

Electrochemically Controlled Ligands Switching in a Ruthenium Cluster Monolayer Assembled on Gold Electrode Surface

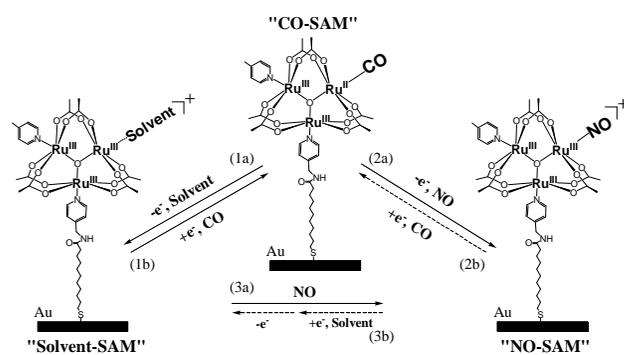
Wei Zhou,[†] Shen Ye^{†,‡}, Masaaki Abe,[§]
Masatoshi Osawa,^{†,‡,¶} Kohei Uosaki[§] and Yoichi Sasaki,[§]

[†]Graduate School of Environmental Earth Science,

[‡]Catalysis Research Center,[§]

[§]Division of Chemistry, Graduate School of Science,
Hokkaido University, Sapporo, JAPAN

[¶]CREST, Japan Science and Technology Agency (JST)



Scheme 1. Electrochemically Controlled Ligand Replacement

Introduction Transition metal complexes and clusters with versatile physical and chemical properties are eminent candidates for the molecular building blocks. Among them, oxo-centered triruthenium complexes of the type $[\text{Ru}_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6\text{L}_6]^{n+}$,¹ which show reversible multi-step electron transfer, have been of significant interest to explore the synthesis of ligand-bridged extended architectures, which is facilitated by site-selective ligand substitution in solution. Recently, we succeeded in constructing a self-assembled monolayer (SAM)² and multilayer³ on gold surface from $[\text{Ru}_3(\mu_3\text{-O})(\text{CH}_3\text{COO})_6(\text{CO})(\text{L}_1)(\text{L}_2)]$, where $\text{L}_1 = \{(\text{NC}_5\text{H}_4)\text{CH}_2\text{NHC}(\text{O})(\text{CH}_2)_{10}\text{S}\}_2$ and $\text{L}_2 = 4\text{-methyl-pyridine}$ (denoted as $[(\text{Ru}^{\text{II}}\text{-CO})\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}]^0$ below. As shown Scheme 1, by electrochemically tuning the electronic state of the Ru central ion in the SAM, we could precisely exchange the ligand with NO, CO and solvent on the Ru^{II} site originally occupied by CO.⁴ These unique electrochemically-controlled surface reactions can applied in the development of novel molecular electronic devices and sensors.

Experimental The synthesis of the complex was described in the reference.¹ The SAM was prepared on the gold surface by immersing the electrode in a 50 μM ethanol solution for ca. 20 hrs at ca. 20°C. The gold film (~50nm) was chemically deposited on a Si prism.⁵ *In-situ* infrared measurement was employed to trace the reaction process. Aqueous (0.1 M HClO₄) and non-aqueous solutions (CH₃CN or 1,2-dichloroethane with 0.1M n-Bu₄NPF₄) were used for CV and IR measurements.

Results and Discussions

1. Original SAM

CV of 1e⁻ redox reaction between $[(\text{Ru}^{\text{II}}\text{-CO})\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}]^0$ (0.3V) (underline represents the stable species and its rest potential, the same as below) and $[(\text{Ru}^{\text{III}}\text{-CO})\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}]^+$ as well as the related *in situ* IR spectra were shown as solid line in Fig. 2a and a', respectively.

2. CO Dissociation and Solvent SAM

By electrochemical oxidation at +0.8V, the CO-SAM will lead to the dissociation of the CO ligand, which may be replaced by a solvent molecule, and the forming of solvent SAM. CO peak is absent from the IR (Fig. 2a', dotted line), while CV of solvent-SAM represents the 1e⁻ redox between $[(\text{Ru}^{\text{III}}\text{-solvent})\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}]^+$ (0.3V) and $[(\text{Ru}^{\text{II}}\text{-solvent})\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}]^0$ (Fig. 2a, dotted line).

3. CO Re-introduction

State of $[(\text{Ru}^{\text{III}}\text{-solvent})\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}]^+$ (0.3V) does not react with CO molecule in solution, while the reduced state of $[(\text{Ru}^{\text{II}}\text{-solvent})\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}]^0$ at -0.3V recalls CO. Similar CV (Fig. 2b) and IR spectrum (Fig. 2b') to Fig. 2a

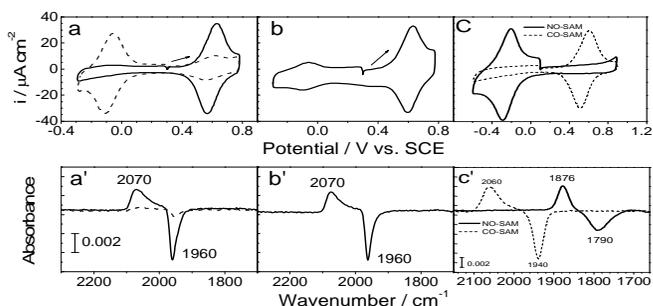


Figure 2. CVs and IR spectra at +0.8V for (a, a'): CO- (solid) and solvent-SAM (dotted) in 0.1M HClO₄; (b, b'): after solvent-SAM contact with CO at -0.3V for 30 min (c, c'): CVs and *in situ* IR spectra of CO-SAM before (dotted) and after (solid) contact with NO at +0.8V for 1hr in 1,2-dichloroethane. Scan rate: 500 mV/s.

and a' confirmed that CO replaces solvent and re-binds to Ru cluster. The electrochemical control realized the switching process of CO ligand (1a and 1b in scheme 1) on the SAM efficiently.

4. NO Introduction

When the CO-SAM is controlled as $[(\text{Ru}^{\text{III}}\text{-CO})\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}]^+$ to react with the NO molecule in a 1,2-dichloroethane solution, a new 1e⁻ redox peak between $[(\text{Ru}^{\text{III}}\text{-NO})\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}]^+$ (0.2V) and $[(\text{Ru}^{\text{II}}\text{-NO})\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}]^0$ appears at -0.25V (Fig. 2c, solid line) as well as related IR peaks of NO ligand appear at 1876 and 1790cm⁻¹ (Fig. 2c', solid line). An unchanged surface charge after the reaction indicates a high conversion efficiency, which was hard to achieve in conventional ligand exchange in solution.

5. Further Study

Stability and ligand conversion efficiency of the SAM is crucial to its application development. Detailed studies on monolayers as well as multilayers are still in process.

References

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