Particle size dependence of the charging of Au nanoparticles immobilized on a modified ITO electrode

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Title Running Head: Size dependent charging of Au nanoparticle

Abstract

Citrate-stabilized gold nanoparticles (Au-NPs) of a nearly spherical shape with four different diameters (3.7, 11.0, 21.7, and 40.8 nm) were immobilized on a 4-aminobutylsiloxane monolayer-modified indium-tin oxide (ITO) electrode. From the results of coulometric measurements using potential step sequences, the number of electrons per particle to be transferred to attain a new equilibrium state after applying a potential step was found to increase in proportion to the square of the diameter. The double layer integral capacitance of the Au-NP surface per unit area in the potential range from -0.4 V to 0.6 V (Ag/AgCl/sat'd KCl) is *ca.* $70 \mu\text{F cm}^{-2}$, being independent of the particle size. The differential capacitance of the Au-NP surface is a function of the potential with a maximum at 0.32 V, while the function is again independent of the particle size. The kinetics of the charging was discussed using the analysis of the potential step transient current. The potential dependent shift of the plasmon absorption band obtained by constant-potential and potential-modulated transmission-absorption spectroscopic measurements revealed that a smaller Au-NP exhibits a greater blue-shift of the plasmon band when applying more negative potentials, being in line with the Mie-Drude theory.

Keywords: Au nanoparticle; ITO electrode; Plasmon absorption; Transmission spectroscopy; Potential step coulometry

1. Introduction

The unique optical and electronic properties of noble metal nanoparticles are multi-faceted. Nanoparticles (NPs) of Ag and Au exhibit plasmon absorption bands in the visible wavelength region. The absorption spectrum is sensitive to various factors such as particle size [1–3] and shape [4,5], the electron density on particle [6–9], the dielectric properties of the surrounding medium [10–13], aggregation state and interparticle interaction [14,15]. The change of the particle charge occurs in a solution phase when electrons are injected or ejected by soluble reductants or oxidants, respectively. For the NPs immobilized on an electrode surface, the particle charge can be regulated by potential control as well [6-12,14,16-17]. On an electrode, the change of the particle charge can be estimated by coulometric measurements. It has been theoretically and experimentally established that optical properties of a NP are governed by the charge on it. On the basis of the Mie theory, the increase of the electron density on a NP results in the increase in the plasma frequency of the electrons in the NP, leading to a blue-shift of the plasmon absorption band [2,11]. For nano-sized Au-NPs, for example, hexanethiol-protected Au-NP ($\text{C}_6\text{S-Au}_{147}$) with its diameter, d , of 1.62 nm [18] and octanethiol-protected Au-NP ($\text{C}_8\text{S-Au}_{247}$, $d = 2$ nm) [19], the differential pulse voltammograms show evenly spaced, high-resolved peaks. Each peak corresponds to a one-electron transfer process per particle due to quantized double-layer charging. The capacitance of such particles is of the order of sub-attoFarad, which in turn is several $\mu\text{F cm}^{-2}$ if being normalized to the surface area and taking into account the low dielectric constant of the protection layer. For larger NPs, the particle surface charging takes place in similar manner as a bulk metal.

Ung and coworkers have investigated the relationship between the plasmon peak position and surface charge density for Ag-NPs [6]. They modeled and measured a quantitative relationship between the spectral shift and the surface charge density for 11.3 nm Ag-NPs dissolved in an aqueous solution. The number of transferred electrons and the double-layer capacitance of the Ag/water interface were estimated by the potential dependent plasmon absorption spectral shift to be 1790 electrons particle⁻¹ (per 1.1 V) and $80 \pm 10 \mu\text{F cm}^{-2}$, respectively. This result was in good agreement with the values of 1600 ± 200 and 1650 ± 500 electrons estimated electrochemically by the use of the Cottrell equation and

cyclic voltammetry, respectively. In our previous report, the number of electrons per particle transferred for a 11.5 nm Au-NP immobilized on an indium-tin oxide (ITO) electrode was directly estimated in an aqueous solution by the use of the potential step coulometry to be approximately 1500 electrons $\text{V}^{-1} \text{particle}^{-1}$, which corresponds to an Au/solution interfacial integral capacitance of *ca.* $60 \mu\text{F cm}^{-2}$ [16]. This capacitance value is of the same order of magnitude as the double-layer capacitance of a bulk Au electrode, in line with the above mentioned results for Ag-NPs in solution by Ung and coworkers [6].

Clarification of size-dependent properties of an Au-NP is of importance for its application as a functional nano-material. Elucidation of the optimal size is indispensable for the use as an optical signal enhancer and a catalyst. For example, size dependencies of enhancement of optical signals [20-23], molecular adsorption and cross-linking structure formation [24], and catalytic activities for reduction of organic compounds [25] have been extensively studied. The key factors of the size dependence include not only the surface density of coordinatively unsaturated Au atom [25] and electronic structure of NPs but also the charging-discharging properties of the particles. Especially when one immobilizes Au-NPs on a conductive solid surface and uses them to fabricate a nano-electrode ensemble, the size-dependent Au-NP double-layer charging should be among the most fundamental factors to quantitatively control the electrochemical characteristics.

The aim of this work is to clarify the size effect on the changes of the particle charges of citrate stabilized Au-NPs using both electrochemical and spectroelectrochemical methods in the range of d of approximately 4–40 nm. We quantify the difference of particle charge between equilibrium states at two electrode potentials. Citrate stabilized Au-NPs are targeted, because their syntheses are quick and easy to attain variable but nearly mono-dispersed diameters and they are most widely used for immobilization on electrode surfaces. We use Au-NPs immobilized on a 4-aminobutylsiloxane (ABSiO)-modified ITO electrode in an aqueous solution at pH 7.0. We focus on the particle size dependence of the number of electrons per particle transferred, the capacitance of a particle and its potential dependence, the charging kinetics, and the plasmon absorption spectral shift with potential. The potential-modulated transmission-absorption (PMTA) spectrum is used for sensitive detection of the plasmon absorption band of a Au-NP with a diameter of a few nanometers.

2. Experimental

Table 1

Chemicals. Hydrogen tetrachloroaurate(III) tetrahydrate (Wako), trisodium citrate dihydrate (Kanto), sodium borohydride (Aldrich), 4-aminobutyltriethoxysilane (Gelest), dipotassium hydrogen phosphate (Kishida), potassium dihydrogen phosphate (Kishida), and all other chemicals were of reagent grade and used as received. Water was purified through a Milli-Q Plus Ultrapure water system coupled with an Elix-5 kit (Millipore). Its resistivity was over 18 M Ω cm.

Preparation of Au-NPs. Citrate-stabilized Au-NPs were prepared by the water-phase reduction of AuCl_4^- in reference to previous papers [9,26]. The size of product Au-NP was controlled by the concentration ratio of $[\text{AuCl}_4^-] : C(\text{Na}_3 \text{ citrate}) : C(\text{NaBH}_4)$ and temperature (Table 1). The diameter was statistically calculated using over 100 particles in the transmission electron microscopy (TEM) images. Although the particles were multi-faced reflecting the crystalline structure, their shapes could be geometrically approximated as spheres. For UV-vis spectroscopic measurements, a spectrophotometer (Hitachi U-3000) was used. The TEM diameters and the wavelengths of plasmon absorption maximum of the colloidal solution, λ_{soln} , also were shown in Table 1. The colloidal solutions of Au-NPs stored in a refrigerator at 4 °C were stable for at least 1 year without any change of the absorption spectra and without precipitation.

Preparation of modified ITO electrode. A surface-flat ITO electrode (surface resistivity, 6.2 Ω/sq , R_a -roughness < 1 nm; Kuramoto Seisakusho CO., LTD.) of a surface area of 1.50–1.61 cm^2 was cleaned in 1% aqueous solution of Vista #50, a neutral detergent from Inui Medics Co., Osaka, Japan, for a period of 3 min under sonication and rinsed with a copious amount of water and then ethanol. Then, the electrode was immersed in an ethanolic solution of 0.1 M 4-aminobutyltriethoxysilane for 15–30 min to prepare an amine-terminated siloxane (ABSiO)-monolayer modified electrode. After the modified electrode was rinsed copiously with ethanol and subsequently with water, it was immersed in a Au colloidal solution for a period of $t_m = 30\text{--}180$ min. After it was rinsed well with water,

the Au-NPs deposited on the rear glass surface were wiped off completely. The amount of immobilized NPs was estimated from the plasmon absorption peak absorbance, $A_{\max}$, on an assumption that the particle absorption coefficient on the electrode surface is equal to that in the colloidal solution.

Electrochemical measurements. All the electrochemical measurements were conducted using a Ag/AgCl (saturated KCl) reference electrode and a coiled Au wire counter electrode in an Ar gas (>99.998%) atmosphere at 23 ± 2 °C. All the potentials are cited with respect to this reference electrode. The base electrolyte solution used in electrochemical measurements was 0.1 M phosphate buffer (Pi) solution of pH 7.0 prepared from potassium salts.

Potential step coulometry measurements. Potential step coulometry measurements were conducted using a Huso Electro Chemical System (HUSO, HECS326 Digital Universal Signal Processing Unit equipped with a HECS326-1 head box, response time 0.5 μ s) as described in our previous paper [16]. After an equilibration period of 90 s at the initial potential $E_i = -0.4$ V, the potential was stepped to a sequence of final potentials E_f ranging from -0.38 to 0.60 V. The sampling interval of the current was 0.25 ms. The charge was obtained by the time integration of current transient. Within the potential range used, the plot of the charge as a function of time t at $t > 0.8$ s was linear regardless of E_f , ensuring that we could obtain the charge to reach new equilibrium after the step. The intercept to the time zero line of the straight line fit of charge in the range of 0.8–1.0 s was equated to $Q(E_f)$, the charge amount required to charge the interface to equilibrium.

Spectroelectrochemical measurements. A UV–vis spectrophotometer (U-3000, Hitachi) equipped with an optical integration sphere of a diameter of 60 mm (ISN-470, Hitachi) was employed to measure the transmission-absorption spectrum. The modified ITO electrode was vertically inserted in a quartz cuvette of a light path length of 10.0 mm. The electrode surface was perpendicular to the incident light. The cuvette was filled with the base solution, in which reference and counter electrodes were put in so as not to intermit the light path. For the PMTA spectral measurements, the quartz cuvette was placed in the home-made optical system so that the monochromatic light irradiates the ITO electrode perpendicularly. The potential modulation used for the PMTA measurements is described as

$$E = E_{dc} + E_{ac} = E_{dc} + \Delta E_{ac} \text{Re}[\exp(j\omega t)] \quad (1)$$

where E_{dc} and E_{ac} are, respectively, the dc and ac potentials, ΔE_{ac} is the amplitude of the potential modulation, $j = \sqrt{-1}$, $\omega = 2\pi f$, where f is the modulation frequency, and t is the time. The instruments and procedures for the PMTA measurement were the same as described elsewhere [17]. The transmitted light was focused to a photomultiplier (Hamamatsu R928). The signal from the photomultiplier representing the transmitted light intensity in response to E_{ac} was subjected to the phase-sensitive detection by a lock-in amplifier (EG&G model 5210) to obtain both real (in-phase component with respect to E_{ac}) and imaginary (90° out-of-phase component) parts of the ac transmitted light intensity, ΔI . Simultaneously, the signal from the photomultiplier was monitored by an A/D converter and was time-averaged to obtain the dc intensity of transmitted light, I_{dc} . The ac components, both real and imaginary parts, normalized by I_{dc} , were defined as the PMTA signals and designated by $\Delta I/I$. The spectrum of the real part of $\Delta I/I$ represents the absorption spectrum at more negative potential in the modulated region from which the spectrum at more positive potential is subtracted [17].

3. Results and Discussions

The structure of the modified ITO electrode (ITO/ABSiO/Au-NP) was schematically depicted in Fig. 1. Au-NPs were immobilized on the modified ITO electrode through electrostatic interaction between negatively charged Au-NPs and the positively charged ABSiO layer and/or adsorption interaction of terminal amine groups to the Au-NP surface.

Fig. 1

Fig. 2

With an increase in t_m , the plasmon absorption band became gradually greater. Typical absorption spectra for ITO/ABSiO/Au-NP ($d = 21.7$ nm) measured at 0.0 V are shown in Fig. 2. The immobilized amounts of the Au-NPs on a modified layer were

5.6×10^{10} particles cm^{-2} for $t_m = 30$ min and 8.2×10^{10} particles cm^{-2} for $t_m = 60$ min. These values correspond, respectively, to approximately 23% and 34% of the amount of a two-dimensional hexagonal close-packing structure. Because a new absorption band at longer wavelengths than 700 nm did not appear and the wavelength of the plasmon absorption maximum of Au-NPs on the ITO electrode, λ_{max} , was insensitive to the immobilized amount, aggregation of Au-NPs was unnecessary to be considered for all four different particles.

Fig. 3

Table 2

Fig. 3 shows the plots of $\Delta Q(E_f)$ before and after the immobilization of Au-NPs on an identical ABSiO-monolayer-modified ITO electrode. The obtained charge relative to -0.4 V, $\Delta Q(E_f)$, was greater in the presence of the particles than in the absence. The particle charge equilibrated at E_f relative to that at -0.4 V is presumably equal to the difference of $\Delta Q(E_f)$ between in the presence and absence of the particles, provided that the charge required to charge the space charge layer of the semiconductive ITO was unchanged by particle immobilization [16]. The change of the total charge on the particles per 1 V change of E for the Au-NP coverages of 23% and 34% was, respectively, 58 and 87 $\mu\text{C cm}^{-2}$ when being normalized to the total surface area of the Au-NPs with spherical shape assumption with a diameter of d . Here, the change of the total charge was equated to the difference of $\Delta Q(0.6 \text{ V})$ between before and after the Au-NP immobilization. Using the amount of Au-NPs obtained from A_{max} , the number of electrons per particle transferred, q , was estimated to be approximately 6.5×10^3 electrons V^{-1} particle $^{-1}$ for both Au-NP coverages of 23% and 34% (Table 2) in the potential range from -0.4 to 0.6 V. Note that no redox response was observed in this potential range in voltammograms. Assuming that the surface area of a Au-NP is the same as that of a sphere with a diameter of 21.7 nm and the charging takes place totally at the Au-NP surface, the value of 6.5×10^3 electrons V^{-1} particle $^{-1}$ corresponds approximately to an integrated capacitance of $70 \mu\text{F cm}^{-2}$. This capacitance value is of the same order of magnitude as the double-layer capacitance of a bulk Au

electrode. For four different diameters of Au-NPs, potential step coulometry measurements were conducted for more than two different coverages of Au-NPs. It was found that the value of q does not depend on the coverage.

Fig. 4

Fig. 4 shows the dependence of q upon d as a log-log plot. The values of q were obtained from both the change of total charge on the particle per 1 V change of E (from -0.4 to 0.6 V) by the uses of potential step coulometry measurements and the amounts of Au particles estimated from $A_{\max}$. The least squares fitting calculation using all 10 points in the plot to a straight line gave rise to a slope of 2.1, revealing the fact that q is proportional to the square of d . This results points to surface charging of Au-NP with a size-independent double layer integral capacitance per unit surface area. Actually, when the particle diameter was in the range in 3.7 to 40.8 nm, the integral capacitance values fell in the range of $69 \pm 12 \mu\text{F cm}^{-2}$ (as average and deviation for in total 10 data points) regardless of d .

Fig. 5

Two charging processes, charging of the space charge layer of the ITO and charging of the immobilized Au-NPs, take place in parallel. Therefore, the differentiation of the difference of $\Delta Q(E_f)$ between before and after the Au-NP immobilization with respect to E_f gives rise to differential capacitance of Au-NPs, $C_{\text{diff}}(E)$, as a function of E . Because $\Delta Q(E_f)$ was taken at an equilibrium state after the potential step, $C_{\text{diff}}(E)$ represents the differential capacitance at the zero-frequency limit obtained by positive-going measurements. Fig. 5 shows the plot of $C_{\text{diff}}(E)$ obtained from lines a and c in Fig. 3. Because line a shows the Mott-Schottky type dependence without any additional features, the potential dependent features of line b can be regarded exclusively due to the charging of Au-NPs. The $C_{\text{diff}}(E)$ - E curve (line b) exhibits a shoulder around -0.15 V and a peak around $+0.3$ V. Note that this potential dependent curve shape is found to be common over all the diameters and the coverages of Au-NPs on the electrode. The electrolyte solution contains various anions: trace amounts of Cl^- and citrate (these were present when synthesizing Au-NPs), and

oxidation products of BH_4^- as well as 0.1 M phosphate species (H_2PO_4^- and HPO_4^{2-}). In addition, there is a monolayer of amine groups in contact with Au-NPs. All these species are adsorptive to the facets of Au-NPs and their adsorption amounts are potential dependent. Moreover, high concentration of electrolyte solution (0.1 M phosphate buffer) was used. Therefore, the differential capacitance of each facet does not have minimum at the pzc [27]. On the other hand, the adsorptions may be maximum around pzc. The pzc values of low index crystalline planes of the bare Au single crystal electrodes range approximately from -0.05 to 0.35 V [27]. Therefore, the appearance of a C_{diff} maximum at 0.3 V as in Fig. 5 is reasonable. In this context, the shoulder around -0.15 V may also be due to adsorption-desorption or reorientation of adsorbed species. To be emphasized is the particle size independency of the $C_{\text{diff}}(E)$ curve shape. The electrochemical double-layer properties of the Au-NPs do not depend on their diameters in the range of 3.7 – 41 nm, as long as capacitance obtained by the macroscopic measurements is concerned.

Fig. 6

By the use of the current transients recorded in the potential step sequence measurements, we may discuss the kinetics of the charging of Au-NPs. Fig. 6 shows typical current transients for 40.8 nm Au-NPs. In the absence of Au-NP, the transient current, $i(t)$ for ITO/ABSiO, corresponding to the charging current of the space charge layer of ITO, could be fit to:

$$i(t) = i_0 + M \exp(-t/\tau_m) \quad (2)$$

where i_0 is the constant current, M is the pre-exponential factor, t is the time after the potential step, and τ_m is the time constant. In the case of curve a in Fig. 6, $\tau_m = 7.42 \pm 0.01$ ms and R^2 -value as the result of the least-squares fitting was 0.9997 . In the presence of Au-NP (*i.e.* ITO/ABSiO/Au-NP), $i(t)$ could be fit to:

$$i(t) = i_0 + M \exp(-t/\tau_m) + N \exp(-t/\tau_n) \quad (3)$$

where N and τ_n are, respectively, the pre-exponential factor and time constant for the charging process of Au-NPs. In the case of curve c in Fig. 6, $\tau_m = 5.59 \pm 0.04$ ms and $\tau_n = 44.86 \pm 0.07$ ms with $R^2 = 0.9993$. For all the ITO/ABSiO/Au-NP (four different diameters), the fitting to Eq. (3) was successful with R^2 being over 0.9992. These results reveals that both the space charge layer of ITO and Au-NPs charging processes are represented by an exponential decay and that these two components are additive.

The charging process with 5.0%-coverage of 40.8 nm Au-NP (curve b, $\tau_n = 28.65$ ms) is completed in much shorter time than 10.2%-coverage (curve c) in Fig. 6. This tendency that a smaller coverage exhibits shorter τ_n actually applied for all other diameters. The time constant τ_n is likely the product of a capacitance and a resistance ($\tau_n = C_n R_n$). The capacitance of Au-NP corresponds to C_n , and R_n does to the sum of charge transfer resistance (R_{ct}) between ITO and Au-NP and uncompensated solution resistance (R_∞). Assuming that the time scale of the charge transfer is much shorter than the measurement time scale, $R_{ct} \ll R_\infty$, and thus $R_n = R_\infty$ is a constant. Then, C_n , thus τ_n , should be proportional to the product of d^2 and the number of the particles on the electrode surface, keeping in mind that the capacity of Au-NP per unit area is independent of d (Fig. 4). In fact, when we calculated the values of τ_n divided by d^2 and subsequently by the number of immobilized particles, resulting values represent statistical deviation of as little as $\pm 12\%$ for all the cases. This supports above assumption that the charge transfer is fast relative to the time scale of the measurements and that the decay of the transient is determined dominantly by the particle capacitance.

Attempts to more in-depth approach to the charge transfer kinetics based only on the current transients should be discarded, because we need to additionally consider the potential and time-domain dependencies of the particle capacitance (Fig. 5). In order for the kinetics to be discussed more deeply, we are currently underway of detailed investigation using ac impedance and PMTA techniques.

Fig. 7

Fig. 7 shows typical PMTA spectra represented by the real parts measured at four different E_{dc} for the same modified ITO electrode as Figs. 2 and 3 with Au-NPs ($d = 21.7$ nm,

34% coverage). The imaginary parts of the PMTA spectra (not shown here) were of factored mirror images of real parts with respect to the zero line, indicating that the spectra consist of a single component [28]. The peak wavelengths of the positive-going PMTA band, λ_p , are close to the plasmon absorption maximum of the Au colloidal solution (524.0 nm) in the range of E_{dc} from -0.3 to 0.6 V. Actually, the PMTA spectral curve represents the difference of absorption spectra between two constant potentials: the absorption spectrum of the Au-NPs at more negative potential from which that at more positive potential is subtracted within the range of the potential modulation (see Section 2.6 for details). Thus, λ_p in the PMTA spectrum at a E_{dc} was not necessarily equal to λ_{max} in the absorption spectrum at a given constant potential equal to E_{dc} . However, we found that the particle diameter dependence of the peak shift per constant change of E_{dc} , ΔE_{dc} , in the PMTA spectra was in harmony with the shift of the absorption spectrum with the change of the constant potential. Therefore, we may use the shift amount of λ_p in Fig. 7 as the semi-quantitative basis to discuss the relationship among peak shift, ΔE_{dc} , and d .

In Fig. 7, the shift of λ_p to longer wavelengths is obviously observed when E_{dc} becomes more positive. This potential dependence feature was also the cases of 3.7, 11.0, and 40.8 nm particles (Table 2). The peak shift, for example $\Delta\lambda_p = \lambda_p(\text{at } 0.6 \text{ V}) - \lambda_p(\text{at } -0.3 \text{ V})$, is greater for smaller Au-NPs. A quantitative relationship between spectral shift and change of the particle charge amount was previously modeled by Ung and coworkers on the basis of the Mie–Drude optical theory [6]. They correlated the change of dielectric function to the change of the charge to represent the spectral shift in an equation:

$$C = \frac{(\lambda_f^2 / \lambda_i^2 - 1)rF}{3V_m\Delta E} \quad (4)$$

where C is the capacitance, λ_i and λ_f are the plasmon peak maxima, respectively, at two different potentials of E_i and $E_f = E_i + \Delta E$ ($\Delta E > 0$), r is the particle radius, F is the Faraday constant, and V_m is the molar volume. Eq. (4) could be successfully applied in our previous work for a Au-NP of $d = 11.5$ nm [16]. Eq. (4) is rewritten as:

$$(\lambda_f^2 / \lambda_i^2 - 1) = \frac{1}{d} \frac{6CV_m \Delta E}{F} \quad (5)$$

When ΔE is constant, $(\lambda_f^2 / \lambda_i^2 - 1)$ should be proportional to the reciprocal of d , because values of C are approximately the same irrespective of particle diameter in the range in 3.7 to 40.8 nm. Therefore, $(\lambda_f^2 / \lambda_i^2 - 1)$ is predicted to be greater for smaller d . In fact, we confirmed for all the PMTA data obtained in the present work (Table 2) that $(\lambda_p^2(0.6 \text{ V}) / \lambda_p^2(-0.3 \text{ V}) - 1)$ became greater almost in proportion to d^{-1} at a given ΔE as well as with the increase in ΔE at a given d , maintaining the value of C as being $70 \mu\text{F cm}^{-2}$. These results demonstrate the validity of the use of Eq. (5) at least as a semi-quantitative guide to connect between the spectral shift and the amount of charging.

4. Conclusions

The particle diameter dependence of the amount of charging-discharging and PMTA spectra for spherical Au-NPs immobilized on an aminobutylsiloxane monolayer-modified ITO electrode were studied. The number of electrons injected into four different Au-NPs with diameters 3.7, 11.0, 21.7, and 40.8 nm were estimated using the results of potential step coulometry. Obtained values were proportional to the square of the diameters of the particles, reflecting the charging of the Au-NP surface, whose double-layer property is size independent. The differential capacitance as a function of electrode potential and current transient features in response to the potential step are also size independent. The potential dependent change of the PMTA spectra depended on the particle diameter. For a smaller particle, the shift amount of the plasmon peak wavelength of the PMTA band is greater per constant change of potential.

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FIGURE CAPTIONS.

Fig. 1. Schematic model of the aminobutylsiloxane (ABSiO) monolayer-modified ITO electrode with immobilized Au-NPs (presentation not in correct scale).

Fig. 2. Typical absorption spectra of a modified ITO electrode with two different coverages of Au-NPs ($d = 21.7$ nm) at 0.0 V in 0.1 M phosphate buffer (pH 7.0). The coverages were 5.6×10^{10} particles cm^{-2} (solid line, a) and 8.2×10^{10} particles cm^{-2} (broken line, b).

Fig. 3. Plots of relative charge $\Delta Q(E_f) = Q(E_f) - Q(-0.4 \text{ V})$ obtained by a sequence of potential step chrono-coulometry as a function of E_f for the same modified ITO electrode as Fig. 2. Line a (solid square, ■), before immobilization of the particles; line b (open circle, ○) and c (solid circle, ●), after the immobilization of Au-NPs of 5.6×10^{11} particles cm^{-2} and 8.2×10^{10} particles cm^{-2} , respectively. Current transients in response to the potential steps ($E_i = -0.4 \text{ V}$, $E_f = -0.4 \text{ V} + n \times 0.02 \text{ V}$ with $n = 1$ to 50) were used to obtain $Q(E_f)$. See Section 2.5 for details.

Fig. 4. Plot of the number of electrons per particle transferred when a 1.0 V potential step was given as a function of particle diameter for ABSiO-ITO electrodes with immobilized Au-NPs in 0.1 M phosphate buffer (pH 7.0). The immobilization amount were 1.1 and 1.3×10^{12} particles cm^{-2} ($d = 3.7$ nm), 3.0 and 3.6×10^{11} particles cm^{-2} ($d = 11.0$ nm), 2.0 and 2.8×10^{11} particles cm^{-2} ($d = 11.5$ nm), 5.6 and 8.2×10^{11} particles cm^{-2} ($d = 21.7$ nm), and 3.5 and 7.1×10^9 particles cm^{-2} ($d = 40.8$ nm).

Fig. 5. Plot of $C_{\text{diff}}(E)$ as a function of E obtained from Fig. 3 by differentiation. Line a: ABSiO monolayer modified ITO electrode before Au-NP immobilization. Line b: after Au-NP ($d = 21.7$ nm) immobilization with a coverage of 5.6×10^{10} particles cm^{-2} . For line b, the charging amount for ITO space charge layer was subtracted before differentiation.

Fig. 6. Current transients as the results of the potential step from -0.4 V to 0.6 V . The area of the ITO electrode was 1.58 cm^2 . For lines a-c, see the list in the inset box. A 5%

coverage corresponds to 3.5×10^9 particles cm^{-2} .

Fig. 7. Typical potential-modulated transmission-absorption (PMTA) spectra (real part) measured at four different E_{dc} for the same modified ITO electrode as Figs. 2 and 3 with a coverage of 34% ($d = 21.7$ nm). Conditions of PMTA measurements were $\Delta E_{\text{ac}} = 99$ mV and $f = 14$ Hz. E_{dc} values are given in the inset box.

Table 1. Preparation conditions and properties of Au-NPs used in the present work.

Conditions of Au-NP colloidal solution preparation			
$[\text{AuCl}_4^-]^{[\text{b}]} : \text{C}(\text{Na}_3 \text{ citrate}) : \text{C}(\text{NaBH}_4)$	Temperature / °C	d / nm	λ_{soln} / nm
1 : 3.75 : 1.74	rt ^[a]	3.7 ± 0.8	505.5
1 : 5 : 0	100	11.0 ± 0.8	520.0
1 : 5 : 0	100	11.5 ± 1.1	521.0
1 : 3 : 0	100	21.7 ± 5.2	524.0
1 : 1.32 : 1.19	rt	40.8 ± 6.4	533.0

d : particle diameter determined by TEM, λ_{soln} : plasmon absorption maximum of the colloidal solution.

[a] Room temperature

[b] $[\text{AuCl}_4^-] = 2.56 \times 10^{-4}$ M for 3.7 nm Au-NP, and $[\text{AuCl}_4^-] = 1.10 \times 10^{-3}$ M for other Au-NPs.

Table 2. Summary of particle diameter dependence.

Method	Parameter					
	d / nm		3.7 ± 0.8	11.0 ± 0.8	11.5 ± 1.1	21.7 ± 5.2 40.8 ± 6.4
	Au colloidal solution					
UV-vis	$\lambda_{\text{soln}} / \text{nm}$		505.5	520.0	521.0	524.0 533.0
	ITO/ABSiO/Au-NP					
UV-vis	$\lambda_{\text{max}} / \text{nm}$		534.3 ± 0.8	538.5 ± 1.0	520.5	537.8 ± 0.3 532.0 ± 0.5
	A_{max}	Run 1:	0.00649	0.0624	0.0352	0.114 0.0468
		Run 2:	0.00774	0.0737	0.0483	0.168 0.0955
	$\Gamma_{\text{Au}} / \text{particles cm}^{-2} \text{ [a]}$	Run 1:	1.1×10^{12} (13%)	3.0×10^{11} (32%)	2.0×10^{11} (21%)	5.6×10^{10} (23%) 3.5×10^9 (5%)
		Run 2:	1.3×10^{12} (15%)	3.6×10^{11} (38%)	2.8×10^{11} (29%)	8.2×10^{10} (34%) 7.1×10^9 (10%)
PSC ^[b]	$q / \text{electrons V}^{-1} \text{ particle}^{-1}$	Run 1:	1.5×10^2	1.4×10^3	1.5×10^3	6.5×10^3 2.9×10^4
		Run 2:	1.8×10^2	1.5×10^3	1.5×10^3	6.5×10^3 2.9×10^4
PMTA ^[c]	$\lambda_{\text{p}} (\text{at } 0.6 \text{ V}) / \text{nm}$		534	534	536	526 525
	$\lambda_{\text{p}} (\text{at } -0.3 \text{ V}) / \text{nm}$		496	515	522	516 516
	$\Delta\lambda_{\text{p}} / \text{nm}$		38	19	14	10 9

λ_{max} : the plasmon absorption maximum of Au-NPs on an ITO electrode, A_{max} : the plasmon absorption peak height, Γ_{Au} : the immobilization amount of Au particles, q : the number of electrons per particle transferred per 1 V, λ_{p} : the peak wavelength of the positive-going PMTA band, $\Delta\lambda_{\text{p}}$: $\lambda_{\text{p}}(\text{at } 0.6 \text{ V}) - \lambda_{\text{p}}(\text{at } -0.3 \text{ V})$ for real part

[a] Γ_{Au} was estimated by using A_{max} (% with respect to the 2D hexagonal close-packing structure).

[b] PSC: potential step coulometry

[c] Data for Run 2 is given.

Fig. 1. A. Toyota and T. Sagara

Fig. 2. A. Toyota and T. Sagara

Fig. 3. A. Toyota and T. Sagara

Fig. 4. A. Toyota and T. Sagara

Fig. 5. A. Toyota and T. Sagara

Fig. 6. A. Toyota and T. Sagara

Fig. 7. A. Toyota and T. Sagara