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Electron and Ion Transport through Multilayers of Au Nanoclusters
Covered by Self-Assembled Monolayers

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Abstract

Two types of gold nanoclusters (GNCs), one covered by self-assembled monolayers
(SAMs) of mercaptoundecanoic acid (MUA), hexanethiol (C₆SH), and ferrocenylhexanethiol
(FcC₆SH), MHF-GNC, and the other with MUA and C₆SH, MH-GNC, were used for the
construction of ten GNC layers of two different sequences on an MUA modified Au(111)
surface based on the carboxylate/polycation (poly(allylamine hydrochloride) : PAH)/
carboxylate electrostatic interaction. MHF-GNC was placed either as the layer closest
to the gold electrode, i.e., the first layer, or as the outermost layer with MH-GHC in the other
layers. A quasi-reversible redox peak with a constant charge corresponding to the redox of the
ferrocene moiety of the MHF-GNC monolayer was observed at both electrodes, showing
electrons and perchlorate ions could be transferred through the MH-GNC/PAH multilayers.
Cross-sectional transmission electron microscopy revealed that the size of the immobilized
GNC was almost same as that in solution and well-separated GNCs were dispersed rather
uniformly within the polymeric matrix. The incorporation of perchlorate ion upon the
oxidation of the ferrocene moiety of the MHF-GNC was demonstrated by electrochemical
quartz microbalance measurement. Based on the above results, the charge transfer mechanism
in the GNC multilayers was discussed.
INTRODUCTION

The formation of ordered mono- and multi- layers of both organic and inorganic materials on solid substrates with various functionalities has been a subject of intensive research in view of the possible applications in a wide variety of fields in nanotechnology and nanoscience.

One of the good candidates as a building block for the multilayer formation is metal and semiconductor nanoclusters because they have various interesting characteristics, which are different from those of the bulk materials. Since the report by Brust et al. [1], gold nanoclusters (GNCs) covered by self-assembled monolayers (SAMs) of alkanethiols have attracted many research groups [2-14] because SAM-covered GNCs have a high stability and those of a certain size with a narrow size distribution can be prepared relatively easily. GNC with special functionalities can be constructed by using thiol molecules with special functional groups. One can utilize the rich references on alkanethiol SAMs with various functionalities [15,16] including ours [17-20].

Several groups have already reported the formation and the properties of the GNC multilayers on solid surfaces [6,10-12a,12c,13,14,21]. For example, Murray et al. constructed the GNC mono- and multi- layers and reported the quantized charging and dynamics of electron transfer between the GNCs [10-12]. The electrostatic layer-by-layer (LBL) assembly method has been applied not only for the multilayer formation of oppositely charged polyelectrolytes [22], for which this method was originally developed, but also to construct nanoparticle multilayers [12c, 23, 24] by alternatively immersing the charged substrate surface into oppositely charged GNC and ionic polymeric solutions with a rinse after each deposition. Combining the versatility of polymeric materials with GNCs by LBL sequential formation of ordered nanostructures offers significant advantages such as usage of environmentally-friendly aqueous solution, low cost, high throughput. However, the studies of the electron transport within the multilayer of GNCs covered by thiol molecules containing
electroactive groups are rather limited. Recently, we have constructed the multilayers of GNCs covered by mixed self-assembled monolayers with an electrochemical active group, ferrocene, based on this versatile technique, and investigated their electrochemical properties [26,27]. In these reports, we found that the electric charge due to the redox of a ferrocene (Fc)/ferricenium cation (Fc+) couple linearly increased with the number of layers up to a certain number of layers. Preliminary results of the electrochemical characteristics of two types of the GNC multilayers with the Fc attached GNC either only at the outermost layer or at the closest layer to a gold substrate were also reported in these works to clarify the charge transfer mechanism within the multilayers. Electron was proposed to be transferred between ferrocene and the gold electrode through the GNC cores.

The understanding of electron transfer mechanism at the multilayer modified electrode/electrolyte interface is very important not only for fundamental surface science and electrochemistry but also for the design and fabrication of advanced electronic, optical and sensing nanodevices. In this study, we have investigated the electron transport properties within the multilayers of two GNCs, one covered by self-assembled monolayers of mercaptoundecanoic acid (MUA), hexanethiol (C6SH), and ferrocenylhexanethiol (FcC6SH), MHF-GNC, and the other with MUA and C6SH, MH-GNC, with various sequences constructed based on a carboxylate/cationic polymer (poly(allylamine hydrochloride): PAH)/carboxylate electrostatic interaction on a Au(111) surface. It is shown that all the ferrocene groups within the multilayer are electrochemically active even when the Fc attached GNC existed either only at the outermost layer or only at the closest layer to a gold substrate with 1 - 9 layers of GNC without Fc groups. This means electron and perchlorate ion can be transferred through the GNC multilayers and electron transfer between the ferrocene moiety and the Au(111) electrode takes place through the GNC cores by hopping. Cross-sectional transmission electron microscopy has revealed that no aggregation of the GNC within the multilayers. The incorporation of perchlorate ion upon the oxidation of the ferrocene moiety
of the MHF-GNC is demonstrated by electrochemical quartz microbalance (EQCM) measurement. Based on the above results, the charge transfer mechanism in the GNC multilayers is discussed.

EXPERIMENTAL

Hydrogen tetrachloroaurate (HAuCl$_4$, 99.99 %), sodium tetrahydroborate (NaBH$_4$), ethanol (superpure grade), methanol (superpure grade), hexanethiol (C$_6$SH, superpure grade), calcium hydride (CaH$_2$), dichloromethane (ultrapure grade), perchloric acid (ultrapure grade), and sulfuric acid (ultrapure grade) were purchased from Wako Pure Chemicals. Tetra-n-octylammonium bromide (TOAB) was obtained from Tokyo Kasei Kogyo. Tetra-n-butylammonium perchlorate (TBAP, for polarography use) was obtained from Nacalai Tesque, and 11-mercaptoundecanoic acid (MUA, 97%) and toluene (spectroscopy grade) were obtained from Dojindo Laboratory. All chemicals except for dichloromethane and TBAP were used as received. Dichloromethane was distilled twice with CaH$_2$ to remove any residual water. TBAP was recrystallized from methanol more than twice. Ferrocenylhexanethiol (FcC$_6$SH) was synthesized by a previously reported method [27]. Ultrapure water was obtained using a Milli-Q water purification system (Millipore) and ultrapure N$_2$ (99.999 %) was obtained from Air Water.

A gold single crystal was prepared from a gold wire (99.999 %, φ = 1 mm, Tanaka Precious Metals) by Clavilier’s method [29]. It was cut to expose the (111) face, mechanically polished, and then annealed at 800 °C for 8 h in an electric furnace (Denken, KDF S-70) under an ultrapure N$_2$ atmosphere. Gold substrates used for the EQCM measurements were prepared by the vacuum evaporation of 10 nm thick titanium followed by 100 nm thick gold onto a 5 MHz quartz crystal plate (double-side polished) kept at 300 °C with an evaporation rate of less than 0.01 nm s$^{-1}$. This procedure is known to provide a highly ordered Au(111) phase with wide terraces [30]. For the XPS measurements, a gold disk
(99.99 %, φ = 8 mm, thickness = 3 mm, Tanaka Precious Metals) was used as the substrate after mechanical polishing and electrochemical treatment by cycling the potential between -0.2 and +1.5 V vs. Ag/AgCl in 0.1 M H₂SO₄. All the gold substrates were annealed by a hydrogen flame and cooled in air just before dipping in the thiol solution.

Two types of GNCs covered with mixed alkanethiol SAMs, one covered by the SAMs of hexanethiol, ferroceny1hexanethiol, and 11-mercaptoundecanoic acid, MHF-GNC, and the other covered by C₆SH and MUA, MH-GNC, were synthesized as follows: First, the C₆SH SAM protected gold nanocluster, H-GNC, was prepared by the method reported by Brust et al. [1]. An aqueous solution of HAuCl₄ (100 ml, 20 mM) was mixed with a toluene solution of TOAB (300 ml, 30 mM). The two-phase mixture was vigorously stirred until all the HAuCl₄ was transferred to the organic layer, i.e., the color of the organic phase changed to dark orange, and C₆SH (0.68 g, 5.8 mmol) was then added to the organic phase. After stirring the mixture for 10 min, a freshly prepared aqueous solution of NaBH₄ (100 ml, 260 mM) was slowly added with vigorous stirring. After further stirring the mixture vigorously for 3 h, the organic phase was extracted by dichloromethane. The volume of the organic residue was reduced to 10 ml in a rotary evaporator, and then 400 ml of ethanol was added to remove the excess C₆SH. After the mixture was kept overnight at -18 °C, the dark brown precipitate was filtered off and washed with ethanol. The crude product was dissolved in 10 ml toluene and precipitated again by adding 400 ml of ethanol. From the ¹H-NMR (Hitachi, R-1900, 90 MHz) measurements, we confirmed that the product was H-GNC. The core size of the H-GNC determined by transmission electron microscopy (TEM) (JEOL, JEM-2000FX) was 1.8 ± 0.4 nm.

MUA and FeC₆SH were introduced onto the H-GNC surface by the place-exchange method [9]. As an example, we describe the procedure for the introduction of FeC₆SH. The H-GNC (0.6 g) was first dispersed in 100 ml of dichloromethane, and then FeC₆SH (0.25 g, 8.3 mmol) was added. The solution was stirred for 3 h at room temperature. After evaporating off
the solvent, the precipitate was washed twice with ethanol and acetone. The crude product was dissolved in 10 ml of dichloromethane and precipitated again by adding 400 ml of ethanol. The 1.8 ± 0.4 nm core diameter of the GNCs determined by TEM did not change after the reagent exchange reactions. As the molar ratios of the alkylthiols on the GNC surfaces varied each time, they were determined each time by $^1$H-NMR. The molar ratios of $\text{C}_6\text{SH} : \text{FcC}_6\text{SH} : \text{MUA}$ on the MHF-GNC surface and of $\text{C}_6\text{SH} : \text{MUA}$ on the MH-GNC surface were determined by $^1$H-NMR as 47 : 19 : 34 and 26 : 74, respectively.

GNCs Multilayers with the following three different arrangements as described in Scheme 1 were formed on the carboxylate-terminated (MUA) SAM-modified gold substrates based on the carboxylate/PAH/carboxylate electrostatic interaction. 1. Multilayer containing only MHF-GNC/PAH (Scheme 1 (a): Au(111)/MUA/(PAH/MHF-GNC)$_n$) was prepared on a Au surface by repeating the two-dip and rinse cycle as reported before [27]. 2. Multilayer of MH-GNC and MHF-GNC with only one layer of MHF-GNC existed in the layer closest to the gold electrode, i.e., the first layer, and MH-GNC in the other layers (Scheme 1(b): Au(111)/MUA/PAH/MHF-GNC/ (PAH/MH-GNC)$_n$). 3. Multilayer of MH-GNC and MHF-GNC with only one layer of MHF-GNC existed only in the outermost layer and MH-GNC in the other layers (Scheme 1(c): Au(111)/MUA/(PAH/MH-GNC)$_n$/PAH/ MHF-GNC). The substrate pre-coated with MUA SAM was dipped in a 2 wt% PAH aqueous solution (pH=6) containing 1 M NaCl for 30 min followed by a Milli-Q water rinse and then dipped in a 0.75 wt% GNC ethanol solution for 30 min followed by a rinse with ethanol. This two-dip and rinse cycle was repeated to construct the multilayers.

Cyclic voltammograms (CVs) were recorded with an automatic polarization system (Hokuto Denko, HSV-100). A potentiostat/galvanostat (Hokuto Denko, HA-151) and a function generator (Hokuto Denko, HB-111) were used for the EQCM measurements, which were carried out in a three-compartment cell. The resonant frequency of the quartz crystal electrode, which was oscillated by a homemade oscillation circuit, was simultaneously
monitored with the electrode potential and current by a frequency counter (Hewlett-Packard, HP53131A) controlled by a personal computer (NEC, PC9821cb2) through a GPIB interface. The frequency stability of the EQCM system was better than 0.1 Hz for a sampling gate time of 0.1 s. Pt wire and Ag/AgCl were used as the counter and reference electrodes, respectively. The measurements were carried out in a 0.1 M HClO₄ aqueous solution, which was deaerated by passing ultrapure N₂ gas through it for more than 30 min before each measurement.

The XPS measurements were performed on a Rigaku XPS-7000 spectrometer using an MgKα X-ray source (1253.6 eV). The take-off angle between the sample surface and the analyzer was fixed at 90 ° in all cases. The narrow-scan spectra of the Fe2p region were taken with a resolution of 0.1 eV and the signals of 64 scans were averaged.

Cross-sectional transmission electron microscopy of a GNC multilayer was carried out using a JEOL electron microscope JEM-2010F with 200 KV acceleration voltage. A multilayer with ten MHF-GNC/PAH deposition cycles was prepared on a silicon wafer with a pre-evaporated Au film of 150 nm. After the multilayer formation, the multilayer was further covered with the evaporated Au and epoxy resin to protect the multilayer for the preparation of a sliced sample.
RESULTS AND DISCUSSION

(1) Structure and electrochemical characteristics of the MHF-GNC/PAH multilayers

Figure 1 shows the cross-sectional micrograph of a multilayer with ten MHF-GNC deposition cycles. The substrate (evaporated Au film), GNC/PAH multilayers, and the protecting layers, i.e., the evaporated Au and epoxy resin, were clearly visible in Fig. 1 (a). From this image, the total thickness of the GNC multilayer with ten GNC/PAH cycles was estimated to be about 58 nm, which is in good agreement with the previous reported value of 51 nm determined by ellipsometry for the same system [27]. This and the higher resolution image (Fig. 1(b)) revealed that the GNCs were dispersed within the polymeric matrix rather uniformly and the well-defined layered structure as illustrated in Scheme 1 was not observed, suggesting a homogenous mixture of the GNCs and PAH in the LBL film rather than the expected vertically ordered structure with sharp interfaces between the two components. This is reasonable because the layered LBL assembly might be obscured in the case of globular nanoparticles alternatively assembled with flexible linear polymeric chains due to the interpenetration between the adjacent layers and high interlayer roughness or by embedding of the GNCs on the polymeric chains. The spherical nanoparticles were separated from each other by the organic shells and the mean size of the immobilized GNC core was about 1.8 ± 0.3 nm, which was almost the same as that of the GNC in solution, revealing the absence of aggregation or reshaping of the linked GNC particles to those of larger core size in the LBL multilayers. The average separation distance of the immobilized GNCs was estimated by measuring the edge-to-edge distances of the particles in the cluster regions in Fig.1 (b). The result yields an almost uniform spacing close to the cluster core size. Similar features are expected for the multilayers with the ferrocene group either existed at the innermost and or outermost layers, since both types of GNCs used for the fabrication of LBL multilayers with PAH spacing layers have same core size and similar activity.

Figure 2 (a) shows the CVs of the electrode modified with MHF-GNC/PAH multilayers
of 1-10 deposition cycles of (Scheme 1 (a)) measured in a 0.1 M HClO₄ aqueous solution at a scan rate of 100 mV s⁻¹. The oxidation and reduction peaks due to the redox of Fc/ Fc⁺ were observed around +360 mV (vs. Ag/ AgCl) in all the cases. The full width at half-maximum (fwhm) of MHF-GNC multilayer modified electrode was constant to be around 90 mV regardless of the GNC deposition cycles, suggesting a simple Langmuir type redox process of the ferrocene moieties. The peak-to-peak separation was less than 60 mV in all the cases, suggesting a facile charge transfer within the MHF-GNC multilayers. The charge of the redox peak linearly increased with the MHF-GNC deposition cycles as summarized in Fig. 2 (b). Note that all charge values in this study are slightly larger than those previously reported [27] because the surface coverage of FeC₆SH in the present system was higher than that of the previous case.

(2) Structure and electrochemical characteristics of the multilayers consisted of both MHF-GNC and MH-GNC with two different sequences

It is impossible to clarify the GNC arrangement in the multilayers with the ferrocene group either existed at the innermost and or outermost layers by the cross-sectional transmission electron microscopy since both types of GNCs used for the LBL multilayer formation with PAH spacing layers had same core size. However, the X-ray photoelectron spectra of the multilayer assembly in the Fe2p region can provide additional structural information concerning the position of MHF-GNC in the multilayer. Figure 3 shows the X-ray photoelectron spectra in the Fe2p region of the two types of multilayer assemblies: (a) Au(111)/MUA/PAH/MHF-GNC/ (PAH/MH-GNC), for n=1, 3 and 5, and (b) Au(111)/MUA/ (PAH/MH-GNC),/PAH/ MHF-GNC for n=1, 3, 5 and 9. No peak was observed even at n=3 in the former (Fig. 3(a)), while the peak intensity did not change with n in the latter (Fig. 3(b)), confirming that the ferrocene group definitely existed at the innermost and outermost layers in the former and the latter systems, respectively, as suggested in Schemes 1(b) and 1(c).

Figures 4 (a) and 4 (b) shows the CVs of the former (n=1, 3, 5, 9) and the latter (n=1, 3,
7, 9) multilayer modified electrodes measured in a 0.1 M HClO₄ aqueous solution at a scan rate of 100 mV s⁻¹. For a comparison, the CV of the Au(111)/MUA/PAH/MHF-GNC, which is equivalent to the assembly of n=0 of the both sequences, is also shown in the both figures. For all the cases, the oxidation and reduction peaks due to the redox of Fe+/Fc⁺ were observed around +360 mV (vs. Ag/AgCl). The peak width and peak-to-peak separation of the redox Fe group increased significantly with the introduction of one PAH/MH-GNC layer then slightly with a further increase of the PAH/MH-GNC layer. The peak-to-peak separation increased from 35mV (n=0), to 75mV (n=1), 100mV (n=5), and 125mV (n=9) for the former, and to 165mV (n=1), 175mV (n=7), and 185mV (n=9) for the latter. However, the charge in these peaks did not depend on n and were 23 - 24 µC cm⁻², which was in good agreement with that of the Au(111)/MUA/PAH/MHF-GNC consisting of only one MHF-GNC/PAH deposition cycle, i.e., the case of n = 0 of the both sequences, as summarized in Fig. 4 (c). All these charge values are slightly larger than that previously reported [27] due to the similar reason as mentioned above. As the charge did not depend on the number of MH-GNC/PAH layers, one could conclude that all the Fe groups in the multilayer on the gold electrode were electrochemically active despite the presence of the PAH/MH-GNC multilayer between the electrolyte solution and the ferrocene moiety in the former and between the gold electrode and ferrocene moiety in the latter.

(3) Charge transfer through the GNC multilayers

Since the redox process of the surface-attached ferrocene group is known to be represented by [28]:

\[-Fe + X⁻ \rightarrow \text{Fe}⁺ X - + e⁻ + \text{solv.}\]

where -Fe and -Fe⁺ are the neutral and oxidized states of the ferrocene group, respectively, X⁻ is the solvated anion in solution, -Fe⁺ X⁻ is an ion pair between the ferricenium cation and the anion, and solv. is a solvent molecule, electron and anion should be transferred between the ferrocene moiety and the electrode, and between the electrolyte solution and the ferrocene
moiety, respectively, upon the redox of the ferrocene group. Thus, the results shown in Figs. 2 and 4 strongly suggest that perchlorate anion, which forms an ion pair with Fe\(^{+}\), is transferred between the electrolyte solution and the ferrocene group at the innermost layer through the 1 - 9 PAH/MH-GNC layers at the Au/MUA/PAH/MHF-GNC/(PAH/MHGNC)\(_n\) (n=1, 3, 5, 9) electrodes and electron is transferred between the ferrocene group at the outermost layer and the gold electrode through the 1 - 9 PAH/MH-GNC layers at the Au/MUA/(PAH/MH-GNC)\(_n\)/PAH/MHF-GNC (n=1, 3, 7, 9) electrodes.

Figure 5 shows the potential dependencies of current and EQCM at the Au/MUA/PAH/MHF-GNC/(PAH/MH-GNC)\(_9\) electrode obtained simultaneously in 0.1 M HClO\(_4\) aqueous solution at a scan rate of 10 mV s\(^{-1}\). Note the current density of Fig. 5 was smaller than the results shown in Fig. 4 because the sweep rate was 10 times smaller in the latter. Significant frequency decrease and increase, i.e., weight increase and decrease, were observed when the current due to the oxidation and reduction of the ferrocene moiety, respectively, flowed. A linear relation was observed between the mass change calculated from the frequency change by using Saubrey’s equation and the charge in the region of the ferrocene oxidation (250 - 550 mV) with the slope of 216 g/mol-electron. Similar EQCM response was observed for the Au/MUA/PAH/MHF-GNC/(PAH/MH-GNC)\(_3\) and Au/MUA/PAH/MHF-GNC/(PAH/MH-GNC)\(_6\) electrodes. The slopes for the mass change - charge relations, i.e., mass per electron: mpe, for the former and the latter were 233 and 177, respectively. Furthermore, the essentially the EQCM response was obtained at the Au/MUA/(PAH/MH-GNC)\(_9\)/PAH/MHF-GNC. These results clearly show that the EQCM response was not affected by the number of the PAH/MH-GNC overlayers, confirming perchlorate ions are transferred between the electrolyte solution and the ferrocene group at the innermost layer through the PAH/MH-GNC. The mpe values obtained for Au/MUA/PAH/MHF-GNC/(PAH/MH-GNC)\(_n\) (n=3, 6, 9) are in good agreement with the value observed at the gold electrode modified with the PAH/MHF-GNC multilayers (245
g/mol-electron) and is much larger than the molecular weight of perchlorate ion (99.5 g/mol), suggesting that each perchlorate ion moves into and is released from the modified layer accompanied by 5 - 7 water molecules upon the oxidation and reduction of the ferrocene moiety, respectively.

At least two possible mechanisms can be considered for the electron transfer between the ferrocene group on the MHF-GNC surface and the gold electrode: one is the direct tunneling between the ferrocene group on the MHF-GNC surface and the gold electrode and the other is the transfer through the core of the MH-GNCs. The distance between the ferrocene group in the outermost layer and the gold electrode in the GNC multilayers with ten deposition cycles was more than 50 nm as evidenced by both cross-sectional transmission electron microscopy and ellipsometry and is far too long for electron to tunnel. Thus, the electron should be transferred not by direct tunneling between the ferrocene group and the gold electrode but through the GNCs by hopping.

In comparison with those of the multilayers with only MHF-GNC, the peak width and the peak-to-peak separation increased significantly with the introduction of PAH/MH-GNC layers in the multilayers with MHF-GNC either as the layer closest to the gold electrode, i.e., the first layer, or as the outermost layer with MH-GHC in the other layers. One possible reason for these peak broadening and the peak-to-peak separation is the slow kinetics for the charge transfer, including the electron transfer between the Au electrode and the Fc moiety and the transport of the perchlorate ion between the electrolyte and the Fc moiety, through these layers. The facile electron transfer through these multilayers was, however, demonstrated by measuring the scan rate dependence of the electrochemical characteristics. Figure 6 and Table 1 shows the CVs and electrochemical parameters, respectively, of the Au/MUA/PAH/MHF-GNC/(PAH/MH-GNC)₃ modified electrode. The peak potential shifted only slightly and the peak current increased almost linearly with the scan rate up to 200 mV s⁻¹, and the corresponding charge was almost independent of the scan rate. Thus, the charge
transfer is indeed facile. Another possible contribution for the peak broadening and the
enlarged peak separation might result from the non-uniform packing arrangement of the
MHF-GNC in these multilayers with different sequences, although we could not provide a
clear evidence for the non-uniform packing of the MHF-GNC. The packing arrangement of
the redox moiety attached GNC in these multilayers should play an important role in the
transport of both electron and ClO₄⁻ within the multilayers and some changes of the
microstructure of these films might take place during the redox process of the Fc groups.
Above results implied that although perchlorate anion and electrons can be transferred
through the MH-GNC/PAH layers so that all the ferrocene groups are electrochemically
active, their transports within the MH-GNC/PAH layers are slower than those in the
PAH/MHF-GNC layers, suggesting the promotion of their transports by the
ferrocene/ferricenium groups in the latter system.

**Conclusion**

Two types of GNCs, one covered by SAMs of MUA, C₆SH, and FeC₆SH, MHF-GNC,
and the other with MUA and C₆SH, MH-GNC, were used for the construction of ten GNC
layers of two different sequences on an MUA-modified Au(111) surface based on the
carboxylate/polycation (PAH)/carboxylate electrostatic interaction. MHF-GNC was placed
either as the layer closest to the gold electrode, i.e., the first layer, or as the outermost layer
with MH-GHC in the other layers. A quasi-reversible redox peak with a constant charge
corresponding to the redox of the ferrocene moiety of the MHF-GNC monolayer was
observed at both electrodes, showing that electrons and perchlorate ions are transferred
through the MH-GNC/PAH multilayers as shown in Scheme 2 for (a) Au(111)/MUA/PAH/MHF-GNC/(PAH/ MH-GNC)ₙ and (b) Au(111)/MUA/(PAH/MH-
GNC)ₙ/PAH/MHF-GNC electrodes.
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References


Table 1  Electrochemical parameters of Au/MUA/PAH/MHF-GNC/(PAH/MH-GNC)₃ modified electrode measured in 0.1 M HClO₄ aqueous solution at different potential scan rate.
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Table 1  W.Song et.al.
**Figure Captions**

Scheme 1. Schematic view of the idealized layer structure of (a) Au(111)/MUA/(PAH/ MHF-GNC)$_n$, (b) Au(111)/MUA/PAH/MHF-GNC/(PAH/MH-GNC)$_n$, and (c) Au(111)/MUA/(PAH/ MH-GNC)$_n$/PAH/MHF-GNC electrodes.

Scheme 2. Schematically idealized model for the charge transfer during the redox of the ferrocene moiety at (a) Au(111)/MUA/PAH/MHF-GNC/ (PAH/MH-GNC)$_n$, and (b) Au(111)/MUA/(PAH/MH-GNC)$_n$/PAH/MHF-GNC electrodes.

Figure 1 Cross-sectional transmission electron micrographs of a (a) MHF-GNC multilayer films with ten deposition cycles on an evaporated Au film on the silicon wafer, and (b) higher resolution image of the GNC/PAH multilayer region.

Figure 2 Cyclic voltammograms of Au(111)/MUA/(PAH/MHF-GNC)$_n$ for n=1-10 measured in 0.1 M HClO$_4$ aqueous solution at a scan rate of 100 mV s$^{-1}$ (a) and relationship between the electronic charge of Fc redox peak and the number of MHF-GNC/PAH deposition cycles (b).

Figure 3 X-ray photoelectron spectra of (a) Au(111)/MUA/PAH/MHF-GNC/(PAH/ MH-GNC)$_n$ for n=1, 3 and 5 and (b) Au(111)/MUA/(PAH/MH-GNC)$_n$/PAH/MHF- GNC for n=1, 3, 5 and 9.

Figure 4 Cyclic voltammograms of (a) Au(111)/MUA/PAH/MHF-GNC/(PAH/MH- GNC)$_n$ for n=1, 3, 5 and 9 and (b) Au(111)/MUA/(PAH/MH-GNC)$_n$/PAH/MHF-GNC for n=1, 3, 7 and 9 measured in 0.1 M HClO$_4$ aqueous solution at a scan rate of 100 mV s$^{-1}$. For a comparison, CV of Au(111)/MUA/PAH/MHF-GNC is presented in both figures as Au(111)/MUA/PAH/MHF-GNC is equivalent to the assembly of n=0 of both systems. (c) Relationship between the electronic charge of Fc redox peak and the number of MH-GNC deposition cycles for the two assemblies.

Figure 5 EQCM response of the Au(111)/MUA/PAH/MHF-GNC/(PAH/MH-GNC)$_n$ electrode measured in 0.1 M HClO$_4$ aqueous solution at a scan rate of 10 mV s$^{-1}$.
Figure 6 Cyclic voltammograms of (a) Au(111)/MUA/PAH/MHF-GNC/(PAH/MH- GNC), measured in 0.1 M HClO₄ aqueous solution at different scan rates.
Scheme 1  W. Song et.al.
Scheme 2  W. Song et al.
Fig. 1 W. Song et al.
Fig. 2 W. Song et al.
Fig. 3  W. Song et.al

(a)

Intensity

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Fe 2p_{3/2}  Fe 2p_{1/2}
Fig. 4 W. Song et al.
Fig. 5 W. Song et al.
Fig. 6 W. Song et. al.