

Surface Modification of Citrate-Capped Gold Nanoparticles Using CTAB Micelles

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The surface of nanoparticles governs the overall properties of the nanoparticles because nanoparticles have a large surface-to-volume ratio. Charge, crystallinity, and chemical properties (such as hydrophilicity) of surfaces determine the stability, structure, and reactivity of nanoparticles.¹⁻¹¹ In this respect, it is essential to have a capability to control and modify the surfaces of nanoparticles.

Among many nanoparticles, gold nanoparticles (AuNPs) are fascinating because of their unique plasmonic properties. Surface plasmons, collective oscillation of conduction electrons, permit a wide variety of applications of AuNPs in spectroscopy, imaging, energy, and biomedicine.¹²⁻¹⁶ AuNPs are typically synthesized using citrate-reduction of Au ions in an aqueous solution, which results in the AuNP surfaces covered with citrate anions.¹⁷ The citrate anions on the AuNP surface are weakly bound and thus easy to replace with more strongly binding thiol ligands. Changing the surface functionality of AuNPs from citrate anions (negative charge) to carboxylate (negative charge) or hydroxyl group (hydrophilic group) has been achieved using the corresponding organofunctional thiol compounds.¹⁸

More challenging in modifying the surface of citrate-capped AuNPs is to impart positive charges to the surface. Simple ligand exchange using thiol with cationic functional groups (*e.g.*, NH₃⁺) generally causes irreversible agglomeration of AuNPs due to multiple electrostatic crosslinking.¹⁹ Another formidable task is to conjugate hydrophobic materials to the AuNPs prepared in an aqueous phase. In this study, we aim to resolve these two issues, which will help us expand our ability to control and modify the surface of citrate-capped AuNPs for further advanced applications.

The molecule of choice for converting the surface charge from negative to positive was cetyltrimethylammonium bromide (CTAB), a cationic surfactant with a positive ammonium head group and a long hydrocarbon tail. CTAB is a commonly used surface ligand in nanochemistry, particularly for the synthesis of gold nanorods or nanocubes.²⁰ CTAB stabilizes Au nanorods by forming a stable bilayer on the surfaces with the cationic head groups exposed to the outside.²¹

When we added a CTAB solution to a solution of citrate-capped AuNPs, we observed an anomalous concentration-dependent response of the AuNPs. Addition of a small amount of CTAB expectedly resulted in aggregation of AuNPs. The cationic CTAB head group binds to the negatively charged

citrate-capped AuNPs *via* electrostatic interaction. Consequently, either surface charge neutralization or hydrophobic interaction causes the AuNPs to aggregate in an aqueous solution. When we increased the concentration of added CTAB, we obtained surprisingly unexpected results. Addition of a large amount of CTAB stabilized the AuNPs rather

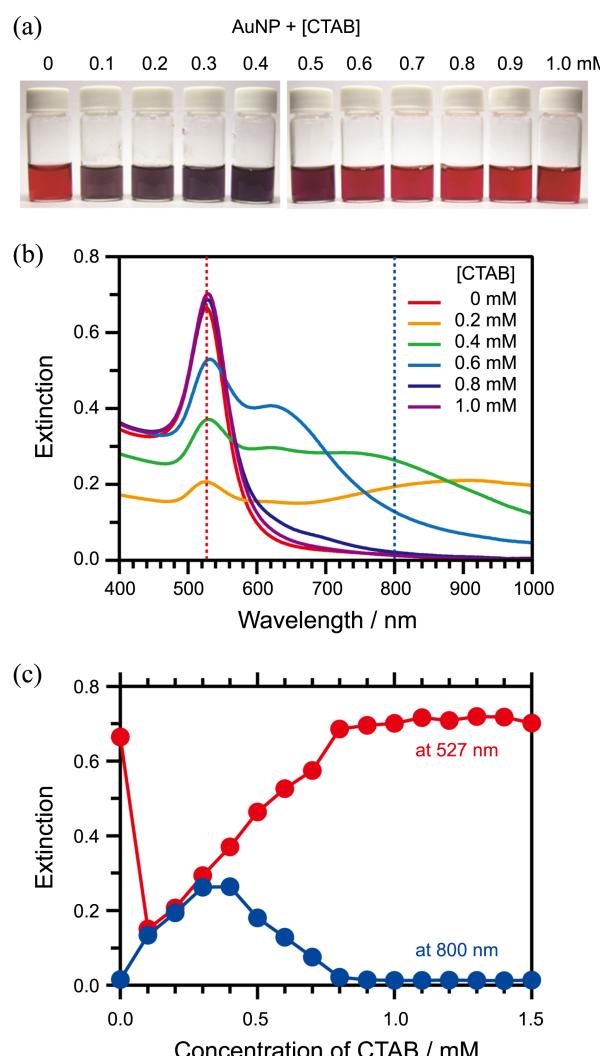


Figure 1. Changes in (a) color and (b) UV-vis spectra of 32 nm AuNP solutions with the addition of increasingly concentrated CTAB. (c) Spectral intensity changes at the characteristic wavelengths for dispersed (527 nm) and aggregated (800 nm) AuNPs as a function of the concentration of added CTAB.

than aggregated them.

Figure 1 displays the changes in color and UV-vis spectra of AuNP (32 ± 3 nm) solutions upon addition of CTAB. The well-dispersed AuNPs exhibit a bright red color due to the localized surface plasmon resonance (LSPR).¹² As aggregation occurs, multiple interactions among the surface plasmons of AuNPs in close proximity shift the LSPR band to a longer wavelength region, resulting in a dark blue color.¹⁹ Figure 1 shows that addition of 0.1 mM CTAB darkens the AuNP solution and yields a redshifted peak. As the concentration of added CTAB increases, the color becomes even darker and the extinction peak attributed to the aggregation further redshifts, indicating the aggravated aggregation. This trend, however, drastically changes as the concentration of CTAB reaches ~ 0.9 mM. AuNPs become stable even though a lot of CTAB has been added. From this point, AuNPs remain dispersed, regardless of the increase in the concentration of added CTAB (Figure 1(c)). Similar concentration-dependent response was observed for the 12 nm AuNPs (Supporting Information).

CTAB is markedly contrasted with other cationic surface ligands in the interaction with AuNPs. Addition of *p*-aminothiophenol, 6-amino-1-hexanethiol, and (11-mercaptopoundecyl)-*N,N,N*-trimethyl ammonium bromide causes AuNPs to aggregate at both low (0.1 mM) and high (1 mM) concentrations (Supporting Information). This control experiment also shows that converting the surface charge of AuNPs from negative to positive through a simple ligand exchange is extremely difficult to achieve.

Addition of high concentration CTAB successfully converted the surface charge of AuNPs with their stability maintained. The zeta potential of the AuNPs changed from -42 ± 2 to $+22 \pm 3$ mV upon addition of CTAB (2.5 mM). This result strongly suggests that CTAB binds to the citrate-capped AuNPs and stabilizes them by surrounding the AuNPs with its cationic head group facing the outside.

Regarding how an excessive amount of CTAB stabilizes the citrate-capped AuNPs and converts the surface potential, two models are conceivable. One is the formation of bilayers (Figure 2(a)). The cationic head group binds to the citrate anions on the AuNP surfaces. Then, hydrophobic interactions among the alkyl chains of CTAB form a bilayer. The cationic head groups in the exterior of the bilayer provide the AuNPs with an overall positive surface charge. The formation of CTAB bilayers has been widely accepted as the stabilization mechanism for Au nanorods.²¹ Nevertheless,

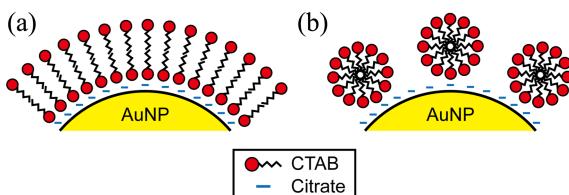


Figure 2. Two possible models for stabilization of citrate-capped AuNPs by the addition of excessive CTAB. (a) Bilayer formation of CTAB on the AuNP surfaces. (b) Adsorption of CTAB micelles on the AuNPs.

this model does not seem applicable to Au nanospheres because it does not explain the abrupt change in the response of AuNPs with the CTAB concentration.

The other possible model for the stabilization of AuNPs by CTAB is the formation of micelles (Figure 2(b)). We note that CTAB is an amphiphilic surfactant with a hydrophilic head group and a hydrophobic tail. It forms micelles at higher concentrations than the critical micelle concentration (CMC). Notably, the CMC of CTAB is 0.92 to 1.0 mM in water.^{22,23} This value is close to the concentration of CTAB at which the AuNPs become stable (Figure 1(c)). Below the CMC, individual CTAB molecules adsorb on the AuNP surfaces with their hydrophobic tails exposed to water, leading to aggregation of the AuNPs. Above the CMC, positively charged CTAB micelles stabilize the AuNPs and change the surface charge to positive, consistent with our observations. Therefore, we believe that it is the formation of micelles that is responsible for the anomalous concentration-dependent response of AuNPs to CTAB.

More conclusive evidence for the stabilization of citrate-capped AuNPs with CTAB micelles comes from cryogenic transmission electron microscopy (cryo-TEM) measurements. The cryo-TEM image obtained from the mixture of citrate-capped AuNPs (12 nm) and CTAB (0.7 mM) clearly shows the CTAB micelles surrounding the AuNPs (Figure 3).

The CTAB micelle-stabilized AuNPs are stable and robust. They remained dispersed without aggregation at least for a month. Subjected to addition of 1,10-decanedithiol (DDT), the micelle-capped AuNPs did not aggregate as opposed to citrate-capped AuNPs (Supporting Information).

The micelle stabilization of AuNPs opens a new way to conjugate hydrophobic molecules to AuNPs in an aqueous solution. CTAB micelles can entrap hydrophobic molecules

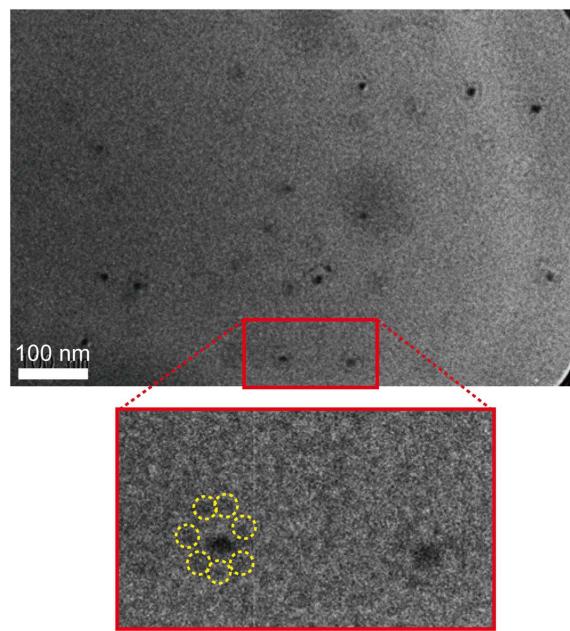


Figure 3. Cryo-TEM image of AuNPs stabilized by CTAB micelles. For better visibility, CTAB micelles surrounding an example AuNPs are marked with yellow dotted circles.

in their interior core in an aqueous phase and deliver them to the AuNP surfaces. Therefore, surface-enhanced fluorescence, surface-enhanced Raman scattering, and photochemical reactions of hydrophobic molecules can be studied using micelle-stabilized AuNPs. Those studies are currently under way in our laboratory.

In conclusion, we found that citrate-capped AuNPs remained stable despite the addition of a large amount of CTAB ($> 1 \text{ mM}$) whereas the addition of a small amount of CTAB caused the AuNPs to aggregate in water. We also observed that the zeta potential of the AuNPs changed from negative to positive upon addition of CTAB. The cryo-TEM measurements showed that the CTAB micelles formed at a concentration above CMC ($\sim 1 \text{ mM}$) stabilized the citrate-capped AuNPs by surrounding them. Surface-capping of AuNPs by CTAB micelles presents a new way to convert the surface potential from negative to positive *in situ* and to conjugate hydrophobic materials to AuNPs in water.

Experimental Section

We adopted the Turkevich and the seeded growth method to synthesize 12 and 32 nm AuNPs, respectively.²⁴ The exact sizes measured by TEM (JEM-2100F, JEOL) were $12.2 \pm 1.1 \text{ nm}$ ($N = 102$) and $31.7 \pm 3.3 \text{ nm}$ ($N = 104$). After the synthesis, the AuNPs were centrifuged and re-dispersed into water to remove residual reagents in solution. The aqueous 32 nm AuNP solutions (0.7 nM, 2 mL) were added to CTAB solutions (Aldrich, > 99%) prepared in different concentrations ranging from 0 to 1.5 mM in 2 mL. Then, the changes in color and UV-vis spectra were measured after the two solutions were mixed and fully equilibrated (15 h).

UV-vis spectra were acquired using Lambda 25 (Perkin-Elmer). Zeta potential was measured using ELS-Z (Otsuka Electronics). The cryo-TEM images were acquired from a thin film of aqueous solution (4 μL) transferred to a lacey supported grid by the plunge-dipping method. The thin aqueous films were prepared at ambient temperature and with humidity of 97-99% within a custom-built environmental chamber in order to prevent evaporation of water from sample solution. The excess liquid was blotted with filter paper for 2-3 s, and the thin aqueous films were rapidly vitrified by plunging them into liquid ethane (cooled by liquid nitrogen) at its freezing point. The sample was observed with a JEOL-JEM-3011 HR instrument operating at 300 kV. The data were analyzed with Gatan Digital Micrograph.

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Supporting Information. Response of 12 nm AuNPs to addition of CTAB, response of AuNPs to addition of other cationic ligands, stability of CTAB micelle-stabilized AuNPs.

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