Electrodeposition Mechanism of Biferrocene Derivative-Attached Gold Nanoparticles

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Recently, preparation methods of stable and size-controlled gold nanoparticles using alkanethiols have been developed, and their special electronic and electrochemical properties have been revealed. One important area of study on nanoparticles is the fabrication of their dimension-controlled assembly for the purpose of making new electronic and optical devices such as quantum wire, single electron device, and nonlinear optical films. Several methods to induce assembly such as self-assembly using mono-dispersed particles; chemical interaction using dithiol, ionic polymers, metal ions, and organic ligands with an adsorptive group, or physical perturbation by electric field or light, have been reported.

We recently reported a novel electrochemical procedure to fabricate redox-active Au[1] and Pd[2] nanoparticle films on electrode substrates using biferrocene (BFc) derivative-attached metal nanoparticles, Au_n-BFc, prepared by a substitution reaction of octyl thiolate-covered metal nanoparticles with the biferrocene-terminated alkanethiol derivative (BFcS). The electrodeposition is achieved by the two-electron oxidation of the BFc units attached to metal nanoparticles. We also found that the electro-reductive deposition of Au nanoparticles was modified with the use of an anthraquinone derivative.[3] This method can be utilized for constructing hetero-layers of metal nanoparticles, and the film thus formed shows novel photoelectrochemical characteristics different from those of a single particle.

These previous results indicate that the metal nanoparticles functionalized with ‘multi-redox’ molecules can be generally aggregated on the electrode by electro-oxidative or reductive reaction. The detailed elucidation of the mechanism itself is of considerable interest, and can contribute to the advanced practical application of fabricated and more ordered metal nanoparticle assemblies. In this study, the electrodeposition mechanism of octyl thiolate-stabilized gold nanoparticles with a 2.3 ± 0.5 nm core diameter modified with biferrocene-terminated alkyl thiolates on their surface (Au_n-BFc) has been investigated using cyclic voltammetry, STM and AFM morphological observation, and electrochemical quartz crystal microbalance (EQCM) of the deposited Au_n-BFc film.

Consecutive potential scans causing two-step one-electron oxidation of the biferrocene units of Au_n-BFc in 0.1 M electrolyte (Bu_4NClO_4, Bu_4NBF_4, Bu_4NPF_6) – CH_2Cl_2 solution produce the adhesive Au_n-BFc film on an electrode. The deposition rate is lower for the biferrocene derivative on one particle (θ_{BFc}) with a smaller modification number and a kind of electrolyte anion; $ClO_4^- \sim BF_4^- >> PF_6^-$.

The STM and AFM images have revealed that the thickness of the Au_n-BFc film grows gradually by increasing the number of cyclic scans, forming many domains *ca.* 80 nm diameter of the assembled Au_n-BFcs. The average inter-particle spacing of neighboring Au_n-BFcs in the film is 7.5 nm, which is longer than the estimated diameter of Au_n-BFc (5.9 nm). Elemental analysis of the film by the prompt γ-ray neutron activation (PGA) method and inductively coupled plasma (ICP) measurement show that the ratio of Au_n-BFc and an anion in the film electrodeposited in 0.1 M Bu_4NBF_4 – CH_2Cl_2 solution of Au_n-BFc (θ_{BFc} = 7.5) can be calculated as 9.3 BF_4^-'s per Au_n-BFc particle. These results indicate that anions surround the charged Au_n-BFc surface in the electro-oxidation process, and the electrolyte species are therefore incorporated among the Au_n-BFc particles.

EQCM measurement suggests that the electrodeposition process of Au_n-BFc is comprised of four processes: adsorption, desorption, assembly, and deposition. The plots of potential vs frequency change for the film prepared in 0.1 M Bu_4NPF_6 – CH_2Cl_2 of Au_n-BFc (θ_{BFc} = 7.5) on an EQCM gold electrode prove the periodical weight change of the film by cyclic potential scans, indicating that the included cations of electrolyte in the film are moved in and out reversibly in a potential range of $E^{0\prime}_2$ of Au_n-BFc.

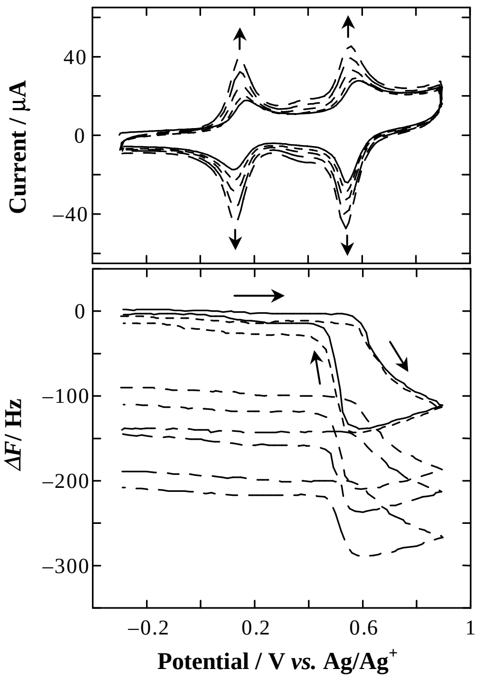

Fig. 1. Cyclic voltammograms (top) and *ΔF*-potential curves (bottom) of 5.2 mM Au_n-BFc (θ_{BFc} = 7.5) at a gold electrode in 0.1 M Bu_4NClO_4 – CH_2Cl_2 at 100 mV/s between –0.3 and 0.9 V vs Ag/Ag^+ in the positive direction with the 1st (solid line), 5th (dotted line), 10th (dashed line), 15th (dot-dashed line), and 20th (2-dot-dashed line) scans.

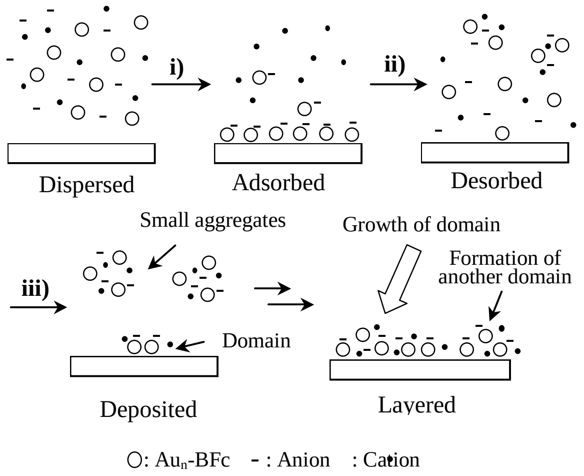

Fig. 2. The illustration of the electrodeposition process in Au_n-BFc solution at the electrode interface (bottom). i) Two-electron oxidation of the BFc sites, ii) set back to the neutral state by two-electron reduction, and iii) repeating the potential sweep.