

Spectroelectrochemical Characterization of Gold Nanoparticles on Electrode Surfaces

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Metal nanoparticles have been recognized to be one of the nano-substances serving a variety of novel functions at electrode/solution interfaces. It is indispensable to clarify the intrinsic and unique properties of the metal nanoparticles to be used in order for novel functional electrified interfaces to be designed.

In this paper, we describe potential dependent UV-visible spectral changes of Au nanoparticles immobilized on organic monolayers coated on an ITO electrode and dynamic behaviors of surface-modified Au nanoparticles at a Au(111) electrode using the results of electrochemical and spectroelectrochemical measurements.

The UV-vis transmission-absorption spectra were measured for a 4-aminobutyl siloxane coated ITO electrode on which citrate-stabilized Au nanoparticles of a 11-nm diameter were immobilized. The nanoparticles showed a potential dependent shift of the plasmon absorption band due to charging-discharging of the particles; at more negative potentials, a sharper and greater absorption peak was observed at a shorter wavelength. This assignment to the charging-discharging process was supported quantitatively by the Mie-Drude model proposed by Ung *et al.* [1] A combined use of potential step chronocoulometry enabled us to estimate the charging amount as being ca. 1500 electrons/V a particle. The spectral change was also tracked by potential-modulated UV-vis transmission-absorption (PMTA) spectroscopy [2]. The frequency dependence of the PMTA signal at $f > 8$ Hz was in line with the ac charging current.

However, when the time scale of the measurement was set longer, the presence of a slow decay of the absorbance was observed. The absorbance change with time after potential step perturbation was a sum of rapid change within 1 s and an exponential decay with a half life ranging from 30 to 150 s. The slow decay response depended on the wavelength, indicating that the spectral curve itself is time-dependent. In a buffered (pH 7) solution of 1.0 M NaClO₄, the slow decay component was negligibly small, whereas in 1.0 NaCl solution, the response totally consisted of the slow decay (Fig. 1). The increase of citrate concentration in the electrolyte solution did not affect the decay curve. These results indicate that very slow surface processes under the influence of anionic adsorption may originate the slow spectral change.

We have synthesized two different surface-modified Au nanoparticles shown in the upper part of

Fig. 2. These particles could be spread on an Ar gas/electrolyte solution (0.05 M KClO₄ + 2 mM KHCO₃) interface with a help of a volatile organic solvent. A Au(111) electrode was horizontally touched to the spread film, and electrochemical and electroreflectance (ER) measurements were made. These particles show potential dependent responses as shown by the differential capacity (C) – potential (E) curves in Fig. 2. In the case of PyMPC-1, the peak around -0.2 V was observed presumably due to the potential dependent reorientation of terminal 4-pyridyl groups on Au(111) surface. [3] On the other hand, PyMPC-2 showed a rise of C at negative potentials. This may be due to the partial adsorption-desorption of the particles on the Au(111) surface. At the potentials near the capacity changes, changes of ER signals were also observed. These observations and implication of ER signal will be discussed in regard to the interfacial dynamics of the metal nanoparticles.

References

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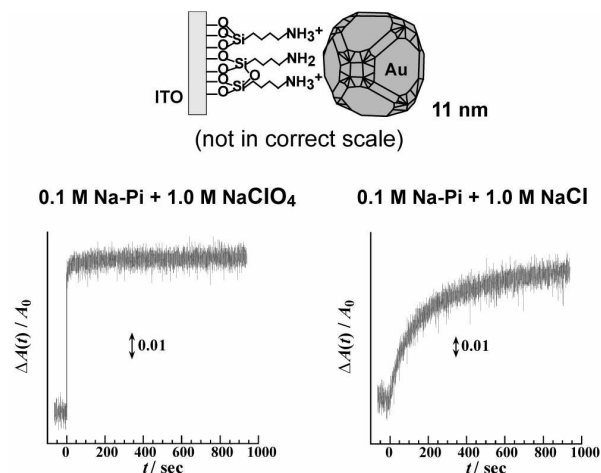


Fig. 1. Schematic picture of Au nanoparticle immobilization (upper) and absorbance changes at 530 nm in response to the potential step from 0.8 V to 0.0 V vs. Ag/AgCl (sat'd KCl).

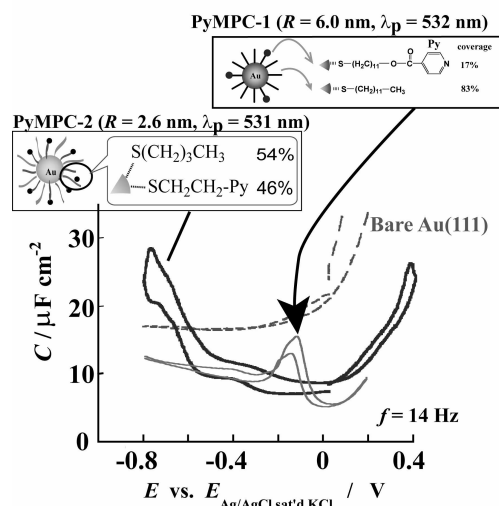


Fig. 2. Structure of surface-modified Au nanoparticles (upper) and C - E curves for Au(111) electrode at a frequency of 14 Hz.