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Synthesis of Novel Dithiolate Co-Protected Alloy Nanocluster and Evaluation of Their Catalytic Activity for Hydrogen Evolution Reaction

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Abstract

Thiolate (SR)-protected gold nanoclusters (Au NCs) have attracted attention as functional nanomaterials because they exhibit size-specific physical and chemical properties that differ from those of bulk metals. In this study, we succeeded in creating novel $Au_{24}Pt$ alloy NC with high stability by replacing the central atom of Au_{25}NC with a platinum (Pt) atom and partially protecting the surface with a dithiolate (SR'S). Furthermore, the new NC with increased metal atom surface exposure showed about five times higher mass activity than conventional $Au_{24}Pt$ NC catalysts, which are known as highly active hydrogen evolution reaction (HER) catalysts. This increase in catalytic activity can be attributed mainly to the changes in the staple structure of the NC surface, which 1) reduced the hydrophobicity of the core surface, exposing the core for easier access to substrates, and 2) facilitated proton adsorption due to the change in the electronic structure of the NC.

1. Introduction

SR-protected Au NCs exhibit size-specific physical and chemical properties not found in the corresponding bulk metals. In particular, alloy NC, in which 24 atoms of Au are doped with one atom of Pt, supported on a carbon black (CB), are known to catalyze highly active HER better than common Pt nanoparticle catalysts and have been actively studied[1]. Here, the ligands protecting $Au_{24}Pt(SR)_{18}$ are 'non-conductive and hydrophobic' and induce a decrease in electrocatalytic activity in aqueous electrolyte. Therefore, we investigated the reduction of the total number of long-chain alkyl ligands by replacing some SR ligands with SR'S ligands. We hypothesized that this could improve the activity without the need to remove the ligand by calcination or other means. In our experiments, we used $Au_{24}Pt(SR)_{18}$ as a precursor and carried out ligand exchange reactions to replace SR ligands with SR'S to synthesize NCs co-protected by SR and SR'S and to evaluate their HER catalytic activity.

2. Experiment (or Theory)

2-phenylethanethiolate (PET) protected $[Au_{24}Pt(PET)_{18}]^0$ was dissolved in toluene as precursor NC, and a 20:1 substance ratio of 4-*tert*-butylbenzenethiol (TBBTH) and 1,3-propanedithiol ($PDTH_2$) were added and reacted at 60 °C to obtain product **1**. The chemical composition and geometric structure of the obtained **1** were determined by electrospray ionization mass spectrometry (ESI-MS), single crystal X-ray diffraction (SC-XRD), and UV-visible absorption spectroscopy (UV-Vis), differential pulse voltammetry (DPV) and high performance liquid chromatography (HPLC) for electronic structure and stability were evaluated. In addition, catalysts with **1** supported on CB (1 wt% of metal) were prepared and their HER activity was evaluated by linear sweep voltammetry (LSV).

3. Results and discussion

The composition of product **1** obtained from ESI-MS is $[Au_{24}Pt(TBBT)_{12}(PDT)_3]^0$, which was attributed to a new NC. **Fig. 1** shows the geometric structure of **1** determined by SC-XRD. **1** has an icosahedral $Au_{12}Pt$ core similar to previously reported **2** ($[Au_{24}Pt(TBBT)_{18}]^0$)[2], but the staple structure covering the core was significantly different: whereas **2** has six $[Au_2(TBBT)_3]$ staples coordinated to the $Au_{12}Pt$ core, **1** has three coordinated $[Au_2(TBBT)_2$-PDT-$Au_2(TBBT)_2]$ staples with two $[Au_2(TBBT)_2]$ cross-linked by PDT. Furthermore, the UV-Vis spectra and DPV results show that **1** and **2** have very different electronic structures, suggesting that these particular differences in staple structure induced the electronic structure change in the visible light region of NC. In addition, in a toluene solution at 80 ºC, the peak in HPLC and UV-Vis spectra of **2** disappeared within 2 hours, whereas the peak of **1** was observed for more than 10 days, indicating that it has high stability. Subsequently, LSV of the obtained catalysts **1** and **2** supported on CB revealed that **1** exhibited 5 times higher HER mass activity than **2** (**Fig. 2**). This increase in catalytic activity can be attributed mainly to the changes in the staple structure of the NC surface, which 1) reduced the hydrophobicity of the core surface, exposing the core and thus facilitating the access of substrates (protons) and 2) facilitated proton adsorption due to changes in the electronic structure of the NC[3].

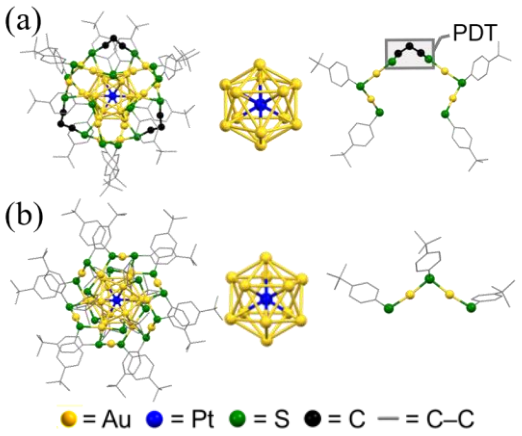

Fig.1 Geometric structures of (a) **1** and (b) **2** determined by SC-XRD (left: full, middle: core, right: staple structure).

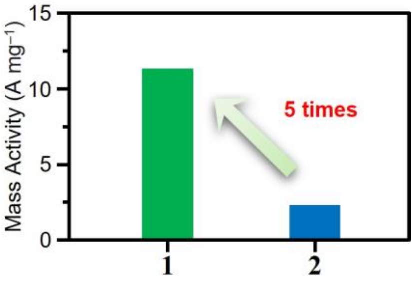

Fig.2 Comparison of mass activity of HER for **1** and **2** (at –0.35 V *vs.* RHE).

4. Conclusions (or Summary)

Novel AuPt alloy NC protected by dithiolate were successfully created. The new NC showed higher stability and approximately 5 times higher HER activity than the previously reported NC. This improvement in activity is thought to be mainly due to the change in the staple structure of the NC surface, which reduced hydrophobicity and facilitated proton access, and the change in the electronic structure of the NCs, which facilitated proton adsorption.

References

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