

学 位 論 文 題 名

Self-Assembled Monolayers of Triruthenium Clusters: Preparation, Characterization and Reactivity

（ルテニウム三核クラスターの自己組織化単分子膜の作製、
キャラクタリゼーション及び反応性）

学位論文内容の要旨

In this thesis, preparation, characterization and reactivity of self-assembled monolayers and multilayers of triruthenium clusters on gold electrode surfaces have been described. The present results demonstrate that the triruthenium cluster is an eminent building block in the construction of functional ordered monolayers and multilayers on gold surfaces. Location controlled nanostructures of the triruthenium clusters provide possibilities to develop nanodevices with novel functions.

In Chapter 1, the general background of the present study has been introduced. Top-down strategy has approached its limit in nanotechnology. Bottom-up strategy such as self-assembly is a promising alternative to the top-down strategy. Through self-assembly, various molecular building blocks can be employed to construct functional nanostructures. Triruthenium clusters are prominent candidates as building blocks due to their well-known properties including multistep electron transfer, ligand-substitution in solution, formation of supramolecular structures. Based on the initial works on the self-assembled monolayer (SAM) of the triruthenium cluster, the objectives of the present study are given.

In Chapter 2, experimental aspects have been described in detail. Synthesis procedures of the triruthenium clusters employed in this study and the construction process of the SAM have been given. The basic principles of vibrational spectroscopic methods such as infrared reflection absorption spectroscopy (IRRAS), surface-enhanced infrared absorption spectroscopy (SEIRAS) and sum-frequency generation (SFG) as well as their applications in electrochemical systems have been stated. Combination of electrochemistry with in situ vibrational spectroscopy is an effective probing technique for the study of SAMs.

In Chapter 3, the structure and the oxidation state of the SAM of the triruthenium clusters have been characterized by using the techniques introduced in Chapter 2. Based on the assignment of IR absorption peaks in the IRRAS spectra of the SAMs, it is concluded that the orientation of the SAMs is perpendicular to the gold surface. The multistep electron transfer behavior has been successfully realized in the SAMs. From the charge estimated in the cyclic voltammogram of the

SAMs, the coverage of the SAM on gold surface is estimated to be 1.0×10^{-10} mol/cm², which is relatively lower than the one of the alkanethiolate with similar length on gold surfaces and is ascribed to the large size of the terminal group. In situ IR and SFG measurements provide detailed structural information about the CO ligand and the acetate bridges in different oxidation states. The largest IR peak shift of the CO absorption is observed in the one-electron oxidation of the Ru moiety in the SAM. This phenomenon confirms the electron localization [Ru₃^{II,III,III}] in the triruthenium cluster on molecular level. For the first time, the electron localization [Ru₃^{II,III,III}] is changed to electron delocalization state such as [Ru₃^{III,III,III}] and [Ru₃^{IV,III,III}] in the other oxidation states as observed by in situ IR measurement. Absorption bands of the acetate ligands observed from SFG measurement, which gives absolute vibrational spectra of the acetate ligands in different oxidation states, also support the conclusion. A tentative model is suggested to explain the IR absorption bands of the acetate bridges, which are correlated with the electron localization in the cluster.

In Chapter 4, electrochemically controlled reversible CO ligand exchange in the SAM of the triruthenium cluster has been realized for the first time. The oxidation state of the triruthenium clusters in the SAM is crucial to the stability of the CO ligand. One electron oxidation of the SAM triggers a CO release process, resulting in a CO free SAM; while one electron reduction of the CO free SAM triggers a CO re-introduction process into the SAM at the original site of the CO. Kinetics of both, the CO release and coordination, have been evaluated by the electrochemical and in situ IR measurements. The reaction rates are significantly affected by the solvent and temperature. The reaction rate decreases greatly with the decreasing temperature, which is an important factor in the control of the ligand exchange process in the SAM. From the reaction rate constants at various temperatures, the reaction activation energies of both processes have been evaluated. Step-scan IR technique has been used to probe the possible intermediates with short life-time at low temperature during the electron transfer process of the Ru cluster moiety in the SAM.

In Chapter 5, immobilization of NO molecule in the monolayer of the triruthenium clusters has been realized under electrochemical control. Different from the CO ligand, NO favors [Ru₃^{III,III,III}] rather than [Ru₃^{II,III,III}]. Only was the CO bound SAM oxidized to [Ru₃^{III,III,III}], can NO binds to the SAM. NO ligand can also bind to a CO free SAM in the state [Ru₃^{III,III,III}]. The different binding ability of NO compared to CO is closely related to the one more electron in NO than CO. Upon one electron reduction of the NO bound SAM, the NO ligand can be replaced by CO or solvent, resulting in ligand exchanges from NO to CO or solvent molecule. The NO bound SAM is sensitive to the visible light irradiation, which leads to the NO ligand release from the SAM. By employing all the electrochemically controlled ligands exchanges realized in the study, it is possible to prepare monolayers comprising mixed ligands. The electrochemically controlled reversible CO, NO and solvent ligand exchange in the SAM has been realized in the present work for the first time.

In Chapter 6, layer-by-layer multilayer of the triruthenium cluster has also been constructed through metal-ligand coordination on the template of the self-assembled monolayer of the triruthenium clusters. The construction process has been characterized by in situ IR spectroscopy.

In Chapter 7, general conclusions of the thesis have been drawn.

From the present study, the importance of the combination of nanomaterial design, nanostructure construction, characterization and the final devices fabrication for the successful applications of molecular building blocks in nanotechnology has been demonstrated.

学位論文審査の要旨

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金属多核錯体は、可逆的多段階多電子移動を示す特徴があり、生体内等での電子移動の機構と速度論を調べるモデル化合物として研究されている。このような機能性分子を電極表面に固定できれば、電子移動に伴う反応過程を分子レベルでより詳細に解明できるとともに、多電子移動の機能性を持つ新しい不均一電極触媒や機能性材料のとしての利用が期待できる。申請者は、自己組織化法により、豊富な酸化還元状態をもつルテニウム金属三核クラスターの自己組織化単分子膜(SAM)と多層膜を金電極表面に固定させ、電気化学測定法の他に、その場赤外分光法および和周波発生(SFG)分光法を用い、機能性薄膜における分子配向・構造と機能性制御を詳細に調べた。

申請者は、オキソカルボキシラト架橋型ルテニウム錯体のチオール誘導体を、金電極表面に SAM として構築し、ルテニウム中心金属の三段階四電子にも及ぶ電子移動反応を電極表面で初めて実現した。ルテニウム中心金属の多電子移動反応に伴い、錯体 SAM の分子構造と電子状態の変化についてその場赤外分光法により明らかにした。ルテニウム中心金属の電子状態の違いにより、配位子の安定性と反応正が大きく異なることを明らかにした。これに基づき、申請者は、電気化学的制御により、錯体 SAM のカルボニル(CO)配位子、一酸化窒素(NO)配位子または溶媒分子を SAM への導入または脱離を可逆的に行うことに成功した。このような表面反応は溶液中における錯体の反応と比べると、高い反応収率かつ短時間で実現できるメリットがある。また、電気化学的制御により、単分子膜とルテニウムクラスター間の共有結合を通じてルテニウムクラスターの多層膜の連続成長に成功した。これらの配位子交換反応を利用することにより、将来、高感度の CO や NO センサーの開発が期待できる。さらに、申請者は分子レベルで反応制御の実現を目指し、これらの配位子交換の反応過程について赤外分光法と SFG 分光法によってその場追跡し、反応に伴う SAM の分子

構造や配向の変化、電子状態の局在化の変化および反応速度について定量的に調べる事が出来た。

こうした申請者の一連の研究は、機能性有機薄膜の分子構造の解析と機能性制御に大きく貢献した。こうした成果は今後、この研究は基礎研究に無論のこと、機能性材料開発やセンサーへの応用も期待できる。審査員一同は、これらの成果を高く評価し、また研究者として誠実かつ熱心であり、独特な発想により研究を推進することや大学院単位取得などを併せ、申請者が博士(地球環境科学)の学位を受けるに十分な資格を有するものと判定した。