

## Spectroelectrochemistry of Au Nanoparticles Immobilized on an Organic Monolayer Modified Electrode

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### Introduction

Ordered assemblies of metal nanoparticles immobilized on an electrode surface provide us with a nano-regulated macroscopic electrode. Such electrodes exhibit unique characteristics based on the nano-specific properties of metal particles at the electrified interface [1]. It is important to clarify the unique functions attained by the immobilization of metal particles on electrode surfaces. We describe herein the potential dependent behavior of Au nanoparticles (Au-NPs) immobilized on an electrode using the results of static and dynamic spectroelectrochemical measurements.

### Experimental

Citrate stabilized Au-NPs with four different diameters (3.7, 11.5, 21.7, 40.8 nm) were immobilized on a siloxane monolayer-modified ITO electrode surface with more than two different coverages. The behavior of Au-NPs was characterized in an aqueous solution at pH 7.0 by combined use of electrochemical and *in situ* UV-vis transmission-absorption spectral methods.

### Results and Discussions

At more negative potentials, a sharper and greater plasmon absorption band at a shorter wavelength was observed [2,3]. This spectral change was found to originate mainly from the charging-discharging process, which amounts to approximately 1500 electrons V<sup>-1</sup> per Au-NP with a diameter of 11.5 nm as being estimated from potential step coulometry, in response to the change of electrode potential. The number of electrons injected into Au-NPs with four different diameters was proportional to the square of the diameters, reflecting the charging of the Au-NP surface, whose double-layer property is size independent. The potential-dependent shift of the peak wavelength of the plasmon absorption band per constant change of potential is greater for smaller particle, being in line with the Mie-Drude theory. Details of these results will be discussed.

**References** [1] A. N. Shipway et al., *ChemPhysChem*, **1**, 18 (2000). [2] A. Toyota et al., *J. Electroanal. Chem.*, **565**, 335 (2004). [3] A. Toyota, T. Sagara, *Electrochim. Acta*, **53**, 2553 (2008).