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## Electrocatalytic Activity for Oxygen Reduction of Multilayer of Pd Coated Gold Nanoclusters

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### Abstract

Multilayers of SAM (Self-Assembled Monolayer)-protected gold nanoclusters (GNCs) were constructed by utilizing electrostatic interaction between cationic polymer (poly allylamine hydrochloride: PAH) and GNCs protected by SAM with anionic carboxyl groups (Mercaptoundecanoic acid: MUA). Electrocatalytically active metal multilayers were formed by depositing small amount of foreign metals on GNCs after removing the SAM. We estimated electrocatalytic properties of GNC multilayers by oxygen reductions.

Key words: GNCs (Au nanoclusters), SAM (Self-Assembled Monolayer), electrocatalysis, oxygen reduction, electrodeposition

### Introduction

Electrocatalysis is of central importance in electrochemistry and plays a vital role in emerging technologies related to environmental and energy-related applications, such as fuel cells and batteries. In particular, the electroreduction of oxygen is one of the most intensively investigated processes in electrochemistry.

This reaction has been drawing considerable attention because of its complex kinetics and the need of better electrocatalysts for fuel cells [1, 2]. Thus, the mechanism of the electrochemical reduction of oxygen has been studied in a variety of well-defined surfaces including Au [3], Ru [4], and Pt [5,6] crystals and Au nanoparticles [7, 8, 9, 10]. The major problem of the oxygen electrocatalysts, however, is slow kinetics of oxygen reduction even at Pt, the best available electrocatalyst.

An important task in electrocatalysis is to discover new materials and electrode designs to decrease the cathode overvoltage of the process as much as possible. A promising approach to solve this problem is to design a bimetallic electrocatalysts [11, 12, 13].

Surface-modified Pd electrodes have been suggested for many electrocatalytic and electroanalytical applications in view of their superior activity. Recently the electrocatalytic oxygen reduction has been investigated at thin Pd layers on Au (111) [14] and Pt (111) [15, 16] electrodes. It has been found that electrocatalytic activity of thin Pd/Au [14] and Pd/Pt [15] overlayer systems shows a strong dependence on the layer thickness of the deposited Pd films, where lower amounts of Pd resulted in higher reduction rates. The challenge of these studies is to develop appropriate

Pd based electrodes, which exhibit very good activity for oxygen reduction (at least as high as Pt); and excellent stability in acid medium. Oxygen reduction on Pd electrode proceeds via 4-electron pathway, as is the case on Pt electrode [2].

We have already reported the construction of SAM-protected GNCs by electrostatic interaction and the electron transfer between GNCs is facile in multilayer of SAM-protected GNCs, showing this system acts as a three dimensional electrode [17, 18].

In this study, small amount of electrocatalytically active Pd was electrodeposited on a SAM-protected GNC multilayer electrode before and after removing SAM by anodic oxidation. We investigated the electrocatalytic properties of Pd/GNC multilayer electrode for oxygen reduction reaction.

### Experimental

Materials : Hydrogen tetrachloroaurate ( $\text{HAuCl}_4$ , 99.99 %), sodium tetrahydroborate ( $\text{NaBH}_4$ ), ethanol (superpure grade), toluene (spectroscopy grade), hexanethiol ( $\text{C}_6\text{SH}$ , superpure grade), sulfuric acid (ultrapure grade), perchloric acid (ultrapure grade), and hydrogen peroxide (superpure grade) were purchased from Wako Pure Chemicals, tetra-n-octyl ammonium bromide (TOAB) was obtained from Tokyo Kasei Kogyo and 11-mercaptoundecanoic acid (MUA, 97%) was obtained from Aldrich. Ferrocenyl alkanethiol ( $\text{FcC}_3\text{SH}$ ) was synthesized by previously reported method. [19] Ultrapure water was obtained using a Milli-Q water purification system (Millipore) and ultrapure  $\text{N}_2$  (99.999%) was obtained from Air Water. Preparation of SAM-protected GNCs : Two types of

GNC protected by mixed alkanethiol SAMs, one covered by mixed SAMs of  $C_6SH$ ,  $FcC_6SH$ , MUA, (MHF-GNC) and other covered by  $C_6SH$  and MUA (MH-GNC) was prepared by the procedures reported previously. [17, 18] The molar ratio of  $C_6SH : FcC_6SH : MUA$  on the MHF-GNC and of  $C_6SH$  and MUA on the MH-GNC surface were determined by  $^1H$ -NMR as 12:10:78 and 43:57, respectively. The core size of the MH-GNC and MHF-GNC were determined using transmission electron microscopy (TEM) (JEOL, JEM-200FX) to be ca. 1.8 nm [17, 18].

Preparation of multilayer of SAM-protected GNCs: A Au single crystal was prepared from a Au wire (99.999 %,  $\phi = 1$  mm, Tanaka Precious Metals) by Clavilier's method. [20] It was cut to expose the (111) face, mechanically polished, and then, annealed at  $800^\circ C$  for 8 h in an electric furnace (Denken, KDF-S-70) under an ultrapure  $N_2$  atmosphere. The ITO substrate was cleaned by immersing it in a 3:1  $H_2SO_4$  (conc.)-  $H_2O_2$  (30 %) solution for 5 s, then thoroughly rinsing it with Milli-Q water and finally drying it with ultrapure nitrogen. Multilayers of SAM-protected GNCs were prepared on a Au surface or ITO surface. The substrate was dipped first in 0.1 M NaOH aqueous solution containing 2 mg  $ml^{-1}$  PAH and for 5 min and then in an ethanol solution containing 0.15 wt% GNC for 15 min with a rinse after each dip.

Electrochemical measurements: A three-electrode cell with hanging configuration was employed for the electrochemical measurements. A Pt wire (diameter 0.5 mm) and a Ag/AgCl were used as counter and reference electrode, respectively. The electrode potential was controlled by a potentiostat (Hokuto Denko, HA-151) and external potential modulation was provided by a function generator (Hokuto Denko, HB-111). Removal of SAM from GNC was achieved by electrochemical oxidative desorption of SAM by repeating the potential cycling between 0 and 1.3 V in 0.1 M  $HClO_4$ . Anodic current peak for oxidative decomposition of the SAM was observed at 1.5 V at the 1st cycle and shifted negatively as the number of potential cycle increased. Pd electrodeposition was conducted in a solution of 0.1 M  $H_2SO_4$  containing 0.1 mM  $PdCl_4^{2-}$  and electrode was stepped from 0.85 to 0.2 V. The charge for one complete monolayer of Pd on Au(111) is ca.  $450 \mu A cm^{-2}$  [21, 22]. The oxygen reduction curves were obtained in 0.05 M or 0.1 M  $H_2SO_4$ .

## Results and Discussion

Figure 1 shows the typical polarization curves at a Pd modified MH-GNC on Au (111) electrode in an oxygen saturated 50 mM  $H_2SO_4$  solution at different scan rates. Included for comparison are CVs for the same Pd/MH-GNC electrode in  $N_2$  saturated electrolyte and of a MH-GNC in oxygen saturated solution. The polarization curve on bare MH-GNC electrode showed negligible electroreduction current and only a small cathodic current started to flow from ca. 0 V, which is presumably associated with the hydrogen evolution reaction. The polarization curves of the electrode on which 1 ML of Pd was deposited showed that when the potential swept from 0.8 V to the negative direction, the

cathodic current started to flow gradually from ca. 0.48 V and continued to increase as the electrode potential became more negative. The peak currents observed at 0.25 and -0.05 V varied linearly with the square root of the scan rate, indicating a diffusion-controlled electrochemical process.

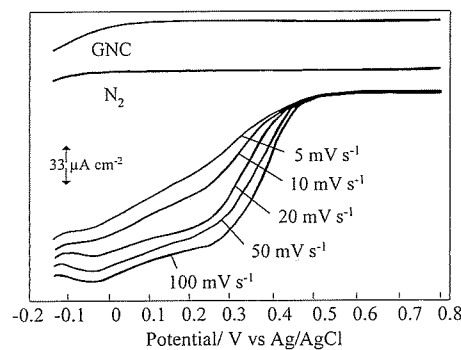


Figure 1. Polarization curves for oxygen reduction at MH-GNC and 1 ML Pd-GNC electrodes in  $N_2$  saturated 0.05 M  $H_2SO_4$  solution and 1 ML Pd-GNC electrode in  $O_2$  saturated 0.05 M  $H_2SO_4$  solution with different scan rates.

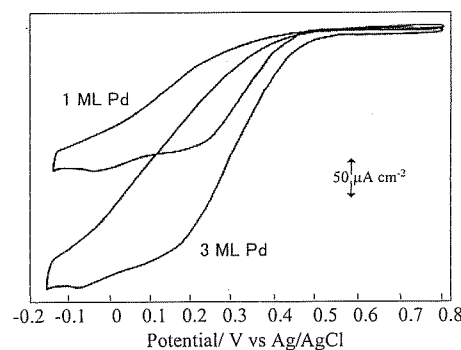


Figure 2. Cyclic voltammograms for oxygen reduction in 1 and 3 ML Pd-GNC electrodes in an  $O_2$  saturated 0.05 M  $H_2SO_4$  solution, at scan rate of  $20 mV s^{-1}$ .

The electrocatalytic activities of 1 and 3 ML of Pd on MH-GNC electrodes for the oxygen reduction reaction in oxygen-saturated 0.05 M  $H_2SO_4$  solution were determined by cyclic voltammetry at a scan of  $20 mV s^{-1}$  as shown in Figure 2. The lower cathodic overvoltage and the higher current density in the case of the electrode with the higher Pd coverage clearly indicate superior electrocatalytic activity towards the oxygen reduction. However, most of the catalytic materials recently investigated for oxygen reduction have lower onset potentials and a higher exchange current density than these results.

The oxygen overvoltages and exchange current densities of the Pd/MH-GNC electrodes were better than the values on Au particles [8], similar to those observed at Pd mesoparticles [23], but lower than the electrocatalytic activity at Pd thin films [14, 15], Pd alloys [24] and Pd nanoparticles [25]. As well known oxygen is

reduced either directly to water through a four-electron transfer or it is first reduced to hydrogen peroxide through a two-electron transfer followed by further reduction to water. The decrease in the electrocatalytic effect, i.e., the shift in the reduction potential and the lower current densities indicate that a slow dissociation of monolayer oxygen took place. In electrocatalysis, the high performance of electrodes is the result of combination of surface reactivity, electronic and ionic conductivity and demonstrate that the oxygen penetration was inhibited by the presence of the thiol SAM, resulting in lower catalytic activity.

Figure 3 shows the polarization curves of 5 layers MHF-GNCs on ITO substrate in an oxygen saturated 0.1 M  $\text{H}_2\text{SO}_4$  solution with a scan rate of  $10 \text{ mVs}^{-1}$ . Numbers in figure indicate the number of potential cycles between 0 and 1.3 V for oxidative desorption of SAM from GNC. 0 cycle means GNC electrode protected by the SAM. Thus, electrocatalytic activity for oxygen reduction was very low at the SAM modified GNC as discussed above. By repeating the potential cycling of oxidative desorption of the SAM, onset potential of cathodic current shifted to more positive potential and cathodic current density increased. The SAMs were gradually desorbed by repeating potential cycling and almost completely desorbed from GNC at ca. 10 ~ 15 cycles [26].

After 30 cycles, onset potential of cathodic current was shifted to ca. 0.25 V, showing electrocatalytic activity of multilayer of GNCs for oxygen reduction was significantly increased by desorption of SAM from the GNC electrode.

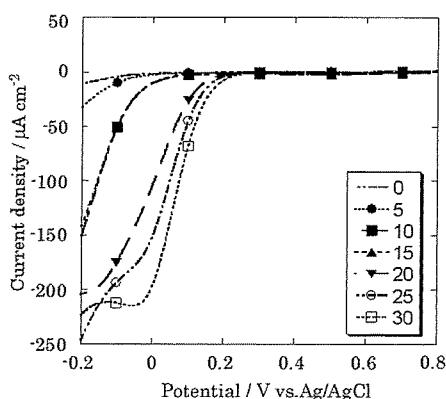


Figure 3. Polarization curves for oxygen reduction in 5 layer of MHF-GNC electrode changing the number of cycles of oxidative desorption of SAM in  $\text{O}_2$  saturated 0.1 M  $\text{H}_2\text{SO}_4$  at scan rate of  $10 \text{ mV s}^{-1}$ .

Figure 4 shows the polarization curves of 5 layers MHF-GNCs on ITO substrate after the SAM desorption and Pd deposition in oxygen saturated 0.1 M  $\text{H}_2\text{SO}_4$  solution with a scan rate of  $10 \text{ mVs}^{-1}$ . Numbers in figure again indicate the number of potential cycles between 0 and 1.3 V for oxidative desorption of SAM from GNC. After each cycle of oxidative desorption of SAM, ca. 1 ML Pd was deposited on GNC surfaces. 0 cycle means GNC electrode protected by the SAM. In the case of 0

cycle GNC Pd deposited electrode, cathodic current started to flow from ca. 0.48 V and continued to increase as the electrode potential became more negative. When Pd was deposited on a GNC electrode after the SAMs were oxidatively removed, onset potential of cathodic currents shifted to more positive potentials and cathodic current densities increased.

However, the relations between the number of oxidative desorption cycles of SAM and electrocatalytic activities of oxygen reduction is not clear at this stage.

This is because Pd deposition is not well controlled, i.e., Pd deposition occur not only on ITO substrate as well as on PAH but also on GNC surfaces.

Further experiments to clarify the effect of the number of GNC layers and/or amount of Pd deposition on GNC surfaces on oxygen reduction reaction are now in progress.

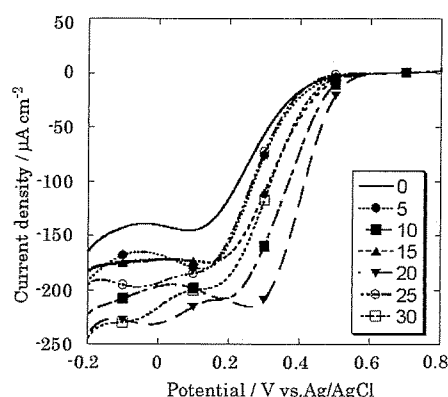


Figure 4. Polarization curves for oxygen reduction in 5 layer of Pd/MHF-GNC electrode changing the number of cycles of oxidative desorption of SAM in  $\text{O}_2$  saturated 0.1 M  $\text{H}_2\text{SO}_4$  at scan rate of  $10 \text{ mV s}^{-1}$ .

## Conclusions

The catalytic activity of the Pd and SAM coated GNC electrode for oxygen reduction reaction have been investigated. It was significantly increased by removing the thiol SAM from the GNC surfaces by oxidative desorption and further by deposition of small amount of Pd (ca. 1 ML) on GNC surfaces. Given the present results it appears worthwhile to pursue more quantitative studies on the preparation of bimetallic clusters and their effects in electrocatalysis.

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