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Electron Transfer

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Observation of Electrochemical Single-Electron-Transfer Events of Gold Nanoparticles in Aqueous Solution in the Presence of Both Ammonium and Sulfonate Surface-Active Agents**

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Metal nanoparticles (MNPs) behave as quantum dots and have attracted much attention in the fields of molecular electronics,[1] catalysis,[2,3] and sensors.[3,4] Recently, biomaterials chemistry has employed MNPs intensively, and MNP-attached proteins and DNAs have been used as DNA sensors,[5] immunosensors,[6] sugar sensors,[7] HIV drugs,[8] and photosensors,[9] and thus the importance of the physical and chemical properties of MNPs in aqueous solution is increasing.

It is known that MNPs smaller than 2.0 nm in diameter have a capacitance C_{CLU} of less than one attofarad (1 aF) per nanoparticle in electrolyte solution, which enables observation of single-electron-transfer events even at room temperature. This phenomenon is called quantized double-layer (QDL) charging, and C_{CLU} is given by Equation (1), where ε is

$$C_{\mathrm{CLU}} = 4\pi\varepsilon\varepsilon_0(r/\mathrm{d})(r+d) \qquad (1)$$

the dielectric constant of the monolayer, ε_0 the permittivity of free space, r the radius of the core, and d the chain length of the monolayer.[10] So far, such unique electron behavior has been observed mostly with gold nanoparticles (AuNPs),[10,11] while for nanoparticles of other metals, such as palladium, platinum, silver, and copper, it was recently reported.[12]

In general, QDL charging can be observed in aprotic organic solvents without difficulty, whereas it is hard to observe in aqueous solution because of the high dielectric constant of water. Chen et al. reported that the QDL charging of AuNPs could be rectified by hydrophobic anions such as PF_6^- and ClO_4^- even in aqueous solution, but the electrochemical response in aqueous media was drastically different from that observed in low-dielectric organic media,[13] and was observed only in a limited regime of positive potential.[14,15] Observation of QDL charging in water is important for applying AuNPs in electrochemical biosensors. Katz and Willner reported that it could be observed in an aqueous solution by condensing hydrophobic magnetic nanoparticles on the electrode surface.[16] In this case, the low dielectric constant of a hydrophobic microenvironment was provided by the attracted magnetic nanoparticles associated with the electrode surface.

One possible approach to constructing a hydrophobic environment on the electrode surface is addition of surface-active agents. Cationic surfactants are adsorbed on the metal surface in the potential region less noble than the point-of-zero charge (PZC), anionic surfactants or bases such as amines in the potential region more noble than the PZC, and combinations of cationic, anionic, and/or neutral (Lewis acid or base) surface-adhesive species exhibit cooperative adsorption on the surface to form a barrier layer, which can prevent electrode reactions such as corrosion.[17] This prompted us to study the effect of surface-active agents on the QDL charging behavior of AuNPs in aqueous solution. Finding conditions that allow QDL charging of AuNPs to be observed in aqueous solution is important for the fabrication of biocomponent-based sensors. Herein we report on the electrochemical properties of AuNPs in aqueous solutions containing hexyltrimethylammonium bromide, sodium dodecylbenzenesulfonate, or a combination thereof. The results demonstrate that the combination of the two reagents is suitable for forming a hydrophobic environment on the electrode to observe QDL charging of MNPs over a wide potential range.

Water-soluble AuNPs with narrow size distribution are requisite for this study. Among several methods to prepare such AuNPs,[18,19] we employed the most convenient one, namely, the reprecipitation method.[19] First, hexanethiol-protected AuNPs $Au_x(SC_6H_{13})_y$ suitable for this purpose were prepared by the Brust method,[20] followed by reprecipitation several times. Then water-soluble AuNPs were prepared by a substitution reaction, and their electrochemical properties in the presence of the surface-active agents investigated.

Figure 1 shows TEM images and size-distribution histograms of $Au_x(SC_6H_{13})_y$ prepared by the water/toluene two-layer method.[20] The diameter of AuNPs reprecipitated from acetone/toluene (24:1) was (1.9 ± 0.2) nm (Figure 1 b), and the diameter from acetone/toluene (7:1) was (1.6 ± 0.2) nm (see the Supporting Information). These diameters were smaller than that of crude AuNPs before reprecipitation ((2.0 ± 0.3) nm; Figure 1 a). The AuNP sizes were also mea-

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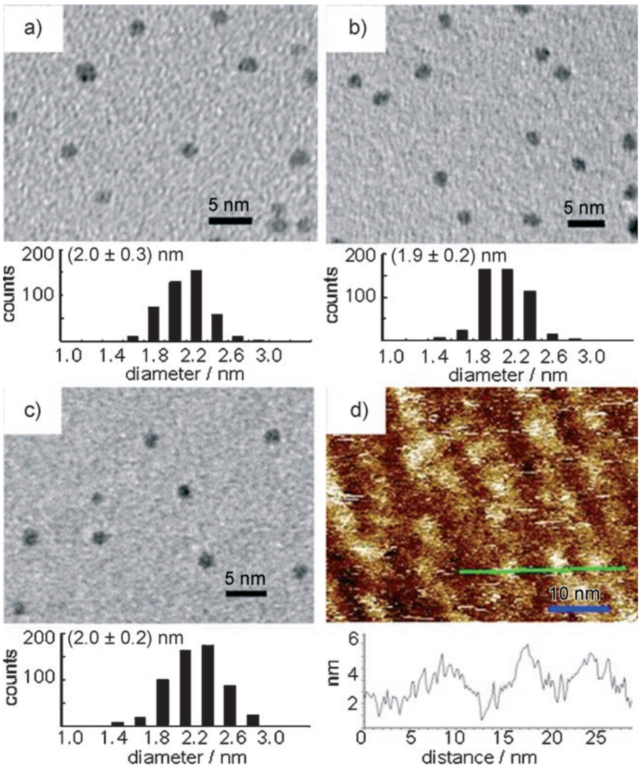

Figure 1. TEM images of $Au_x(SC_6H_{13})_y$ and $Au_x(SC_6H_{13})_y(S(CH_2CH_2O)_3CH_3)_z$: a) $Au_x(C_6H_{13}S)_y$ before reprecipitation. b) $Au_x(SC_6H_{13})_y$ reprecipitated from acetone/toluene (24:1). c) $Au_x(SC_6H_{13})_y(S(CH_2CH_2O)_3CH_3)_z$. d) STM image of a Au electrode modified with $Au_x(SC_6H_{13})_y(S(CH_2CH_2O)_3CH_3)_z$ and the cross-sectional profile (green line in the STM image) along the cross-axis (bottom).

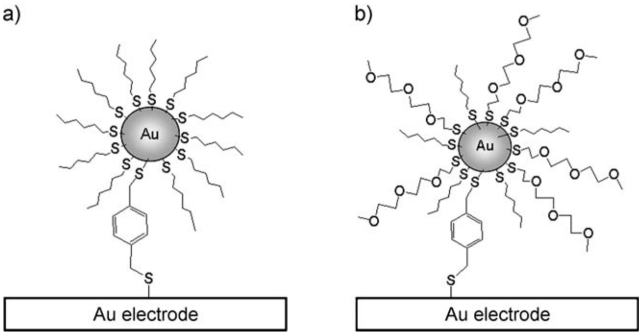

Figure 2. Structures of Au electrodes modified with **1** (a) and **2** (b).

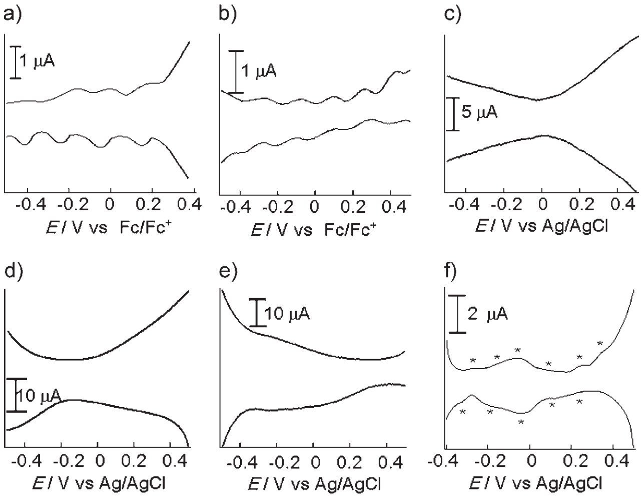

Figure 3. DPVs of **1** and **2** in 0.1 M nBu_4NClO_4/CH_2Cl_2 and 0.1 M Et_4NClO_4/H_2O. a) **1** in CH_2Cl_2, b) **2** in CH_2Cl_2, c) **2** in H_2O, d) **2** in H_2O in the presence of 0.1 M sodium dodecylbenzenesulfonate, e) **2** in H_2O in the presence of 0.1 M hexyltrimethylammonium bromide, f) **2** in H_2O in the presence of 0.1 M sodium dodecylbenzenesulfonate and 0.1 M hexyltrimethylammonium bromide. Asterisks denote peaks ascribed to redox reactions of AuNPs. Rest potential values just before the DPV measurement were −0.13 and −0.13 V versus Fc/Fc^+ for (a) and (b), respectively, and 0.28, 0.17, −0.10, and −0.04 V versus Ag/AgCl for (c), (d), (e), and (f), respectively.

sured by small-angle X-ray scattering (SAXS), which showed sizes consistent with the TEM data (see the Supporting Information). The sizes of (1.9 ± 0.2) and (1.6 ± 0.2) nm correspond to those of Au_{225} and Au_{140} nanoparticles, respectively, which have magic numbers of Au atoms.[21]

Water-soluble AuNPs $Au_x(SC_6H_{13})_y(S(CH_2CH_2O)_3CH_3)_z$ (**2**) were prepared by the thiol-substitution reaction of $Au_x(SC_6H_{13})_y$ with a diameter of 1.9 nm (**1**) with $CH_3(CH_2CH_2O)_3SH$ according to a method described previously.[22] The TEM image of **2** suggested that the diameter of AuNPs did not change in the thiol-substitution process (Figure 1 c). From the ^{1}H NMR spectrum of **2** in $CDCl_3$ a ratio of $C_6H_{13}S$ and $CH_3(CH_2CH_2O)_3S$ moieties attached to Au nanoparticles, that is, y:z in **2**, of 1:3 was deduced.

Immobilization of **1** and **2** on Au/mica plates was carried out by using 1,4-benzenedimethanethiol as a linker ligand (Figure 2). The STM image of the Au/mica surface after immobilization of **2** clearly shows that a monolayer of AuNPs was fabricated (Figure 1 d) with a core-to-core distance of 7–8 nm according to the cross-sectional profile also given in Figure 1 d.

The electrochemical behavior of these AuNP-decorated Au electrodes was investigated by analysis of differential pulse voltammograms (DPVs). In the DPVs in aprotic solvent (0.1 M Bu_4NClO_4/CH_2Cl_2; Figure 3 a,b), well-defined, sequential single-electron charging peaks with intervals of about 0.2 V were observed, as reported previously. These peaks are ascribed to single-electron charging of Au nanoparticles, for which the formal potentials $E^0_{z/(z-1)}$ of the $z/(z-1)$ charge-state couple for QDL capacitance charging are given by Equation (2)[10] where E_{pzc} is the zero-charge potential (i.e., $Z = 0$) of Au nanoparticles, C_{CLU} the AuNP capacitance, and e the electric charge. The nanoparticle capacitances were estimated to be 0.72 and 0.86 aF for **1** and **2**, respectively. The capacitance of **1** is similar to the literature value of 0.71 aF for $Au_x(SC_6H_{13})_y$ with a diameter of 2.0 nm.[14]

$$E^0_{z/(z-1)} = E_{\mathrm{pzc}} + \frac{(z-1/2)e}{C_{\mathrm{CLU}}} \tag{2}$$

The DPV of Au electrodes modified with **2** in 0.1 M aqueous Et_4NClO_4 is shown in Figure 3 c. In this DPV, no significant peaks ascribable to redox processes of the AuNPs were observed. Similarly, no significant redox peaks of the AuNPs appeared in aqueous solutions containing Et_4NBF_4, KNO_3, $NaClO_4$, or NH_4PF_6. Chen and Pei reported the appearance of the peaks of $Au_x(SC_6H_{13})_y$ immobilized on the electrode surface in aqueous solutions containing NH_4PF_6, KPF_6, Et_4NClO_4, Et_4NPF_6, or NH_4ClO_4.[13,14] In these cases, high sensitivity was requisite, and the scale of the observed peaks in the DPV was at most 0.1 μA, much smaller than that in aprotic solvent because of the effect of the high dielectric constant of water.

To make the environment around AuNPs hydrophobic even in water, we examined the effects of various surface-active agents. Figure 3d,e shows DPVs in 0.1M aqueous Et_4NClO_4 containing 0.1M hexyltrimethylammonium bromide and 0.1M sodium dodecylbenzenesulfonate, respectively. In both cases, no significant peaks appeared. This indicates that only one kind of surface-active agent is not enough to make the environment around the AuNPs fully hydrophobic. Then we examined the synergistic effect of the two surface-active agents. In the presence of both 0.1M hexyltrimethylammonium bromide and 0.1M sodium dodecylbenzenesulfonate, sequential peaks ascribed to AuNPs were clearly observed with intervals of about 0.1 V over a wide range between −0.4 and +0.4 V versus Ag/AgCl (Figure 3f). The capacitance of **2** in this aqueous medium, estimated to be 1.25 aF from Equation (2), is higher than that in aprotic media, which is consistent with the results reported previously.[14,23] The DPV of 1,4-benzenedimethanethiol-modified Au/mica in 0.1M aqueous Et_4NClO_4 containing both 0.1M sodium dodecylbenzenesulfonate and hexyltrimethylammonium bromide did not show any peaks (Figure S2 in the Supporting Information); hence the redox peaks in Figure 3f are ascribed to AuNPs. The synergistic effect of the two surface-active agents may be due to the formation of bi- or multilayers due to electrostatic interaction and/or hydrophobic interaction of the two surfactants in enfolding the AuNPs and making the environment around them more hydrophobic.[17] Further analysis of the interfacial structure is in progress.

In conclusion, AuNPs of 1.9 nm in diameter immobilized on an Au electrode show sequential single-electron charging peaks with intervals of about 0.1 V in the potential range between −0.4 and +0.4 V versus Ag/AgCl in an aqueous solution containing both hexyltrimethylammonium bromide and sodium dodecylbenzenesulfonate. This method is very useful for the application of MNPs as electron-counting components in biosensors.

Experimental Section

Hexanethiol-protected Au nanoparticles $Au_x(SC_6H_{13})_y$ were prepared by the Brust method.[20] $Au_x(SC_6H_{13})_y(S(CH_2CH_2O)_3CH_3)_z$ was prepared according to the literature.[22] To prepare the single-sized Au nanoparticles, $Au_x(SC_6H_{13})_y$ (ca. 100 mg) was dissolved in toluene (2 mL), and acetone (2 mL) was added to the mixture, which was kept at room temperature for 1 h in centrifugation tubes. Then, the mixture was centrifuged for 1 h. The precipitate was fritted off and washed with toluene/acetone (1:1). The black solution was divided into 2-mL aliquots in each of two centrifugation tubes. Acetone (6 mL) was added to the mixture, which was kept at room temperature for 1 h. The precipitate was filtered off and washed with toluene/acetone (1:7). Acetone was added to the black solution. The mixture was kept at −4 °C overnight. The precipitate was fritted off and washed with toluene/acetone (1:24). The precipitate from toluene/acetone (1:7) solution was reprecipitated from toluene/acetone (1:1, 1:2, 1:3, and 1:7).

For film preparation,[24] Au/mica plates (gold (100 nm) deposited on natural mica) were used for the electrochemical measurements and annealed with a hydrogen flame just before use. This treatment gave an Au(111)-like surface consisting of Au single-crystal grains of 400–600 nm in diameter. For immobilization of $Au_x(SC_6H_{13})_y$ and $Au_x(SC_6H_{13})_y(S(CH_2CH_2O)_3CH_3)_z$, Au/mica plates were immersed in solutions of 1,4-benzenedimethanethiol (10 mM) in EtOH overnight under Ar, followed by rinsing of the plate with HPLC-grade EtOH and drying by blowing with nitrogen. Then these Au/mica plates were immersed in a solution of $Au_x(SC_6H_{13})_y$ (21 mg) in cyclohexane (50 mL) or of $Au_x(SC_6H_{13})_y(S(CH_2CH_2O)_3CH_3)_z$ (28 mg) in EtOH (50 mL) for one or two weeks, and then washed with cyclohexane or EtOH and dried by blowing with nitrogen.

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