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Spectroelectrochemical Study for Dyes Adsorbed on Gold Nano-Rings Immobilized on an ITO Electrode

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Introduction

Noble metal nano-structures exhibit characteristic optical absorption so-called plasmon resonance, resulting in excitation of collective oscillation of free electrons. This absorption is accompanied by enhancement of electromagnetic field in close proximity of the nano-structure. A gold nano-ring is one of the candidate structures which produce enhanced electric fields in both inner and outer ring surface regions independently [1].

The optical properties of nano-structures are affected by surrounding media (eg. surface protectants, solvents, and inter-structure interaction) and the charge densities on the structures. When metal nano-structures are immobilized on an electrode surface, one can control the optical properties of the modified electrode by potential [2]. We expect that an electrode/metal-nano-structure/electrolyte solution system forms a specific double-layer electric field, inducing unique Stark effects of coexisting dyes.

In this study, we synthesized gold nano-rings and immobilized them onto an ITO electrode. Spectroelectrochemical measurements such as a constant potential transmission spectral measurement were conducted for tracking the spectral response of the ITO electrode/gold-nano-ring/dye system.

Experimental Section

A gold nano-ring was synthesized via replacement reaction of a silver nano-plate by gold using $\text{AuCl}_4^{-}$ as a precursor ($3\text{Ag}^0 + \text{AuCl}_4^- \rightarrow \text{Au}^0 + 3\text{Ag}^+ + 4\text{Cl}^-$). A silver nano-plate was synthesized by reduction of silver nitrate by sodium borohydride in the aqueous solution containing with polyvinylprrolidone (PVP), trisodium citrate, and hydrogen peroxide. Preparation of gold nano-ring was made by addition of HAuCl$_4$ aqueous solution to the silver nano-plate dispersion under vigorous stirring. Thus
obtained gold nano-rings were immobilized on an ITO electrode covered with a monolayer of (3-mercaptopropyl)trimethoxysilane by immersing it in the gold nano-ring dispersion. Electrochemical measurements were conducted using a Ag/AgCl/sat-KCl reference electrode and a coiled Au wire counter electrode.

Results and Discussions

Gold nano-rings synthesized in this study were smaller than 50 nm with circular and triangular shapes (Fig. 1). The dispersion solution contained other shapes as well, such as spherical particle and coin with inner hole of a reduced diameter. Presumably, small gold nano-rings shrank to spherical structures, and replacement reaction occurred at both edge and top faces of silver nano-plate resulted in the reduction of the inner hole diameter.

Spectroelectrochemical response of the ITO/gold nano-ring system was measured in 0.1 M phosphate buffer solution (pH 7.0). As shown in Fig. 2, gold nano-rings on an ITO electrode exhibited a spectral change as a function of the electrode potential. Absorption band around 550 nm was shifted to blue and its absorbance became greater at more negative potentials. This behavior indicates that charging-discharging of the gold nano-ring takes place [2,3].

In the presentation, spectroelectrochemical response of the ITO/gold nano-ring/dye system will be discussed.

Reference