretched length of the ligand polymer. The δ values for various Au-poly(St)s and Au-poly(DE)s are summarized in Fig. 4 and Table 2. As expected from the occupied area determined above, the shorter poly(St) is more closely packed in the shell around the gold core. Taking into account the density of bulk poly(St) ($\sim$1.0 g cm^{-3}), the poly(St) shell around the particle with small δ value is regarded as bulk-like polymer layer rather than the polymer chains surrounded by the organic solvent. Therefore, it is considered that the insolubility of the gold nanoparticle covered with stearyl mercaptan and Au-poly(St) with short poly(St) ($M_n \leq 700$) is derived from less space in the polymer shell enough to dissolve in the organic solvent. The surface of smaller sized gold nanoparticle ($d < 10$ nm) has higher curvature than that of larger one. As a result, the smaller particle was dissolved better than the larger one because of the presence of more space in the ligand shell.

3.3. *Synthesis of larger sized core gold nanoparticle using disodium DL-malate n-hydrate*

In many cases, the synthetic methods of the gold nanoparticle in aqueous media are often based on citrate reduction. Although citrate reduction is a versatile synthetic method and can control the particle size by changing amount of the reagents, the larger sized

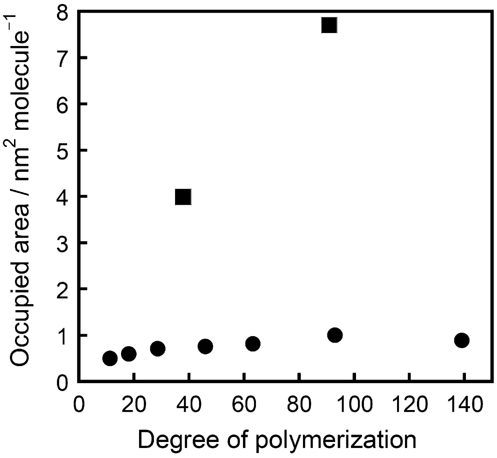

Fig. 3. Relationship between the degree of polymerization of poly(St) (solid circle) or poly(DE) (solid square) and occupied area of the polymers on the gold core prepared using citrate reduction.

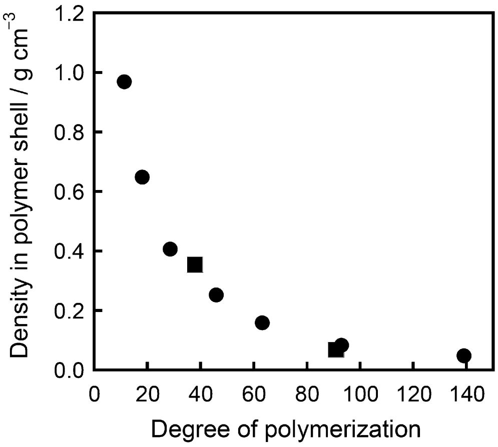

Fig. 4. Relationship between the degree of polymerization of poly(St) (solid circle) or poly(DE) (solid square) and grafting density of the polymers around the gold core prepared using citrate reduction.

particle (>20 nm) is usually obtained with wider size distribution without any treatment such as adjustment of pH in the reaction solution [30]. Seeding growth method can also produce larger sized particle. However the method requires large amount of surfactant and the additional work to prepare the gold nanoparticle. In this section, we explored the facile preparation of larger sized gold nanoparticle using disodium DL-malate *n*-hydrate instead of trisodium citrate. The citrate has three carboxylates that can interact with the gold surface and one hydroxyl group that can be oxidized by the aurate [31]. Meanwhile, the malate has two carboxylates and one hydroxyl group. The difference of the structures is considered to lead to different sized gold nanoparticles.

Fig. 5 shows TEM image and core size histogram of Au-poly(St) prepared using malate reduction. The larger sized and well-spread gold nanoparticles were obtained using malate reduction. The *d* value of the gold nanoparticle prepared by malate reduction was 42 nm, which is more than 3 times larger than that prepared by citrate reduction. Fig. 6 shows TEM images of Au-poly(St) with various polymer chain lengths synthesized using malate reduction. All the samples could also be dispersed in toluene and were well-spread on the copper grid independent on the polymer chain length. These results indicate that malate reduction is regarded as a facile synthetic method to obtain larger sized particle by only replacing trisodium citrate with disodium malate in the standard procedure.

3.4. Synthesis of Au-poly(DE) using malate reduction and its photoreversible optical properties

In this section, we applied malate reduction to prepare the gold nanoparticle covered with photofunctional diarylethene polymers

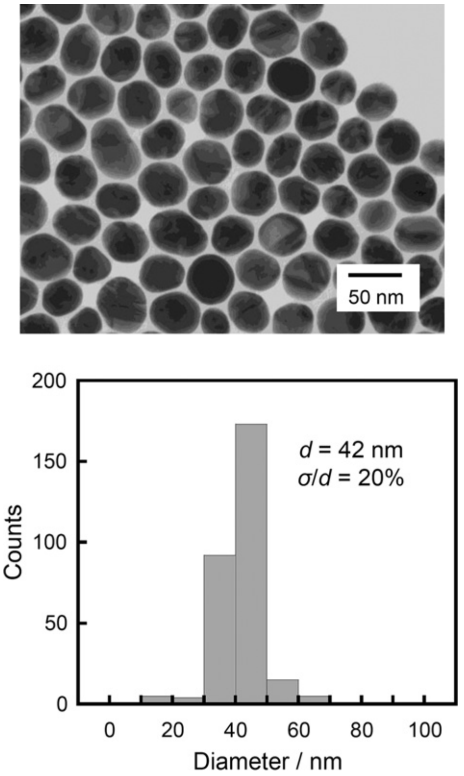

Fig. 5. TEM image and core size histogram of gold nanoparticle covered with poly(St) ($M_n = 2600$) synthesized using malate reduction.

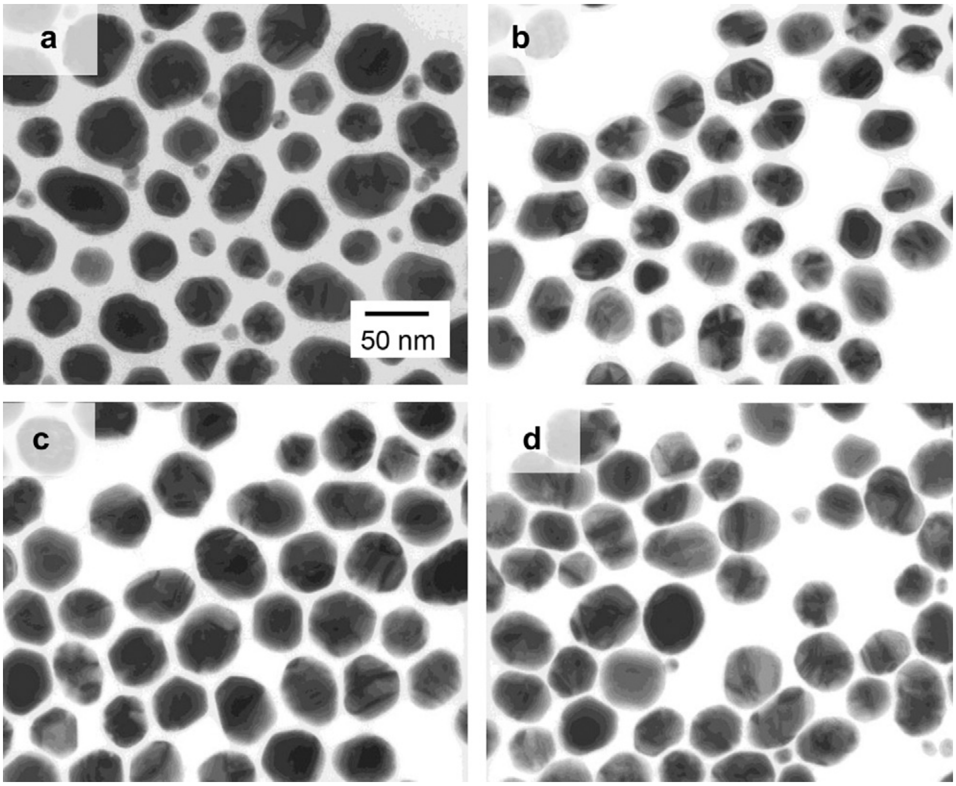

Fig. 6. TEM images of gold nanoparticle covered with (a) poly(St) ($M_n = 14{,}500$), (b) poly(St) ($M_n = 6600$), (c) poly(St) ($M_n = 3000$), and (d) poly(St) ($M_n = 1200$) synthesized using malate reduction.

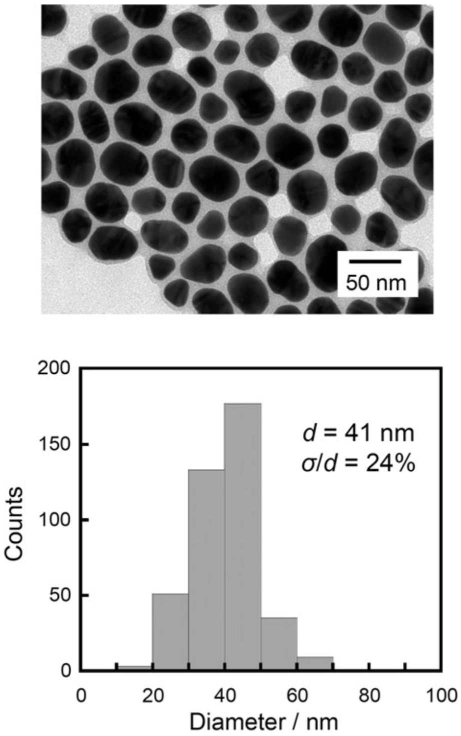

Fig. 7. TEM image and core size histogram of Au-poly(DE) prepared using malate reduction.

(Au-poly(DE)) with ca. 40 nm diameter. Au-poly(DE)s ($d = 6$–22 nm) have been synthesized using citrate reduction and the seeding growth method [20]. They exhibited reversible photochromism and the reversible change in the LSPR band upon alternating irradiation with UV and visible light. However, larger sized Au-poly(DE) ($d > 40$ nm) has not been synthesized so far. It was theoretically shown that the change in the LSPR band strongly depends on the size of gold core. Thus, the larger sized Au-poly(DE) is expected to show much larger shift in the LSPR band upon photoirradiation.

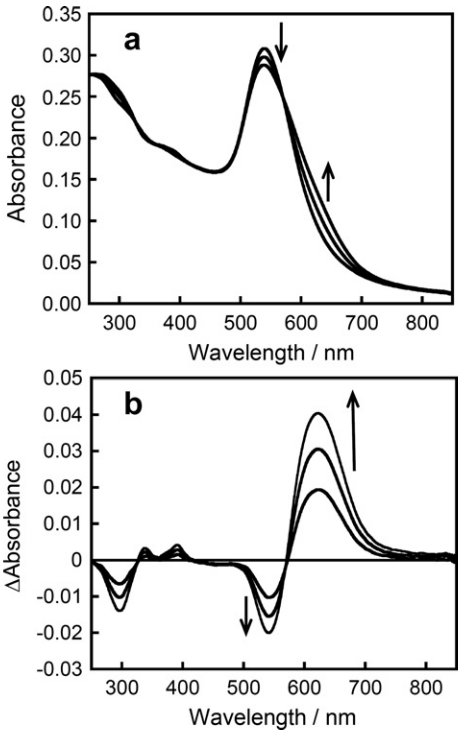

Fig. 8. Changes in (a) absorption spectra and (b) difference spectra of Au-poly(DE) synthesized using malate reduction in THF/water upon irradiation at 313 nm.

Fig. 7 shows TEM image and core size histogram of Au-poly(DE) synthesized using malate reduction, followed by the addition of poly(DE) bearing thiol-end group ($M_n = 37{,}700$). The resulting Au-poly(DE) was well-dispersed in the organic solvent and spread on the grid without agglomeration as well as Au-poly(St), which means the core-shell structure of the gold nanoparticle and poly(DE) successfully prepared. Mean diameter of the resulting Au-poly(DE) was 41 nm, which is similar to that of poly(St) synthesized by malate reduction. This is the largest diameter among the various Au-poly(DE)s that we have synthesized previously. The changes in the absorption spectra and difference spectra of the resulting Au-poly(DE) in THF/water (30/70 vol/vol) upon irradiation at 313 nm are shown in Fig. 8. The difference spectra were obtained by subtracting the absorption spectrum of the initial Au-poly(DE) having the diarylethene open-ring form from each absorption spectrum. The difference spectra have negative Δabsorbance in visible region (∼550 nm), which is derived from changes in the LSPR band of the gold nanoparticle according to the photocyclization reaction of poly(DE) shell [20]. The spectra reverted to initial shape upon irradiation with visible light. The spectral change could be repeated several times. The TEM image of Au-poly(DE) dispersed after UV irradiation was similar to that before UV irradiation. This indicates that the gold nanoparticles do not aggregate even after the photochromic reaction. In our previous study, the spectral dip due to the LSPR band shift of Au-poly(DE) ($d = 6$–22 nm) prominently appeared in the solid state, while that is very small in a solution [20]. However, Au-poly(DE) ($d = 41$) showed large spectral dip even in the solution, which indicates that the LSPR band of the gold core can be reversibly and largely controlled by photoirradiation even in the solution.

4. Conclusion

We examined and developed synthesis of gold nanoparticles covered with hydrophobic polymers by reduction of tetrachloroaurate using various organic acid salts, followed by a ligand exchange reaction. Au-poly(St) with longer polymer chains ($M_n \geq 1200$) was successfully prepared using citrate reduction and well-dispersed in the organic solution independent on the chain length. On the other hand, gold nanoparticle covered with stearyl mercaptan or shorter poly(St) ($M_n \leq 700$) could not be dispersed in the solution. It was found that the insolubility of Au-poly(St) with shorter chains may be derived from high grafting density in the polymer shell around the gold core. The larger sized Au-poly(DE) ($d = 41$ nm) could be easily obtained using disodium DL-malate *n*-hydrate instead of trisodium citrate. The gold core with ca. 40 nm diameter was reproducibly obtained even in the synthesis of Au-poly(DE). The resulting Au-poly(DE) exhibited significant changes in the LSPR band even in the solution.

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