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Electrochemical construction of an alternating multi-layered structure of palladium and gold nanoparticles attached with biferrocene moieties†

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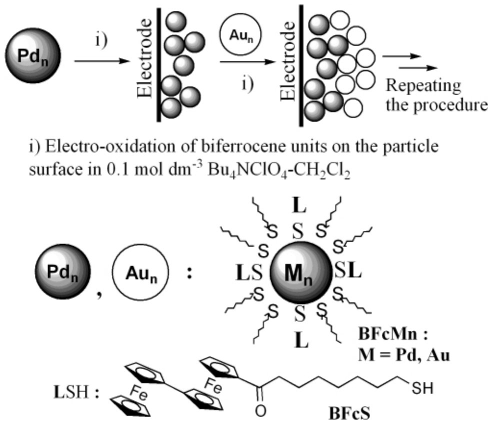
A combination of electro-oxidative deposition of palladium nanoparticles attached with biferrocene-terminated thiolates and that of gold nanoparticles with same thiolates forms a thin redox-active composite film with a layered hybrid structure.

Exploitation of new methods for constructing dimensionally controlled structures of nanometer-sized metal particles[1] is an intriguing subject because such assembled particles are expected to exhibit specific traits that differ from those of isolated single particles due to collective interactions.[2,3] The use of metal nanoparticles chemically stabilized by organic surfactants[4] has been remarkably developed, such that versatile functional interfaces have been formed in the last few years. In the previous studies, we have developed an electrochemical method to construct metal nanoparticle films with a thickness of up to ~ 1 μm by employing multi-redox and photoactive species attached particles.[3,5,6] The electro-oxidative deposition of both palladium and gold nanoparticles modified with biferrocene-terminated thiolates (abbreviated as BFcPd$_n$ and BFcAu$_n$, respectively) can be achieved by two-electron oxidation of the biferrocene units on the particle surface.[5] Deposited particles in the film are densely packed and attached strongly to the electrode, retaining the electroactivity of the biferrocene units.[5,7] This method was shown to be more convenient in terms of fabrication of multilayered films with interlayer interactions, compared to other common methods that utilize chemical binding[8] and electrostatic interaction[9] between particles and ligands (*e.g.*, dithiols, ionic polymers).

Here we demonstrate that the above electrochemical method is an efficient means of constructing novel hetero-layered films of different metal nanoparticles with specific electrochemical behavior in acidic solution. We employed a combination of BFcPd$_n$ and BFcAu$_n$. BFcPd$_n$ with a core diameter of 3.8 (± 0.8) nm, and BFcAu$_n$ with a core diameter of 2.9 (± 0.8) nm, determined by the TEM images, were prepared by 1 : 4 mole feed ratio of the biferrocene thiol derivative (BFcS), 1-(9-thiononyl-1-one)-1′,1″-biferrocene, to octyl thiolate units on the metal nanoparticles in substitution reaction according to the procedure described in our previous reports.[5] The modification number of the biferrocene moieties per particle (θ_{BFc}) was calculated as 26.3 for BFcPd$_n$ (with 325 octyl thiolates) and as 20.8 for BFcAu$_n$ (with 187 octyl thiolates),[10] from the ratio of the peak integrals of the broadened ^{1}H NMR signals between the biferrocene moiety at δ 3.9–4.7 ppm and the methyl group of octyl thiolates. Cyclic voltammograms (CVs) of both BFcPd$_n$ and BFcAu$_n$ at ITO electrode (1×2.5 cm^2) in 0.1 mol dm^{-3} $Bu_4NClO_4–CH_2Cl_2$ showed a two-step 1e$^-$ oxidation derived from the modified biferrocene moieties. The preparation of the composite films was carried out by combining both electrodepositions of BFcPd$_n$ and BFcAu$_n$ in each electrolyte solution (Scheme 1). First, the electrodeposition of BFcPd$_n$ was performed by 25 potential cyclic scans between -0.3 and 0.9 V in a solution of BFcPd$_n$ in $Bu_4NClO_4–CH_2Cl_2$, which was followed by the electrodeposition of BFcAu$_n$ in another electrolyte solution containing BFcAu$_n$ with the same electrochemical condition as the formation of the BFcPd$_n$ film, thus forming the BFcPd$_n$/BFcAu$_n$ composite film. This procedure caused a gradual increase in the peak current (see ESI†), resulting in the formation of the BFcPd$_n$ and BFcAu$_n$ films on ITO. The two-step hetero-electrodeposition procedure was repeated in order to increase the number of composite layers.



Scheme 1 Preparation of BFcPd$_n$/BFcAu$_n$ composite films.

The UV-Vis spectrum of the film thus prepared shows broad absorption bands that grow in intensity with increases in the number of composite layers (Fig. 1). A broad peak at *ca.* 550 nm, which is regarded as the surface plasmon band of the collective BFcAu$_n$, begins to appear quite clearly after the deposition of the second layer of BFcAu$_n$. The CV of the film in a pure electrolyte solution exhibits two redox waves at $E^{0\prime}$ = 0.18 V for BFc$^+$/BFc, and at 0.58 V for BFc^{2+}/BFc$^+$, as shown in the inset of Fig. 1, in which the amount of charge for the two redox waves increases with an increase in the number of composite layers. Fig. 1B shows the XPS spectra of the composite film using the C 1s peak (284.5 eV) as a reference. The Au 4f$_{5/2}$ (87.5 eV) and 4f$_{7/2}$ (83.9 eV) peaks[11] are not detected in the first layer of BFcPd$_n$, although they appear after deposition of the second layer of BFcAu$_n$. In addition, the formation of the third layer of BFcPd$_n$ shelters most of these peaks, suggesting that the prepared films build up an alternately layered structure of BFcPd$_n$ and BFcAu$_n$. The coverage of the BFcPd$_n$/BFcAu$_n$ film, evaluated from the UV-Vis spectra at 510 nm ($\varepsilon = 1.91 \times 10^6$ mol^{-1} dm^3 cm^{-1} for BFcPd$_n$, $\varepsilon = 2.35 \times 10^6$ mol^{-1} dm^3 cm^{-1} for BFcAu$_n$), is 2.69×10^{-11} mol cm^{-2} for BFcPd$_n$ and 1.32×10^{-11} mol cm^{-2} for BFcAu$_n$, corresponds to *ca.* 12 BFcPd$_n$ and 5 BFcAu$_n$ layers, respectively, when we assume that the electrodeposited particles were packed with a spacing of 9.0 and 8.1 nm diameter, as evidenced in our previous studies.[12] Note that the deposition amount of the second layer of BFcAu$_n$ is small compared to that of the first layer of BFcPd$_n$ with reduction of the increasing of the peak currents in the CV at electrodeposition (see ESI†), since electron transfer is rather restricted through the first layer of BFcPd$_n$ on an electrode; however, it is sufficient for

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† Electronic supplementary information (ESI) available: cyclic voltammograms for electrodeposition of BFcPd$_n$/BFcAu$_n$. See http://www.rsc.org/suppdata/cc/b2/b207513j/

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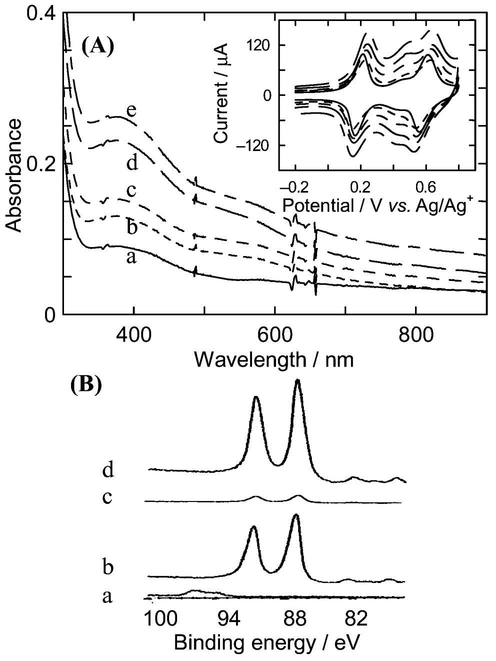

Fig. 1 (A) UV-Vis spectra, (inset) the cyclic voltammograms, and (B) the XPS spectra of BFcPd$_n$ (a), BFcPd$_n$/BFcAu$_n$ (b), BFcPd$_n$/BFcAu$_n$/BFcPd$_n$ (c), [BFcPd$_n$/BFcAu$_n$]$_2$ (d) and [BFcPd$_n$/BFcAu$_n$]$_2$BFcPd$_n$ (e) films. The films were prepared by 25 cyclic potential scans between −0.3 and 0.9 V *vs.* Ag/Ag$^+$ for metal nanoparticle film in a solution of 3.2 μmol dm^{-3} BFcPd$_n$, or BFcAu$_n$, in 0.1 mol dm^{-3} Bu_4NClO_4–CH_2Cl_2 at 0.1 V s^{-1} on ITO.

developing composite film leading to an average 5 BFcM$_n$ (M = Pd, Au) layers above the second layer.

The peculiar electrochemical properties of the BFcPd$_n$/BFcAu$_n$ film on an ITO electrode were observed in 0.5 mol dm^{-3} aq. H_2SO_4 by CV, and the results are displayed in Fig. 2, together with the results of a sole BFcPd$_n$ film and a sole BFcAu$_n$ film. The sole BFcPd$_n$ film undergoes a redox process exhibiting an oxidation peak at *ca.* 1.3 V, which corresponds to the formation of a palladium oxide layer on the particle surface, followed by re-reduction at 0.3 V;[13] the sole BFcAu$_n$ film possesses the same type of oxidation and reduction peaks at *ca.* 1.6 and 0.8 V, respectively. The redox waves of the metal particle films are broader than those of the bulk metal electrode, probably due to the slow electron transfer of the thick layers of particles covered with passive alkyl thiolate chains. In comparison with the CV of the sole-component films, it is clearly seen that the BFcPd$_n$/BFcAu$_n$ film exhibits an oxidation peak at *ca.* 1.3 V, which can be interpreted as the collective oxidation reaction of the BFcPd$_n$ and BFcAu$_n$. On the other hand, the reduction peak appears at *ca.* 0.3 V, which is the same potential as that of the BFcPd$_n$ film, with inhibition of the reduction of the sole BFcAu$_n$ layer at 0.8 V. Furthermore, the current of the reduction peak is quite small compared to that of the oxidation peaks. No appearance of the peak at 0.8 V suggests that the BFcPd$_n$ appears to be sufficiently conductive that it is capable of mediating the oxidation reaction of BFcAu$_n$; however, the electron transfer between the oxidized form of the BFcPd$_n$ and BFcAu$_n$ films is considerably hindered. This implies that electron transfer in the metal nanoparticle films can be controlled by changing the combination of core metal elements in this deposition system.

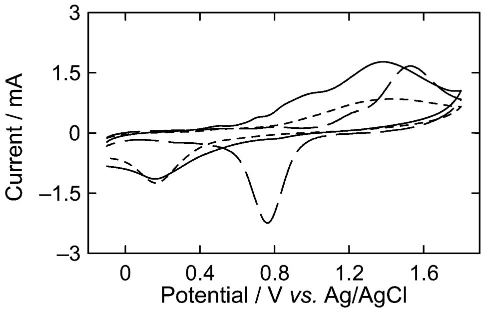

Fig. 2 Cyclic voltammograms of BFcPd$_n$ (dots), BFcAu$_n$ (dashes) and BFcPd$_n$/BFcAu$_n$ (solid line) films in 0.5 M aq. H_2SO_4 at 0.1 V s^{-1}. The films were prepared by 75 cyclic potential scans between −0.3 and 0.9 V *vs.* Ag/Ag$^+$ for each metal nanoparticle layer in a solution of 3.2 μmol dm^{-3} BFcPd$_n$, or BFcAu$_n$, in 0.1 mol dm^{-3} Bu_4NClO_4–CH_2Cl_2 at 0.1 V s^{-1} on ITO.

In conclusion, we have demonstrated that a combined electrodeposition method would be advantageous for arranging dimensionally-controlled hetero-networks of metal nanoparticles. More variation can be introduced into this method in order to achieve additional advanced properties implemented by selecting alternative parameters such as core metal elements, core size, and attached-redox species. Study of relevant alternatives is currently under investigation in our laboratory.

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12 The estimated maximal BFcPd$_n$ and BFcAu$_n$ size including the length of surrounded octyl thiolates (1.0 nm) and biferrocene units (0.8 nm) is 7.4 and 6.5 nm, respectively. In addition to these values, we have considered the particle spacing of 1.6 nm observed by an STM image of the BFcAu$_n$ (d_{core} = 2.2 ± 0.5 nm, θ_{BFc} = 3.6) film, attributed to the immobilized electrolyte among the particles. See refs. 3 and 7.
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