様　式　C－１９、F－１９－１、Z－１９　（共通）

科学研究費助成事業　　研究成果報告書

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研究課題名（和文）Electrodeposition and Characterization of Atomic-Level Metal Clusters

研究課題名（英文）Electrodeposition and Characterization of Atomic-Level Metal Clusters

研究代表者
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研究成果の概要（和文）：今回のプロジェクトの目的は、ユニークな周期的原子めっき法を用いて、導電性ポリマーに原子レベルの金属クラスターを装飾することにより、バイオセンサー用の革新的な触媒材料を開発する。成果には、査読付き論文7本、国際会議12件、国内会議4件での発表が含まれる。7本の発表論文のうち、6本はオープンアクセスの出版物である。さらに、国際会議で1回招待講演を行いました。研究の初期段階に周期的原子めっき法の最適化から始まり、ポリアニリン上の純金属粋クラスター（Au、Pd、Ptなど）の装飾と研究に続きた。昨年度には、研究はPd-Au合金クラスターの装飾に進み、その結果は既に査読付き科学論文として公表されている。

研究成果の学術的意義や社会的意義
Catalytic materials are expected to be a key solution for achieving the Sustainable Development Goals (SDGs). It is anticipated that performance will be enhanced through size reduction. Therefore, the atomic-level catalysts developed in this project will make a significant contribution to the SDGs.

研究成果の概要（英文）：The objective of this 3-year project is to develop novel catalytic materials for biosensors through the decoration of atomic-level metal clusters onto conjugated polymers using a unique cyclic atomic electrodeposition technique. The accomplishments include 7 peer-reviewed papers, presentations at 12 international conferences, and 4 domestic conferences. Of the 7 published papers, 6 are open access publications. Additionally, one of the conference presentations was delivered as an invited talk at an international conference.

The research commenced with the optimization of the original cyclic atomic electrodeposition technique, followed by the preparation and study of atomic pure metal clusters (such as Au, Pd, and Pt) on polyaniline. In the last fiscal year, the research progressed to the deposition of atomic Pd-Au alloy clusters, with the results already published in a peer-reviewed scientific paper.

研究分野：Electrodeposition and Catalytic Materials

キーワード：Electrodeposition　Atomic metal　Conductive polymer　Catalyst　Biosensor

１．研究開始当初の背景

The properties of metal clusters are influenced by their size, or the number of atoms they contain. For instance, the catalytic activity in the oxidation of alcohols is significantly enhanced when the size of the metal cluster is reduced to the nanoscale. Consequently, the reduction of metal cluster size is an important focus in the development of novel catalysts. Additionally, simulation results have indicated that the HOMO-LUMO bandgap of a metal cluster is dependent on the number of atoms, particularly when the atom count is reduced to approximately 10. At this scale, the metal cluster switches between being a semiconductor and a conductor based on whether the number of atoms is even or odd. One possible explanation for this unique phenomenon, obtained from simulations, is the structure of the metal cluster. When the cluster size is reduced to less than 10, there are multiple possible arrangements of the atoms, and these different structures result in varying properties. However, there is still no widely accepted explanation for this even-odd effect. Importantly, due to the challenges associated with preparing and precisely controlling metal clusters composed of less than 10 atoms, there is limited experimental data available on the properties of atomic-level metal clusters.

２．研究の目的

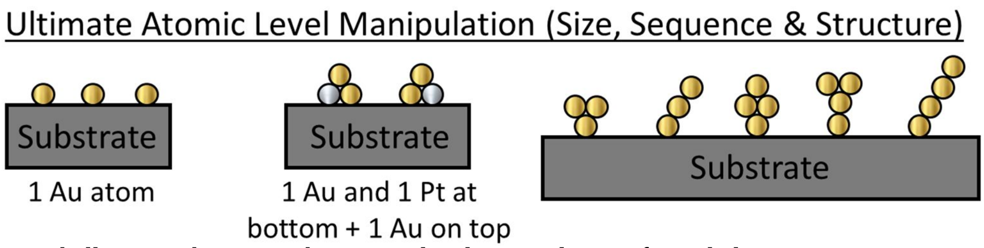

Figure 1 Challenge in this research: Atomic-level manipulation of metal clusters.

The aim of this research is to manipulate metal clusters at the atomic level, including controlling the number, composition, structure, and sequence of atoms within a cluster as illustrated in Fig. 1. To achieve this, a novel cyclic atomic electrodeposition process has been developed, enabling the deposition of metal atoms one-by-one at specific locations to prepare atomic-level metal clusters. Furthermore, the research aims to evaluate and elucidate the extraordinary properties of atomic-level metal clusters, particularly focusing on the even-odd effect.

３．研究の方法

The controlled deposition of metal atoms one-by-one is achieved by precisely managing the location and timing of metal atom formation. In terms of deposition location, the imine groups in polyaniline (PANI) exhibit an affinity for attracting complex metal ions, such as tetrachloroaurate anions ($AuCl_4^-$). Following proper rinsing, a single complex metal ion remains at each imine group in PANI due to the weak attracting force. The timing for initiating reduction of the metal ion in the complex metal ion can be regulated by the potential applied to the PANI. Specifically, tetrachloroaurate anions adsorbed on PANI are reduced to form gold atoms when a potential more negative than +0.8 V vs Ag/AgCl is applied. Through the use of the cyclic atomic electrodeposition process [A1], metal atoms can be electrodeposited one-by-one onto PANI. Previous studies have demonstrated the successful detection of lower aliphatic esters [A2] and propanol gas [A3] using atomic-level pure gold clusters decorated PANI as the working electrode.

４．研究成果

PANI is an excellent support material for noble metal clusters due to its strong electrical conductivity, high stability, large active surface area, and straightforward preparation process. It has been observed that PANI adorned with atomic-level noble metal clusters exhibits notable catalytic activity in the electrochemical oxidation of alcohols. Furthermore, the creation of heterogeneous atomic noble metal clusters is garnering attention as a means to achieve even greater catalytic activity compared to

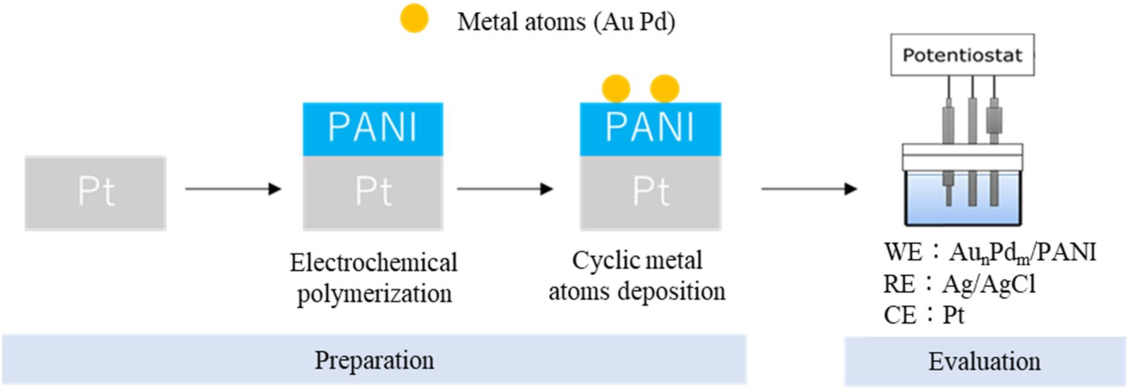

Figure 2 Outline of the atomic metal cluster decoration process.

homogeneous atomic metal clusters. This study investigates the impact of the number of metal atoms and the sequence of the atomic-level deposition step in noble metal clusters on their catalytic activity in the electrochemical sensing of 1-propanol (1-PrOH).

Fig. 2 illustrates the experimental setup, where PANI was electrochemically polymerized onto a Pt disk electrode (ϕ = 3 mm) in a 2 M HBF_4 aqueous solution with 0.1 M aniline. Subsequently, the PANI-coated electrode was modified with mono-atomic, bi-atomic, tri-atomic, or tetra-atomic noble metal clusters denoted as Pd_xAu_y (where x and y represent the number of Pd and Au atoms, respectively). The catalytic activity for electrochemical sensing of 1-PrOH was assessed using cyclic voltammetry (CV) measurements in an aqueous solution containing 0.5 M 1-PrOH and 1 M KOH.

The CVs depicted in Fig. 3 indicate that the catalytic activity of atomic metal clusters consisting solely of Pd was greater for the Pd_2 and Pd_4 adorned PANI electrodes compared to the Pd_1 and Pd_3 adorned PANI electrodes, demonstrating the odd-even pattern effect as previously reported [A1]. Atomic level metal particles are reported to show a size effect in the electronic properties, which is the Kubo effect. In a study by simulations, the HOMO-LUMO bandgap is reported to fluctuate as the size changes, and even-numbered atomic pure Au clusters are semiconductor while odd-number atomic pure Au clusters are conductor. In this study, the odd-even size effect observed in the catalytic activity is believed to be related to the Kubo effect. When considering the

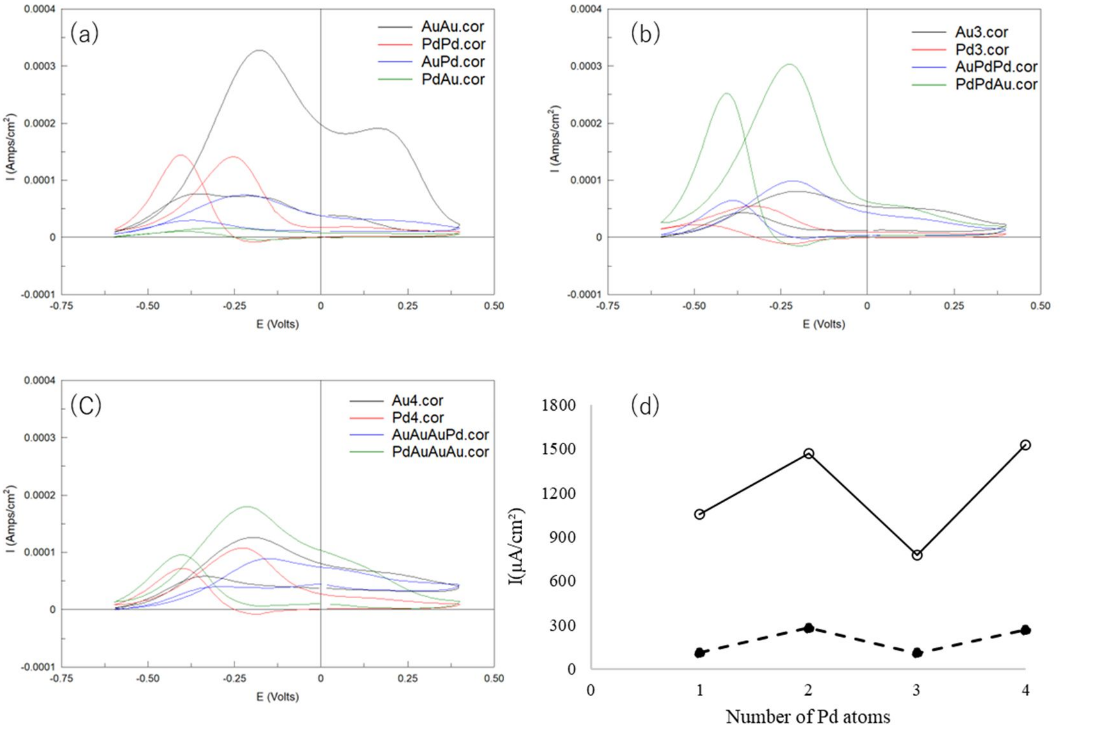

Figure 3 CVs for (a) bi-atomic, (c) tri-atomic, and (d) tetra-atomic metal clusters. (d) A summary of peak current densities for atomic pure Pd clusters, and the solid line shows the 1st oxidation peak and the dashed line shows the 2nd oxidation peak.

catalytic activity of PANI decorated with different size, decoration sequence and composition of the atomic metal cluster, the odd-even size effect was only observed in atomic pure metal clusters

For the bi-atomic, tri-atomic and tetra-atomic metal clusters, three similar general trends were observed. At first, the catalytic activity in the oxidation of 1-propanol was affected by the decoration sequence. The catalytic activity was high when the same metal was decorated in the first two cycles of the atomic electrodeposition process. For tri-atomic and tetra-atomic metal clusters, the third cycle had to be the decoration of a different metal to retain a high catalytic activity. Secondly, the catalytic activity for the oxidation in the region of the second peak was high when the Au content is higher than the Pd content in the atomic metal clusters. Lastly, the current density ratio was also related to the composition, which a high current density ratio was obtained when the Pd content is higher than the Au content.

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２．論文標題 Decoration of atomic PdxAuy (1<=x+y<=4) clusters on polyaniline in electrochemical sensing of 1-propanol	５．発行年 2024年
３．雑誌名 Surface and Coatings Technology	６．最初と最後の頁 130762～130762
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.surfcoat.2024.130762	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

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〔図書〕　計0件

〔産業財産権〕

〔その他〕

－

６．研究組織

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７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関