Surface Potential Change of Cationic Nanoparticles by Polymer Coating

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Keywords: nanoparticles, CTAB, polyethylene glycol, zeta-potential, dynamic light scattering

1. Introduction

Recently, various types of nanostructures containing structured surfaces and particles have been widely developed. Semiconducting/metallllic nanoparticles, in particular, are promising candidates as new functional materials not only as catalysts but also as durable materials for use in novel optical sensors [1] and other devices. [2] Methods for their production have also been widely developed. These methods are usually classified into two types: “top-down” methods and “bottom-up” methods. The authors’ group have been investigating the bottom-up methods primarily. [3,4] Among many types of metallic nanoparticles are used in many kinds of chemical sensors. [5] In these cases, a common detergent cetyltrimethylammonium bromide (CTAB) is often used as a stabilizer for AuNPs with shapes such as cubes, cuboctahedra, octahedra, and rods. [6-10] Among these AuNPs, gold nanorods (AuNRs) are the most frequently used AuNPs. The presence of CTAB is important for nanoparticles synthesis; however, it is cytotoxic in nature. [10] Its strong attachment to the surface of AuNPs has been demonstrated in the literatures [11,12] (e.g., an ~8-nm-thick rigid layer on AuNPs has been reported by Wang et al. [11]). Some research groups have reported their attempts to modify CTAB coatings to other polymeric surfactant coatings. [12-14] These groups focused on AuNRs because of their potential biological applications. In some cases, isotropic AuNPs exhibit a high positive charge density caused by CTAB cations. Highly surface-charged particles are strongly affected by a change in ionic strength. For some biological applications, we would prefer to avoid volatile organic contaminants and handle AuNPs only in the aqueous phase.

In this paper, we describe a simple surface modification of CTAB\textsuperscript{(1)}-coated AuNPs (referred to as CTAB\textsuperscript{(1)}-AuNPs, hereafter) with two polymers (Scheme 1) in an aqueous solution. The two polymers used are poly(sodium 4-styrenesulfonate) (PSS\textsuperscript{(2)}) and polyethylene-glycol bisphenol A epichlorohydrin copolymer (PEG\textsuperscript{(3)}). In order to avoid sample loss, we tried the method omitting the often-used biochemical process "dialysis". We have focused on these two polymers because of their properties of decreasing charge density/repulsion for stabilizing particles and the softness of the polymer chain coating, which contrasts with the rigid CTAB\textsuperscript{(1)}. [11]

![Scheme 1](https://example.com/scheme1.png)

For comparison, we also used sodium dodecyl sulfate (SDS\textsuperscript{(4)}) as a low molecular weight, negatively charged ionic coating agent.

2. Experimental

All chemicals, such as CTAB\textsuperscript{(1)} (Sigma),
AuNPs were synthesized via a common seed-mediated growth method. [8] HAuCl₄·3H₂O was dissolved in an aqueous solution of CTAB(1) and reduced with ice-cooled sodium borohydride to form a “seed solution.” After 1 h, a “growth solution” was prepared with additional HAuCl₄·3H₂O and diluted "seed solution". This mixture was reduced by the addition of ascorbic acid in aqueous CTAB(1) solution. The obtained CTAB(1)-AuNPs were subsequently mixed with an aqueous solution of another coating agent (2-4). Each mixed solution was stirred for 1 h, centrifuged (6.8 kref, 10 min), and then washed twice with H₂O. We hereafter refer to CTAB(1)-AuNPs treated with coating agent (2-4) as coating agent (2-4)-AuNPs.

UV-vis-NIR spectra of AuNPs were measured using a Jasco V-670 spectrophotometer. The zeta-potential (ζ) (hereafter abbreviated as ZP) was determined with an ELSZ-1000 (Otsuka Electronics). Each Hydrodynamic diameter (hereafter abbreviated as HD) was measured at 25 °C by the dynamic light scattering (DLS) method using a DLS-8000 (Otsuka Electronics). Microscopic images and EDX measurements were recorded with either an HD-2000 (Hitachi) or a JEM-2100F (JEOL) operating at 200 kV.

3. Results and discussion
3.1. UV-vis-NIR spectra of AuNPs

![Normalized absorption spectra of AuNPs treated with coating agents (1-4): CTAB(1)-AuNPs (solid line) and CTAB(1)-AuNPs treated with PSS(2) (dotted line), PEG(3) (broken line), and SDS(4) (dotted-chain line).](image)

Each absorption spectrum was recorded and normalized at the λ_max of the AuNPs' band; the results are presented in Fig. 1. During the treatment with the coating agents (2-4), a portion of the AuNPs aggregated and attached to the walls of the container or were washed off. Therefore, the concentration of AuNPs decreased to some extent. Thus, the baseline of each normalized spectrum appeared to shift upward compared to that of CTAB(1)-AuNPs. After the treatment, a blue color gradually appeared on the walls of PEG(3)-AuNPs. Nevertheless, the λ_max of the AuNPs' band was approximately the same for each AuNPs solution. In some cases, as long-term preservation was observed to be problematic, it needs to be improved.

3.2. Zeta-potential measurements

The ZP values of the coating agents (1-4) and the AuNPs treated with the coating agents were measured. The observed ZPs are listed in Table 1. CTAB(1) samples were the only ones that exhibited positive values, slightly more than those of Au cubes reported in the literature (+23.2 mV). [6] This result implies that CTAB(1) salt ionization ratios of the surface layer on the AuNPs differ. For PSS(2) samples, the observed value of the ZP in the presence of AuNPs was −25 mV lower than that observed in the absence of AuNPs. This result suggests that PSS(2)-AuNPs were completely charged negative with high coverage of PSS(2).

![Table 1. ZPs (mV) of each coating agent (1-4), CTAB(1)-AuNPs, and coating agent (2-4)-AuNPs, coating agent only AuNPs†‡§.](image)

*AuNPs correspond to CTAB(1)-AuNPs or coating agent(2-4)-AuNPs. † Values were recorded as soon as possible because each coating agent showed irreversible adsorption onto the electrodes and the polystyrene cell walls during the measurements, especially in the case of CTAB(1). ‡Particles gradually aggregated on the polypropylene microtube walls during storage. Small amounts of sediments were observed for other AuNPs.

Although the ZP in the presence of AuNPs was approximately −40 mV, the ZP of PEG(3) appeared to be close to zero. This highly negative potential value probably arises from an excess amount of anions around the AuNPs in solution.

Based on the change in the ZP of SDS(4)-AuNPs compared to that of SDS(4), SDS(4) appears to form hybrid complexes with CTAB(1) [16] and to attach to NPs by mixing with CTAB(1)-AuNPs.

3.3. DLS measurements

The DLS results are summarized in Table 2. The average HD of CTAB(1)-AuNPs was 55.6 nm.
and was very similar to that of PSS(2)-AuNPs (53.4 nm). Gole et al. [12] reported an increase of ~3.4 nm in the diameter of CTAB(1)-coated AuNRs after being treated with PSS (under experimental conditions that differ from ours). The HDs of PEG(3)-AuNPs in aqueous solutions are larger than those of CTAB(1)- and PSS(2)-AuNPs.

Table 2. HDs (nm) of particles in each surfactant (1-4) and CTAB(1)-AuNPs or coating agent (2-4)-AuNPs.

<table>
<thead>
<tr>
<th>Coating Agent</th>
<th>HDs (nm)</th>
<th>Coating Agent</th>
<th>HDs (nm)</th>
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<tbody>
<tr>
<td>CTAB(1)</td>
<td>241†</td>
<td>PSS(2)</td>
<td>55.6</td>
</tr>
<tr>
<td>PEG(3)</td>
<td>124</td>
<td>SDS(4)</td>
<td>108</td>
</tr>
<tr>
<td>SDS(4)</td>
<td>219†</td>
<td>AuNPs†</td>
<td>194</td>
</tr>
</tbody>
</table>

† Each coating agent sample showed small (d2 nm, corresponding to a monomer/oligomer peak), intermediate (100-200 nm, micelles), and large (e800 nm, corresponding to a higher complex) peaks. The listed values are those for middle-sized peaks because of their supposed nature. Each AuNPs sample also showed small (d10 nm), intermediate (50-200 nm), and large (e500 nm) peaks. The intermediate peaks values are listed. †Values were not stable because of the adsorbing nature of each coating agent.

One possible reason for this larger HDs is that the hydrophobic parts (“bisphenol A” moiety in PEG (3)) form a hybrid structure with CTAB(1) to stabilize the particles. The source of the high negative charge on the AuNPs in PSS(2)-AuNPs and SDS(4)-AuNPs is certainly attributable to the presence of PSS(2) and SDS(4), respectively. The reason for the high negative charge of PEG(3)-AuNPs, as reported in Table 1, is unclear. According to the DLS results, the diameter of PEG(3)-AuNPs was large, which suggests the occurrence of a hydrodynamic effect between PEG moiety and water or CTAB(1) molecules in their aqueous solutions. In the transmission electron microscopy (TEM) images (shown later in Fig. 2), the observed diameters of the AuNPs didn’t substantially differ.

3.4. Microscopic observation of AuNPs

CTAB(1)-AuNPs used in this investigation were rather polydisperse. The typical TEM images that were observed are presented in Figs. 2 and 3. We observed primarily hexagons and small AuNRs with aspect ratios less than ~3. Fig. 2 shows a typical projection view of a hexagonal particle. This image indicates that the particle’s shape would be cuboctahedral/octahedral. As Kim et al. [10] described, depending on the stage of particle growth, the {100} faces are blocked with CTAB(1) because of their strong ability to bind to {100}. TEM images of each of the AuNPs are presented in Figure 3. Because carbon deposition occurred rapidly during the microscopic observations, images were taken within a short time. In Figure 3, the diameters of the particles appear to be similar, in contrast to their HDs reported in Table 2.

Fig. 2. A typical TEM image of hexagonal shaped CTAB(1)-AuNPs on a copper TEM grid.

Fig. 3. TEM images of CTAB(1)-AuNPs and coating agent (2-4)-AuNPs: a) CTAB(1)-AuNPs, b) PSS(2)-AuNPs, c) PEG(3)-AuNPs, and d) SDS(4)-AuNPs (scale bars:100 nm).

PSS(2)-AuNPs were dispersed better than others. The particles in other samples were closely packed. In the case of PEG(3)-AuNPs, in particular, NPs tended to form multilayers, even in areas with relatively small populations of NPs. Compared to the other samples, SDS(4)-AuNPs tended not only to aggregate but also to connect to one another, which may be related to the strong interaction between CTAB(1) cations and SDS(4) anions. [16] Average particle diameters of the AuNPs calculated from TEM images are 44.7 ± 3.2 nm, 44.1 ± 3.1 nm, 43.9 ± 3.3 nm, and 42.3 ± 6.5 nm for CTAB(1)-, PSS(2)-, PEG(3)-, and SDS(4)-AuNPs, respectively. Based on these calculated values, the average diameters of the AuNPs determined from TEM did not substantially differ. Because we didn’t use chemicals that induced digestive effects, such effects and other surface chemical reactions could be excluded in these cases.

Fig. 4 shows the typical overlay images of Br K-line maps and bright-field images for CTAB(1)- and PSS(2)-AuNPs (images for PEG(3)- and SDS(4)-AuNPs are not shown because no significant changes from the images in Fig. 4 are observed). From the Br K-line maps, a decrease in
the amount of Br was not evident, probably because of the limited measurement time, the initial Br K-line intensity, and the existence of Au-Br bonds. Thus, Br was detected in all cases. The situations in aqueous solutions and those on the carbon-supported cellulose nitrate membrane on copper TEM grids certainly differ. The source of negative charge on PEG(3)-AuNPs in our case was suggested to be Br\(^-\), the CTAB(1) counter-anion.

![Fig. 4. Typical EDX (Br K) mapping images of (a) CTAB(1)-AuNPs and (b) PSS(2)-AuNPs.](image)

We also measured and investigated the EDS spectra (data not shown) of each AuNPs. In the case of PEG(3)-AuNPs, two different areas were detected. One area contained many AuNPs and the other contained only polymer chains. Br L-lines were observed in both areas, indicating that the Br\(^-\) ions were attached to PEG(3) polymer surface.

The differences between the microscopic images and the DLS/ZP results for the solutions may arise from the solvent evaporation process. In solutions, particles can exhibit charges (either positive or negative). However, when samples are in a dried state, i.e., solid state, the charges on the AuNPs are compensated by the counter charges of the substrate or other molecules in the solutions. In the case of PEG(3), because the polymeric chain is highly hydrophilic, AuNPs are coated not only by the molecules of the coating agent, but also by numerous water molecules. Therefore, the HD would grow to be much larger than those of CTAB(1)- or PSS(2)-AuNPs. In the solid phase (as is the case of samples prepared for microscopic observations), AuNPs are dried by solvent evaporation.

The conditions around the AuNPs in a solution could be controllable by changing the method that is used to wash them. However, the ZP measurements indicated the presence of negative charges, which indicates that the number of anions located within the HD of the NPs should be larger than the number of cations. In this study, AuNPs were initially coated with CTAB(1). To maintain the negative ZP of the AuNPs after they have been coated with neutral PEG(3), the NP surface must contain more anions than cations. Br mapping is observed to be an ineffective method for tracing CTAB(1) cations (counter ion is Br\(^-\)) because of polymer-CTAB(1) or polymer-Br\(^-\) interactions. SDS(4) showed strong interactions with CTAB(1) partly aggregated on the TEM grids.

Based on these results, we observed some interesting relationships between polymer and particle charges. We expect to improve the mixing and washing procedures in future.

**Acknowledgement**

We thank Dr. Yamada and Dr. Takei (MANA/NIMS) for their assistance with the TEM observations and Dr. Minowa and Dr. Li (M&MS/NIMS) for their assistance with the DLS/ZP measurements. We are grateful to Dr. Shimizu and Ms. Tanaka for providing the EDS results. This study was financially supported by the East Asia Joint Research Program of the Japanese Science and Technology Agency.

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