

Controlled Formation, Charge Transport, and Redox-/Photoinduced Reactivities of Layer-by-Layer Molecular Cluster Assemblies on Gold

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Introduction. Development of controlled formation of monolayers and multilayers on electrode surfaces using functional molecular components is of prime importance in the design and synthesis of molecule-based devices, switches, and sensors, that work at electrochemical interfaces and at the solid state. In particular, layer-by-layer strategy to form multilayers by depositing molecular building blocks onto pre-organized self-assembled monolayers (SAMs) has proven useful in preparing layered architectures with enhanced properties.

Here we report on our successful construction of layer-by-layer nanostructures on a gold electrode using a redox-active metal cluster molecule, in which the electrode potential modulation precisely controls to drive the multilayer growth. We show that the series of multilayers display extensive electronic coupling between the linked molecular units, thus allowing facile multi-electron transport to occur at interfaces.

Characterizations and Redox- and Photoinduced Reactivities of the SAMs. Close-packed SAMs of a CO-bound Ru₃ complex [Ru₃(O)(CH₃COO)₆(4-methylpyridine)(CO){py-CH₂NHC(O)(CH₂)₁₀S-}₂] (**1**) were prepared on an Au(111) electrode (*S* = 0.082 cm²) as described previously.^[1] The terminal CO was eliminated when the attached Ru^{II} center is electrochemically oxidized to Ru^{III}, and the monolayer containing a kinetically-labile, H₂O-binding site was formed.

Photoirradiation at the SAMs in 0.1 M HClO₄ aq. solution also triggered the loss of CO to form the H₂O-terminated SAMs, which was kinetically monitored.^[2]

Further, *in situ* scanning tunneling microscopy (STM) was successfully used to image the SAMs at a single molecule resolution as well as to directly probe the redox states of the molecules and the ligand-displacement processes on surface.

Multilayer Formation. Cyclic voltammetry (CV) was used to follow the multilayer formation processes. Since the redox potentials are substantially different between the “CO-bound” and “CO-free” cluster molecules, the surface species are quantitatively evaluated by observing charge under the CV. Here we used a trinuclear ruthenium complex [Ru₃(O)(CH₃COO)₆(4,4'-bipyridine)₂(CO)] (**2**) as a molecular building block. The Ru₃ core in **2** formally contains two Ru^{III} sites and one Ru^{II} site in which the CO ligand occupies the latter position. This class of molecular clusters has been known to display well-defined redox processes in solution, and the terminal ligand displacement character is precisely controlled by the redox state of the {Ru₃O} cluster core.

Immersion of SAM-covered Au electrode into a solution of **2** resulted in the coordination of **2** to the H₂O-

terminated binding site in **1** within the SAMs through the formation of a Ru^{III}-N(bpy) bond to afford CO-terminated bilayers. By employing surface reactions, *i.e.*, repeat of interfacial CO dissociation and incorporation of the building block **2**, we succeeded in preparing molecular multilayers up to five layers on the Au electrode surface. The expected molecular structures in the multilayers are fairly relevant to a range of bipyridine- or pyrazine-bridged, extended structures ever characterized.^[4] A plot of charge (*Q*) under the voltammetric waves from the aqua-terminated mono- and multilayers against the number of layers (*n*). The linear correlation with the slope *Q/n* = 1.4 × 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 the multilayers. Fourier-transform infrared reflection-absorption (FT-IRRA) spectroscopy measurements further supported the quantitative generation of the present molecular multilayers.

Interfacial Charge Transport. Charge transport behavior in the series of multilayers with CO and H₂O termini was investigated by CV. For example, in the H₂O-terminated 5-layer, a single redox wave (*E*_{1/2} = +0.01 V), which is ascribed to the {Ru₃^{II,III,III}/Ru₃^{III,III,III}} redox change was observed. The charge transport should be balanced by the transport of ClO₄⁻ anions during the redox cycle. The anodic and cathodic current intensities linearly increased with the increase of scan rates, consistent with the feature of surface-confined redox centers. The separation between the anodic and cathodic peak potentials for the 5-layer (0.03 V) was quite small, indicating that the charge transport across the large distance molecular wires is substantially facile, due possibly to a significant degree of electronic conjugation between the cluster units through bpy. The rather broad redox wave (full-width at half-maximum, 0.21 V) suggests the presence of a significant degree of lateral interactions and/or electronic communications between linked Ru₃ cluster cores that occur through the linking bpy ligands.

Ligand Displacement Processes. The CO dissociation reactions in the monolayer and multilayers are all well described by the first-order kinetics with rate constants similar to each other (1.2 × 10⁻² s⁻¹ for the monolayer, while 2.0–7.2 × 10⁻² s⁻¹ for the multilayers at 298 K). The negligible dependence of the CO-dissociation character in the multilayer will facilitate to efficiently construct more extended nanostructures on surfaces.

References

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