Spontaneous Rapid Growth of Triruthenium Cluster Multilayers on Gold Surface. Cyclic Voltammetric In Situ Monitoring and AFM Characterization

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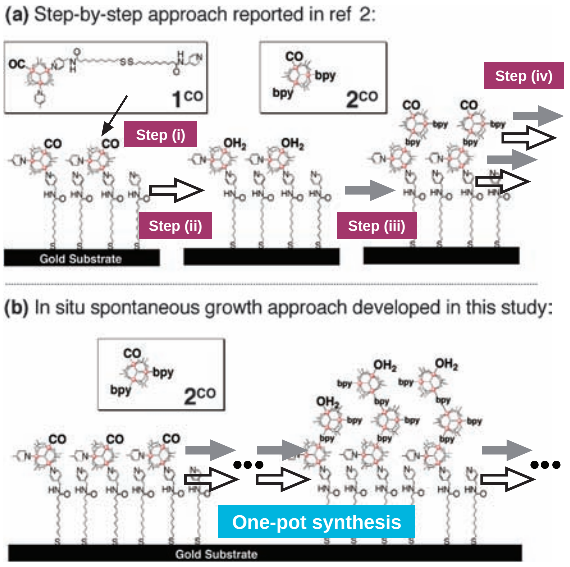
An in situ approach for rapid growth of multilayers of redox-active triruthenium cluster complexes has been developed under electrochemical potential control of the gold electrode, the formation process being successfully probed by cyclic voltammetry and AFM images.

Constructions of molecule-based multilayers on a solid surface is among the most promising bottom-up approach to the well-designed and defined nanoscale structures towards nanostructured functional materials.[1]

We have previously reported a quantitative construction of a series of up to pentalayers of a triruthenium $Ru_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6$ unit on gold surfaces in a layer-by-layer fashion.[2] The multilayers consist of an assembly of molecular wires that contain the triruthenium cluster moieties bridged by aromatic 4,4′-bipyridine (bpy) through the Ru–N bond. Although the preparative methodology has proven to be useful to obtain fully ordered and well-defined multilayers, it requires a series of multiple workups and appears to be rather time-consuming. This step-by-step procedure shown in Scheme 1a is summarized as follows. (i) Formation of densely packed self-assembled monolayers of the $Ru_3^{II,III,III}$ complex, $Ru_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6\text{(mpy)(CO)(L)}$ ($\mathbf{1^{CO}}$) (mpy = 4-methylpyridine; L = $C_5H_4N\text{-}(CH_2)_{10}S\text{–}$), by immersing the gold electrode in an ethanol solution of $Ru_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6\text{(mpy)(CO)(LH)}$ (5×10^{-5} mol dm^{-3}). This step gives a densely packed monolayers ($\mathbf{1^{CO}}$/Au) (1.3×10^{-10} mol cm^{-2}).[3–7] (ii) Electrochemical one-electron oxidation of $\mathbf{1^{CO}}$ to $Ru_3^{III,III,III}$ on Au by applying the electrode potential at +0.80 V vs. Ag/AgCl in 0.1 M $HClO_4$ aq solution (M = mol dm^{-3}), leading to spontaneous CO dissociation and subsequent formation of aqua complex SAMs ($\mathbf{1^{aq}}$/Au), in which ca. 45 min is required for the complete conversion. (iii) Replacement of the H_2O ligand in $\mathbf{1^{aq}}$/Au by the monodentate bpy of $Ru_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6\text{(CO)(bpy)}_2$ ($\mathbf{2^{CO}}$) (bpy = 4,4′-bipyridine) by soaking the $\mathbf{1^{aq}}$/Au electrode in a solution of $\mathbf{2^{CO}}$. This bilayer formation requires the longest time among all the steps, in which quantitative layering (i.e., complete formation of the Ru–bpy bond at the interface) takes 4 days at ambient conditions. (iv) Repetition of the steps (ii) and (iii) that allows further increase in the layer number.



Scheme 1. Fabrication of triruthenium cluster multilayers on gold surfaces.

Herein, we report an exceptionally facile in situ approach to prepare multilayers on the electrode surface as shown in Scheme 1b, so that all the steps required for the cluster-layering (steps (ii)–(iv) in Scheme 1a) proceed spontaneously in a one-pot manner. The new approach described here is quite simple and fast (within several hours), and avoids multiple workup, thereby providing a highly efficient strategy to prepare coordination-based nanoarchitectures at an electrochemical interface. As noted below, the multilayer growth proceeds preferentially on the newly added sites rather than unreacted site, so that the multilayers formed are of the non-uniform type.

The multilayers were formed by placing $\mathbf{1^{CO}}$/Au SAMs in contact with an aqueous 0.1 M $HClO_4$ solution of $\mathbf{2^{CO}}$ (0.2×10^{-3} M) by applying the electrode potential at +0.8 V. This potential allows spontaneous CO dissociation from $\mathbf{1^{CO}}$ attached to the electrode surface. Once monodentate bpy ligand in $\mathbf{2^{CO}}$ is bound to the bottom SAMs to form the bilayer, the CO is lost from the top layer as well. The activated top layer is ready to accept another diffusing molecule $\mathbf{2^{CO}}$ in the electrolyte media, thus allowing spontaneous multilayer growth to proceed (Scheme 1b).

The spontaneous growth of multilayers was demonstrated by measuring cyclic voltammograms (CVs) within the same electrochemical cell. CVs of the multilayers show only one redox wave at −0.05 V that is ascribed to the $Ru_3^{II,III,III}$/$Ru_3^{III,III,III}$ process (Figure 1a). The redox wave responsible for the carbonyl complex $\mathbf{2^{CO}}$, which is expected to locate at +0.6 V vs. Ag/AgCl,[2] is not at all observed, suggesting that complex $\mathbf{2^{CO}}$ becomes fully converted to the aqua complex once it is bound to the top of the underlying layer.

Figure 1b presents time-dependent change in charge under the redox wave, showing that the triruthenium redox moieties are layered on the electrode surface during electrolysis. Significantly, only 3 h are enough to build up more than six layers (in average).[2] Saturation behavior is found with time after approxi-

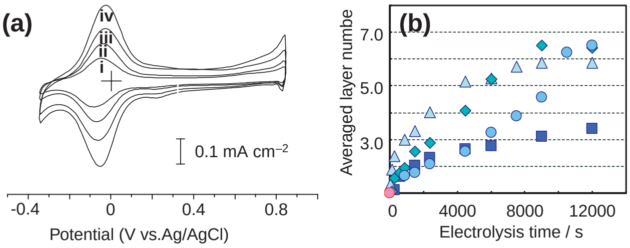


Figure 1. Monitoring of multilayer growth. (a) CVs recorded at 2400 (i), 5000 (ii), 9000 (iii), and 12000 s (iv). Electrolyte solution: 0.1 M $HClO_4$ aq in the presence of $\mathbf{2}^{\mathrm{CO}}$ (0.2 mM). Scan rate: 0.5 V s^{-1}. Working electrode: $\mathbf{1}^{\mathrm{CO}}$/Au. Counter electrode Pt wire. Reference electrode: Ag/AgCl. (b) Plot of charge against the electrolysis time. Multilayers are constructed onto the base layer of single-component $\mathbf{1}^{\mathrm{CO}}$/Au (circles), double-component $\mathbf{1}^{\mathrm{CO}}$–hexanethiol/Au (diamond), $\mathbf{1}^{\mathrm{CO}}$–decanethio1/Au (triangles), and $\mathbf{1}^{\mathrm{CO}}$–dodecahexanethiol/Au (squares).

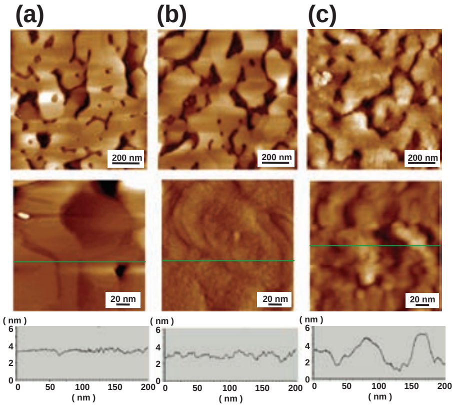


Figure 2. AFM images of (a) Au on mica (Au(mica)), (b) **1**/Au(mica), (c) multilayers constructed under multiple growth conditions on Au(mica).

mately 6 equiv (Figure 1b), which is discussed later.

The AFM images of the present multilayers (Figure 2) were observed by using gold thin film on mica. The height difference on the film with the accumulated 6.5 equivalent units was evaluated to be 50 Å, while that of the monolayers was ca. 5 Å. Since the size of the triruthenium unit is estimated to be ca. 10 Å,[8,9] it is assumed that the layer structure should be bent or laid down over the surface.

We have found that rate of the in situ multilayer growth is tuned by using two-component mixed SAMs (**1** plus varied length alkanethiol molecules) as a base layer.[10] Alkanethiols employed here are hexanethiol, decanethiol, and hexadecanethiol, which are shorter, equivalent, and longer in length, respectively, as compared to $\mathbf{1}^{\mathrm{CO}}$, if the methylene chains are assumed to be the "all-trans" conformation. As shown in Figure 1b, $\mathbf{1}^{\mathrm{CO}}$–hexanethiol/Au and $\mathbf{1}^{\mathrm{CO}}$–decanethiol/Au SAMs grow faster than the single-component $\mathbf{1}^{\mathrm{CO}}$/Au SAMs until the saturation behavior is observed at ca. 6 ML. It appears, however, that in $\mathbf{1}^{\mathrm{CO}}$–dodecahexanethiol/Au SAMs the multilayer growth is significantly retarded, reaching at even lower layers (ca. 3-ML thickness). The accelerated/retarded growth observed for the mixed SAMs strongly indicates that the surrounding alkanethiol molecule is an important factor in controlling the reactivity of buried transition-metal centers at the interface.

The morphology difference is also reflected by multilayer redox potentials since the reduction/oxidation process is associated with dynamic movement of electrolyte anions for charge neutralisation.[7] When the neutral $Ru_3^{II,III,III}$ moiety is one-electron-oxidized to $Ru_3^{III,III,III}$, the redox moiety becomes positively charged so that one equivalence of anion is incorporated in the vicinity of the cationic triruthenium moiety. It is observed that the $E_{1/2}$'s of all multilayers shift to the positive direction as compared to the $E_{1/2}$ of the monolayer, the extent of the potential shift appearing to be smaller for the one-pot growth layers (+0.045 V) than that of more compact uniform multilayers prepared by the step-by-step approach (+0.090 V).[2] This may indicate that the multilayer in the latter largely perturbs dynamics of the electrolyte anions across the compact film but the one in the former may allow more significant cation–anion mutual interactions due at least in part to large exposure of the redox moieties to the electrolyte media.

In summary, spontaneous rapid growth of triruthenium cluster-based multilayers has been observed for the first time by employing simultaneous CO dissociation and bpy-coordination reactions in situ under electrochemical potential control. In addition, larger surface area prepared on the solid surface may find a considerable use of the present architectures, for instance, for highly active heterogeneous catalysts.[11]

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