Clusters Layered on Au Surfaces

Electrochemically Controlled Layer-by-Layer Deposition of Metal-Cluster Molecular Multilayers on Gold**

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The ordered and controlled location of molecular compounds on electrode surfaces is essential for the nanometer-scale design of electrochemical interfaces in view of fundamental electron-transfer studies and several lines of applications, such as molecular electronic devices, optical devices, and sensors.[1] Furthermore, layer-by-layer deposition of molecular units onto preorganized self-assembled monolayers (SAMs) has proven to be useful in preparing layered architectures with enhanced properties.[2] Although a significant progress has been made for atomic-scale depositions (such as underpotential deposition and atomic layer epitaxy)[3] or molecular 2D assembly,[4] an "electrochemical-control strategy" to prepare layer-by-layer 3D structures from molecular building blocks is currently unavailable. Herein we report on the successful construction of layer-by-layer nanostructures on a gold electrode by using a redox-active metal-cluster molecule,[5] in which the electrode potential modulation precisely controls the multilayer growth. We show that the series of multilayers display extensive electronic coupling between the linked molecular units, thus allowing facile multielectron transport to occur at interfaces.

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[**] This work was supported by Grant-in-Aids for Scientific Research on Priority Area of "Electrochemistry of Ordered Interfaces" (Nos. 09554037 and 09237106) and No. 09740483 from the Ministry of Education, Science, Sports and Culture, Japan. Financial support from the Sasakawa Scientific Research Grant from the Japan Science Society (to M.A.) and PRESTO, Japan Science and Technology Corporation (JST) (to S.Y.) is gratefully acknowledged. We thank Prof. M. Osawa (Catalysis Research Center, Hokkaido University) for valuable discussions.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200351334

Our synthetic approach is outlined in Figure 1 and the detailed procedures are provided in the Experimental Section. In the approach, we use a trinuclear ruthenium complex $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(bpy)_2(CO)]$ (**1**, bpy = 4,4′-bipyridine; Figure 1)[6] as a molecular building block. The Ru_3 core of **1** formally contains two Ru^{III} sites and one Ru^{II} site, in which the CO ligand occupies the latter position.[7,8] This class of molecular clusters is known to have well-defined redox processes in solution, and the character of the terminal-ligand displacement is precisely controlled by the redox state of the core of the $Ru_3(\mu_3\text{-}O)$ cluster.[9]

With the aim of constructing molecular multilayers, we prepared close-packed SAMs of a CO-bound Ru_3 complex on an Au(111) electrode[10] (Figure 1 a) as described previously.[11] The terminal CO is eliminated when the attached Ru^{II} center is electrochemically oxidized to Ru^{III}, and the monolayer containing a kinetically-labile water molecule shown in Figure 1 b is formed (step 1).[11] Immersion of the monolayers shown in Figure 1 b into a solution of **1** results in the coordination of **1** to the monolayer binding site through a single Ru^{III}–N(bpy) bond to afford CO-terminated bilayers shown in Figure 1 c (step 2). We have successfully prepared molecular multilayers up to five layers, by repeating interfacial reactions (steps 1 and 2) alternately (Figure 1). The bpy- and pyrazine-bridged extended structures that have been characterized[12–14] are relevant to the expected molecular structures in our multilayers.

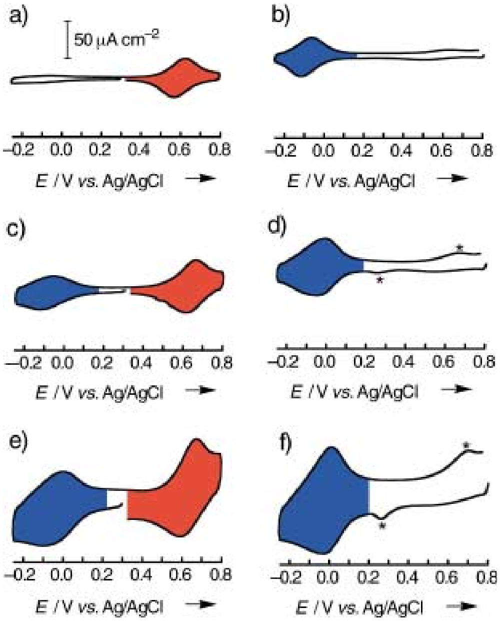

Figure 2. Cyclic voltammograms, recorded in an aqueous solution of 0.1 M $HClO_4$, of monolayers and multilayers sequentially prepared on an Au electrode: a) CO-terminated monolayers; b) water-terminated monolayers; c) CO-terminated bilayers d) water-terminated bilayers; e) CO-terminated trilayers; f) water-terminated trilayers. Red and blue waves correspond to redox couples from the Ru_3 cores with CO and those without CO, respectively. Scan rate = 0.5 V s^{-1}.

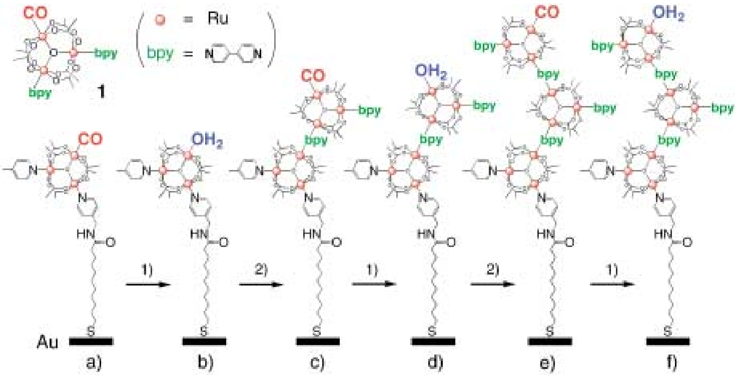

Figure 1. Schematic representation of sequential growth of layer-by-layer multilayers on an Au surface. Only a single molecule attached to Au is shown. Inset: trinuclear ruthenium complex **1**, used as a redox-active molecular building block. Conditions: Step 1: Electrolysis at +0.80 V versus Ag/AgCl for 45 minutes or less, 0.1 M $HClO_4$, 298 K; Step 2: Immersion into an aqueous solution of **1** (0.2 mM), in dark, 4 days, 298 K.

Cyclic voltammetry was used to follow the multilayer-formation processes. As the redox potentials are substantially different between the "CO-bound" and "CO-free" cluster molecules,[7,8] the surface species were quantitatively evaluated by cyclic voltammetry. A series of cyclic voltammograms (CVs) obtained for the monolayers, bilayers, and trilayers with and without CO, which were sequentially prepared on an Au electrode are depicted in Figure 2 a–f. As established previously,[11] the close packed CO-terminated monolayers (the surface coverage $\Gamma = 1.4 \times 10^{-10}$ mol cm^{-2}) result in a $Ru^{II/III}$ couple at the half-wave potential ($E_{1/2}$) of +0.59 V versus Ag/AgCl in contact with an aqueous solution of 0.1 M $HClO_4$ (Figure 2 a, red wave). This couple is ascribed to the site at which CO is bonded. When electrolysis is conducted at +0.80 V so that the Ru^{III} redox state is generated, CO dissociation proceeds from the monolayer which gives rise to a redox couple at $E_{1/2} = -0.09$ V (Figure 2 b, blue wave). The CO-terminated bilayers (Figure 2 c) show a redox wave at $E_{1/2} = +0.64$ V ($\Gamma = 2.0 \times 10^{-10}$ mol cm^{-2}) from **1** coordinatively introduced as a second layer.[15] Complex **1** dissolved in 0.1 M $(C_4H_9)_4NPF_6$-CH_3CN exhibits a reversible redox wave at +0.68 V. An additional wave observed at $E_{1/2} = -0.09$ V ($\Gamma = 1.1 \times 10^{-10}$ mol cm^{-2}) is ascribed to the $Ru^{II}Ru_2^{III}/Ru_3^{III}$ process arising from the underlayer, which is free from CO.[11] Upon subsequent electrolysis (+0.80 V), the CV (Figure 2 d) shows evidence of losing CO from the top layer. The increase in charge and the presence of two waves (shaded waves in Figure 2 c and d) accompanied with an electrochemical release of CO, provides evidence of clean ligand transformation while maintaining the structural integrity at the surface. It should be noted that unlike CO-free multilayers, the CO-terminated multilayers completely block the coordination of **1** under identical conditions. The CO dissociation from the monolayer and multilayers all obey first-order kinetics with rate constants similar to each other, ranging from 1.2×10^{-2} s^{-1} for the monolayer to 2.0–7.2×10^{-2} s^{-1} for the multilayers at 298 K.[16] The negligible dependence of the CO-dissociation character on the multilayer generation is important in effectively extending the nanostructures on surfaces.

Figure 3 shows a plot of charge (Q) from the CVs of the water-terminated mono- and multilayers against the number of layers (n). The linear correlation with the slope $Q/n = 1.4 \times 10^{-10}$ mol cm^{-2}, which is consistent with the monolayer coverage used here, is in full accordance with the picture of quantitative generation of multilayers. Each molecular backbone, in principle, is flexible with respect to the rotation around the Ru–N coordination bonds to form the disordered morphology of the film. On the basis of the quantitative-growth feature observed here, however, we rationalize that this effect is minimized because of extensive lateral interactions as a result of the close-packed molecular assembly present in this case.

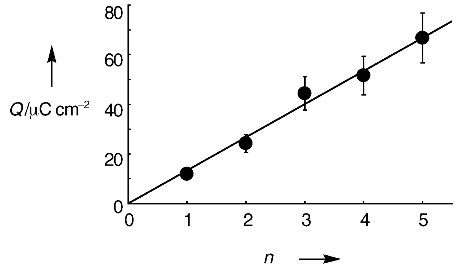

Figure 3. A linear correlation of charge (Q), obtained from the redox wave around −0.1 V, against the number of layers (n) for the series of water-terminated monolayer ($n = 1$) and multilayers ($n = 2$–5).

Fourier transform infrared reflection absorption (FTIRRA) spectroscopy measurements further support the quantitative generation of the molecular multilayers.[17] For the CO-terminated multilayers, the acetate band intensities along with aromatic ring vibration bands arising from bpy ligands (1700–1500 cm^{-1}) increase as the deposition cycle of **1**[18] is increased, while the intensity of the ν(CO) band remains virtually constant (see Supporting Information). The band area was used to evaluate the multilayer growth. We find that the relative intensity ratio $I\{\nu_s(\mathrm{COO})\}/I\{\nu(\mathrm{CO})\}$ linearly increases as the deposition cycle is increased (Figure S1).[19] If we assume that the infrared intensity is not significantly affected by the distance between the surface-confined molecular units and the surface, the trend observed in this case does illustrate the quantitative growth character of our system. Further characterizations, including ellipsometric measurements, are now in progress.

The electron transport behavior of the pentalayer without the top CO is shown in Figure 4. A series of CVs recorded at varying scan rates involve a single redox process ($E_{1/2} = +0.01$ V), which is ascribed to the (0/+1) redox change for each Ru_3 unit, corresponding to the (0/+5) redox change for the entire molecule; ClO_4^- anions balance the charge during the redox cycle.[20] It appears that anodic and cathodic current intensities linearly increase with the increase of scan rates, consistent with the feature of surface-confined redox centers.[21] The separation between the anodic and cathodic peak potentials (ΔE_p) for the pentalayer (0.03 V) is quite small (Figure 4), thus indicating that the electron transport across the large distance molecular wires is substantially facile, because of a significant degree of electronic conjugation between the cluster units through bpy. The rather broad redox wave (full-width at half-maximum, $\Delta E_{1/2} = 0.21$ V) may be attributed to significant lateral interactions and/or the presence of electronic communications between linked Ru_3 cluster cores through bpy. We note that multiple redox cycling for the series of CO-free multilayers does not alter the redox response, and they are stable for days in aqueous electrolyte solution and under atmospheric conditions.

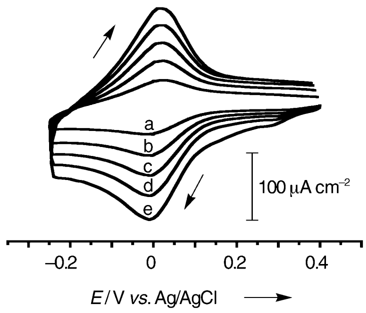

Figure 4. Scan rate dependence of redox waves for the water-terminated pentalayer. Scan rate: a = 0.1, b = 0.2, c = 0.3, d = 0.4, and e = 0.5 V s^{-1}.

In conclusion, we present herein a new method to prepare molecular multilayers with high redox activity, in which layer-by-layer nanostructural growth is controlled by the electrode potential applied. Since our approach can be applied, in principle, to other redox molecules, it will open significant possibilities for the design of new 3D molecular architectures on surfaces, which will be of considerable use in molecular electronics and electrocatalysts.

Experimental Section

Electrochemistry and FTIRRA spectroscopy: Cyclic voltammetry and electrolysis experiments were performed by using Hokuto Denko HA-301 electrochemical systems with an Au(111) electrode ($S = 0.082$ cm^2) covered with monolayers or multilayers as a working electrode, a Pt coil as a counter electrode, and an Ag/AgCl (saturated NaCl) as a reference electrode. An aqueous solution of 0.1 M $HClO_4$ was used as an electrolyte. FTIRRA spectra of monolayers and multilayers were recorded at 298 K in dry air on a Bio-Rad FTS-60A/896 spectrometer equipped with an MCT detector and a Harrick grazing angle reflection accessory.[22] The samples for FTIRRA measurements were prepared on an evaporated Au substrate (thickness, ~200 nm) developed on a Ti-coated (~20 nm) glass plate.

Multilayer preparation procedures: Preparation of CO-terminated monolayers on an Au(111) electrode (Figure 1 a) and subsequent conversion to water-terminated monolayers (Figure 1 b; step 1) were reported previously.[11] To form bpy-linked CO-terminated bilayers (Figure 1 c), the Au electrode covered with the water-terminated monolayer was immersed into an aqueous solution of **1** (0.2 mM, prepared just before use) in the dark at 298 K without potential control (step 2). After four days, it was removed from the solution and rinsed copiously with Milli-Q water. The bilayer formation on the Au electrode was then confirmed by recording CV (only a single cycle) in contact with 0.1 M $HClO_4$ at 0.5 V s^{-1} in the potential range between +0.80 and −0.25 V and scanning from

+0.30 V (rest potential to the negative direction). To form water-bound bilayers (Figure 1 d), the electrode potential was held at +0.80 V, while keeping the same electrochemical setup in which the oxidation state $\{Ru^{III}Ru^{III}(Ru^{III}\text{-}CO)\}$ was generated (step 1). During the electrolysis experiment, CVs were recorded at certain time intervals (10–300 s), as in the case of monolayers,[11] to monitor the CO dissociation process; complete ligand transformation (step 1) typically required 45 min of electrolysis. Alternate procedures were continued to extend the multilayer generation.

Received: March 5, 2003 [Z51334]

Keywords: cluster compounds · electron transport · multilayers · nanotechnology · surface chemistry

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[15] A larger amount of charge of the CO-bound cluster relative to the CO-free cluster (here the 1:1 stoichiometry is expected) arises from physical adsorption of **1**, which was not removed from the surface by rinsing with water. This situation is also encountered for the following CO-terminated multilayers.

[16] The kinetic aspect of the CO dissociation from the multilayers will be detailed in our future publication.

[17] The CO-terminated monolayer (prepared on an evaporated Au substrate) shows a $\nu(CO)$ band at 1948(s) cm^{-1}, $\nu_{as}(COO)$ bands at 1613(s) and 1574(m) cm^{-1}, and $\nu_s(COO)$ band at 1431(s) cm^{-1}. All these infrared spectroscopic features are similar to the triruthenium derivatives[23a] as well as their monolayers prepared on Au.[23b] Upon electrolysis, the intensity of the $\nu(CO)$ band decreases significantly.

[18] Selected IR data of **1** (KBr pellet): 1942(s) $[\nu(CO)]$, 1609(s) and 1568(m) $[\nu_{as}(COO)]$, and 1420(s) cm^{-1} $[\nu_s(COO)]$.

[19] The relative intensity ratio of the two peaks is examined rather than their absolute intensity, because desorption of Au from the Au substrate surface was apparent during the immersion process for deposition, which directly affects the intensity of the infrared band.

[20] We confirm that by using the trilayer without CO the replacement of the electrolyte solution from 0.1 M $HClO_4$ to 0.1 M H_2SO_4 results in a positive shift of $E_{1/2}$ by 0.05 V.

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