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Coupled dynamics of Au-nanoparticles and surfactants driven by potential control on a Au(111) electrode surface

Kenji Izumi¹, Takamasa Sagara²*

¹Department of Materials Engineering and Molecular Science, Graduate School of Science and Technology, ²Department of Applied Chemistry, Faculty of Engineering, Nagasaki University, 1-14 Bunkyo-machi, Nagasaki 852-8521, Japan Tel: +81-95-819-2676, E-mail: sagara@nagasaki-u.ac.jp

Introduction

Au-nanoparticles (Au-NPs) exhibit various physicochemical and optical characteristics in contrast to bulk Au. If we can regulate reversible changes of assembling structure of Au-NPs on an electrode surface by potential control, the changes may be applicable to novel functions of nano-devices that can electrochemically switch, for example, charging-state and locally-enhanced optical electric field. We previously reported potential-driven dynamic processes of a Au-NP, the surface of which is modified with an adsorption-desorption active terminal group, on a Au(111) electrode [1].

It is known that some surfactants exhibit potential-driven phase transitions of their monolayer-level adsorption layers on a Au single crystal electrode surface [2]. If the phase transition can be coupled with the movements of Au-NPs in coexistence, we may realize enhanced and synchronized dynamics of Au-NPs. In this work, we aim at providing alkanethiol-protected Au-NPs with dynamic interfacial behavior by potential control in the presence of a water-insoluble neutral surfactant or water-soluble anionic one. We describe herein the preliminary examination of aforementioned coupled behavior using the results of electrochemical and spectroelectrochemical measurements.

Experimental

We used a hexanethiol monolayer-protected Au-NP with a 3.1 nm-average diameter. As the surfactants, octadecanol (C₁₈OH) and sodium dodecylsulfate (SDS) were used. An anneal-cooled Au(111) single crystal electrode was brought into horizontal contact with Ar gas/0.05 M KClO₄ solution interface and set in a hanging meniscus (H-M) configuration to make electrochemical and electroreflectance (ER) measurements. These measurements were carried out by the use of a Ag/AgCl/sat-KCl reference electrode in Ar gas atmosphere at room temperature.
Results and Discussions

For a Au(111) electrode covered with a Au-NP/C_{18}OH mixed film, interfacial differential capacitance-potential curve (C-E curve) and ER voltammogram (ERV) are shown in Fig. 1. In Fig. 1-A, C-E curve shows low capacitances at $E > 0.0 \text{ V}$ regardless of the existence of Au-NP, indicating that C_{18}OH forms a compact adsorbed phase near the potential of zero charge (pzc) of the Au(111) electrode. Small ER signals in this potential region (Fig. 1-B), presumably due to the potential induced change of surface electron density, are in line with the low capacitance. In the range of $-0.2 \text{ V} < E < 0.2 \text{ V}$, a drastic change of C value and appearance of an ERV peak reflect the phase transition of C_{18}OH adsorbed layer. Even in the coexistence of Au-NPs, capacitance reaches the same value as that for a bare electrode at $-0.7 \text{ V}$, indicating simultaneous desorption of Au-NPs with C_{18}OH from the electrode surface.

For the Au-NP/SDS system, desorption of both Au-NPs and SDS at negative potentials were observed as in the case of Au-NP/C_{18}OH. In contrast, a steep increase of capacitance, exceeding the value of the bare electrode, was observed from 0.2 V to more positive potentials in the presence of SDS. This is likely due to charging-discharging of the Au-NPs. Interestingly, this critical onset potential lies in between two phase transition potentials of SDS on a Au(111) electrode.

In summary, movements of Au-NPs directly associated with original phase transition behavior of two different surfactants were not clearly observed. The majority of Au-NPs used in this work may be beyond the smaller size limit exhibiting measurable plasmon absorption. Although ER methods enabled us to shed light in more depth on the interfacial behavior, additional methods to directly track the dynamics of small Au-NPs should be explored.

References