

Short-time preparation and electrochemical properties of a single layer of tetraoctylammonium bromide capped Au nanoparticles on dithiol self-assembled monolayer-modified Au electrode

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Abstract

Short time immobilization of densely packed tetraoctylammonium bromide (TOAB) stabilized gold nanoparticles (AuNPs) were established on a Au electrode modified with a self-assembled monolayer (SAM) of 1,6-hexanedithiol (HDT) or 1,4-benzenedimethanethiol (BDMT). The quartz crystal microbalance experiment showed that a complete single layer coverage of TOAB-AuNPs on both SAMs was achieved within 20 min. AFM images demonstrated that the immobilized TOAB-AuNPs on the SAMs were densely packed and the AuNPs film thickness was 6-7 nm. The electronic communication between the immobilized AuNPs and the underlying bulk electrode was confirmed by cyclic voltammetry and electroreflectance spectroscopy. A reversible electron transfer reaction was observed for both $[\text{Fe}(\text{CN})_6]^{4-/3-}$ and $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ at TOAB-AuNPs immobilized on HDT (Au/HDT/AuNPs) and BDMT (Au/BDMT/AuNPs) modified electrodes. The electroreflectance spectra show a red-shifted strong positive-going plasmon resonance bands at 551 nm and 584 nm, respectively, for the Au/BDMT/AuNPs and Au/HDT/AuNPs electrodes. The observed reversible redox response for the solution redox species and red-shifted plasmon resonance bands for the immobilized AuNPs again indicated that the AuNPs were immobilized on the SAMs in a densely packed manner. An advantage of TOAB-AuNPs modified electrode prepared by short time immersion over citrate-stabilized AuNPs modified electrode was demonstrated by the enhanced oxidation of ascorbic acid (AA) at these electrodes. The oxidation of AA was shifted to 90 mV less positive potential with higher oxidation current at TOAB-AuNPs modified electrode when compared to citrate-stabilized AuNP modified electrode.

Keywords: TOAB-capped gold nanoparticle; Cyclic voltammetry, 1,4-Benzenedimethanethiol; 1,6-Hexanedithiol; Electroreflectance spectroscopy

1. Introduction

Gold nanoparticles (AuNPs) are considered as one of the most stable and promising nanomaterials with great technological importance mainly due to their unique size-dependent electronic, chemical, and optical properties [1-3]. It is well established that AuNPs immobilized on electrode surfaces exhibit interesting electrochemical properties [1-4]. The distinct electrochemical properties of AuNPs were demonstrated by several electroanalytical applications including electrocatalysis [5], biosensors [6], and protein electrochemistry [7]. Three strategies have been commonly used to immobilize AuNPs on electrode surfaces. The first strategy is the formation of a single layer of AuNPs through covalent or electrostatic linkage on an organic thin film such as self-assembled monolayer (SAM) terminated with a thiol or amino functional group coated on electrode substrates [8,9]. The second one involves the preparation of organized multilayer of AuNPs by a layer-by-layer self-assembly method using molecules terminated with suitable functional groups [10-12]. The third strategy is the direct deposition of AuNPs on electrodes by electrodeposition [13].

The preparation of densely packed AuNPs modified electrode is often desired for catalysis and electronics. To date, one of the most widely used AuNPs for the modification of electrode surface is citrate capped AuNPs (C-AuNPs) [14-18]. Immobilization of C-AuNPs was usually carried out by immersing the electrodes modified with suitable linker molecules into the colloidal solution of C-AuNPs for longer than 12 h [9,12,14-18]. It was found that even after 12 h immersion, a complete coverage of AuNPs was not achieved using C-AuNPs due to repulsive forces in between the surface confined AuNPs and also with free AuNPs in solution [16]. A general approach to increase the AuNPs coverage includes the use of additional linker molecules to attach extra nanoparticles on the electrode surface [10-12]. Natan and co-

workers have extensively used C-AuNPs for the preparation of AuNPs multilayer assemblies on different substrates [12,14,15]. For example, they immersed a mercaptosilane coated glass substrate into C-AuNPs solution for 50 min for the preparation of the first layer of AuNPs, and alternatively immersed it in mercaptoethylamine and C-AuNPs solutions for, respectively, 15 and 50 min each to prepare multilayer of AuNPs [12]. It has been shown that after the deposition of 7 to 8 layers of AuNPs, the multilayers eventually become conductive and the voltammogram of $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ in solution becomes reversible, whereas below 7 layers of AuNPs reversible voltammogram was not obtained [12]. On the other hand, Schiffrin and co-workers extensively used tetraoctylammonium bromide (TOAB) stabilized AuNPs (TOAB-AuNPs) to prepare multilayer assemblies of AuNPs on glass, indium tin oxide (ITO) and polycrystalline Au substrates coated with either mercaptotrimethoxysilane or dithiols [19-21]. For the preparation of the first layer of AuNPs, they immersed the modified substrates in TOAB-AuNPs solution for several hours [21] or overnight [20] and subsequently immersed in the TOAB-AuNPs solution for 3 h to form the second layer of AuNPs [20]. They have shown that 4 layers of the AuNPs are required to see a reversible response for $[\text{Fe}(\text{CN})_6]^{4-/3-}$ in solution [21]. Recently, few reports have been published for the preparation of a single layer of C-AuNPs on SAMs of thiols terminated with amino or thiol functional group that shows a quasi-reversible or reversible response for the solution dissolved redox species [12,22-24]. To sum up, a reversible or quasi-reversible response for a solution dissolved species was achieved at the surface of multilayer assemblies of AuNPs [8-10] and a single layer of AuNPs immobilized on dithiol modified electrodes by several hours immersion [12,22-24].

Herein we report a short time immobilization of a densely packed TOAB-AuNPs single layer on SAMs of 1,4-benzenedimethanethiol (BDMT) and 1,6-hexanedithiol (HDT) coated on Au electrodes. Quartz crystal microbalance (QCM) and atomic force microscopy (AFM) studies

supported that immobilization of densely packed AuNPs is achieved within 20 min immersion on both BDMT- and HDT-SAMs modified Au electrodes into the colloidal solution of TOAB-AuNPs in toluene. The obtained electrode with immobilized AuNPs showed a reversible response for $[\text{Fe}(\text{CN})_6]^{4-/3-}$ and $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ redox couples in aqueous solution. Further, the good electronic communication between the AuNPs and the underlying bulk electrode was confirmed by strong positive-going electroreflectance signal observed at the plasmon resonance band region for the immobilized AuNPs by the potential modulated UV-visible reflectance spectroscopy.

2. Experimental Section

2.1. Chemicals

Water was purified through a Milli-Q Plus Ultrapure water system (Millipore Co.) to 18.3 M Ω cm. $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (Wako), 1,4-benzenedimethanethiol (Wako), 1,6-hexanedithiol (TCI) and tetraoctylammonium bromide (TCI) as well as all other chemicals were of the highest grade commercially available and used as received. Phosphate buffer solution (pH 7.2) was prepared from the potassium salts.

2.2. Preparation of TOAB- and citrate-stabilized gold nanoparticles

TOAB-AuNPs were prepared in toluene by the reported two-phase method [25]. An aqueous solution of $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (500 mg in 40 mL) was mixed with a solution of TOAB in toluene (3.06 g in 100 mL). The two-phase mixture was vigorously stirred until tetrachloroaurate was completely transferred into the organic phase to give a deep orange solution. Then a fresh aqueous solution of sodium borohydride (525 mg in 30 mL) was added slowly while stirring. The deep orange color of the organic phase immediately turned to ruby red. After further stirring for 12 h, the organic layer was extracted and washed with Millipore water for three times and

then dried over anhydrous sodium sulfate. The solution was diluted to 250 mL with toluene before use. The TEM image (Supporting Information, Fig. S1) and surface plasmon resonance band at 524 nm indicate that an average size of the AuNPs is 5-7 nm.

C-AuNPs with a size of ~4 nm were synthesized by the reported method [26].

2.3. Immobilization of AuNPs

Polycrystalline Au electrodes (BAS) with a geometrical surface area of 0.0201 cm² were polished with alumina powder slurries (0.6 μm and 0.03 μm) to a mirror finish and sonicated in water for 10 min. The characteristics of polished Au electrodes were checked by cyclic voltammetry in 0.05 M H₂SO₄ before surface modification. The real surface area of the two electrodes used in this work was found to be 0.0211 cm², determined by integration of the cathodic peak for the reduction of the oxide layer. The cleaned Au electrode was immersed in ethanolic solution of 10 mM 1,6-hexanedithiol (HDT) or 5 mM 1,4-benzenedimethanethiol (BDMT) for 3 h. The HDT or BDMT modified electrode was rinsed with ethanol, then immersed in toluene for 20 min, and soaked in TOAB-AuNPs in toluene for 20 min. Then the electrode was washed with toluene, followed by ethanol and then water, and used for electrochemical and electroreflectance (ER) measurements in the phosphate buffer solution.

2.4. Instrumentation

A quartz spectroelectrochemical cell was used for both voltammetric and ER measurements. Electrochemical measurements were carried out using AuNPs immobilized dithiol SAMs modified Au as a working electrode, Ag/AgCl (KCl saturated solution) as a reference electrode, and a Au wire coil as a counter electrode. Cyclic voltammograms (CVs) were recorded using a computer controlled BAS 100B/W electrochemical analyzer. The instrumentation used for ER measurements is described elsewhere [27]. The ER signal is defined

as the ac component of the reflectance divided by the time-averaged reflectance and designated as $\Delta R/R$. Both the real part (in-phase component with respect to E_{ac}) and the imaginary part (90° out-of-phase component) of $\Delta R/R$ were monitored simultaneously as a function of the incident light wavelength, λ . A lock-in-amplifier (EG & G, model 5210) was employed for the phase sensitive detection of the signals. UV-visible spectra were recorded with a U-3000, Hitachi spectrophotometer. An AT-cut quartz plate with overlaying Au coats at both sides (MSQ-1001QR, Meidensha Co.) with a fundamental resonance frequency of 10 MHz was used as a QCM tip by combining a resonator (MSQ-1001SC, Meidensha) and a frequency analyzer (Universal Counter, Agilent 53131A). One side of the Au film surface was exposed to the solution for the weight change measurements. The QCM tip, the surface of the Au film of which was modified with an HDT or BDMT monolayer, was first equilibrated in stirred toluene, and then colloidal solution of TOAB-AuNPs solution was injected into toluene under stirring. All the electrochemical, spectral, and QCM measurements were carried out at $23 \pm 2^\circ \text{C}$.

The size of the AuNPs was determined with a JEM-100S transmission electron microscope (JEOL). Atomic force microscope (AFM) observation was made in ambient conditions using a scanning microprobe system (SPI 3800N, Seiko Instrumental Co.) with a Si_3N_4 probe.

3. Results and Discussion

3.1. Immobilization of TOAB-AuNPs onto Au/BDMT and Au/HDT electrodes

Fig. 1

Curve a in Fig. 1 shows the absorption spectrum of TOAB-AuNPs in toluene, exhibiting a plasmon absorption band at 524 nm. Curves b and c show the absorption spectra of the colloidal AuNPs after 20 min immersion of BDMT-modified Au (Au/BDMT) and HDT-modified Au

(Au/HDT) electrodes, respectively. For curves b and c, except for a decrease in the absorbance from curve a (original solution), no shift in the plasmon resonance absorption band was observed. The immersion of Au/BDMT or Au/HDT electrodes never affected the optical property of the original AuNPs colloids. Note that prior to the immersion of Au/BDMT and Au/HDT electrodes into TOAB-AuNPs toluene solution, both of them were immersed in toluene for 20 min. When omitting this immersion procedure, we observed a significant decrease in the absorbance intensity of the colloidal solution of TOAB-AuNPs at the plasmon resonance band in addition to the color change from wine red to blue. Particularly, we observed significant changes for colloidal solution of AuNPs in which the Au/HDT electrode was immersed. It is likely that during the monolayer formation some of the dithiol molecules might be physisorbed on the SAM surface [28] and these loosely bound dithiol molecules might have desorbed from the electrode to the colloidal solution of AuNPs, resulting in an enormous decrease in the absorbance and change of color from wine red to blue due to aggregation. These changes observed in the present study are similar to those reported in a recent paper for a solution of TOAB-AuNPs after mixing certain ratio of 1,9-nonanedithiol [29]. On the other hand, we have not observed any color change or significant change in the absorbance when the electrodes were pretreated with toluene for 20 min.

3.2. Characterization by QCM and AFM

Fig.2

The amount of AuNPs deposited on Au/HDT electrode was quantitatively estimated by QCM. Fig. 2 shows the frequency changes associated with the deposition of TOAB-AuNPs on an HDT modified QCM Au electrode. Upon injection of AuNPs toluene solution into a stirred toluene solvent, immediate initiation of steep decrease in the resonance frequency was observed. This suggests that the immobilization of AuNPs on HDT is fast. The frequency change down to

plateau region corresponds to ca. 1028 ng (ca. 1.2×10^{12} particles cm^{-2}). Assuming that the AuNPs (6 nm diameter) form a nanoparticle layer in a 2D hexagonal close packing structure, a surface coverage of 3.2×10^{12} particles cm^{-2} is expected. This fact indicates that the experimental surface coverage of AuNPs is ca. 38%. It is worth to compare this surface coverage of TOAB-AuNPs with the reported value for C-AuNPs on HDT modified electrode [30]. Although immobilization of C-AuNPs on HDT is a rapid process, the surface coverage was found to be only 0.36% [30]. In this case, the negatively charged AuNPs electrostatically repel each other and are well-separated on a substrate once being adsorbed [30]. Thus, less coverage of C-AuNPs was observed at HDT modified electrode. However, in the case of TOAB-AuNPs, the observed higher coverage of AuNPs is attributed to the facile nature of TOAB ligand stabilizing the AuNPs similar to 4-dimethylaminopyridine stabilized AuNPs [31] and insignificant electrostatic repulsion between TOAB-AuNPs.

Fig. 3

The surface morphology and size of the deposited TOAB-AuNPs on HDT modified QCM electrode used in Fig. 2 was examined by AFM. Tapping mode and 3D images of AuNPs are shown in Fig. 3. It can be seen from the image of Fig. 3A that the immobilized AuNPs were densely packed and were mostly spherical in shape. The height of the AuNPs film is 6-7 nm (Supporting Information, Fig. S2). The surface morphology of the AuNPs is similar to that observed for multilayer AuNP films formed by repeated AuNPs adsorption using linker molecules [31].

3.3. Electrochemical characterization of immobilized AuNPs

The redox markers, $[\text{Fe}(\text{CN})_6]^{4-/3-}$ and $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ are well-suited to examine the electronic communication between the immobilized AuNPs and the underlying electrode surface, because their voltammetric responses are sensitive to the state of electrode surface modification.

Fig. 4A

Fig. 4A shows CVs obtained for 1 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ in 0.2 M phosphate buffer solution at bare and surface modified Au electrodes at a scan rate of 50 mV s^{-1} . A well-defined voltammogram with 70 mV peak separation (ΔE_p , the difference between anodic and cathodic peak potentials) was observed for ferricyanide at a bare Au electrode (dashed curve a). On the other hand, the electron transfer reaction was markedly hindered at Au/BDMT electrode (curve b). The absence of appreciable faradaic current at this electrode indicates that BDMT SAM is densely packed on Au electrode. Although toluene was used as a solvent for the preparation of SAMs on Au electrodes in the past [31,32], we tested whether toluene has any impact on the integrity of the structure of BDMT during the immobilization of AuNPs in toluene. To avoid this, prior to immobilization of AuNPs, we have immersed this electrode in toluene for 20 min. It can be seen from curve c that the barrier property of the electrode was slightly altered after being treated with toluene. The observed response of this electrode towards ferricyanide is consistent with the spectral and color changes of colloidal AuNPs as discussed above (*vide supra*).

The alteration of the SAM barrier property by toluene is due to the dissolution of loosely bound dithiols into toluene [28]. Further immersion of this electrode into toluene no longer alters the barrier properties. Curve d shows the CV obtained for Au/BDMT/AuNPs electrode after 20 min immersion in the colloidal solution of AuNPs. Obviously, this electrode exhibits a reversible

voltammetric response for ferricyanide. The peak separation of 70 mV was observed at this electrode and the redox current was slightly higher than at bare Au electrode. The CV obtained for ferricyanide at this electrode was highly stable upon repeated potential cycling. Similar reversible voltammetric response for ferricyanide was also observed at Au/HDT/AuNPs electrode. The CVs obtained for ferricyanide at both these electrodes were highly stable upon repeated potential cycling. The electron transfer reaction of $[\text{Ru}(\text{NH}_3)_6]^{3+/2+}$ was also studied at the AuNPs immobilized electrodes. We observed a reversible redox response with $\Delta E_p = 70$ mV at both the electrodes (Figure not shown). Natan and co-workers [10] have shown that reversible response for ferricyanide was attained only after the 7th layer of C-AuNPs was formed on the electrode substrate. On the other hand, Schiffrin and coworkers [19] attained reversible response for ferricyanide after the 4th layer of TOAB-AuNPs was formed. Recently, few papers have been published for the immobilization of AuNPs on electrodes modified with alkanedithiols and 1,4-benzenedimethanethiol [22,23]. In these papers, only quasi-reversible response for ferricyanide was achieved even after 12 h immobilization [22,23]. In the sharp contrast, we achieved a reversible response for ferricyanide within 20 min immobilization of TOAB-AuNPs on both Au/HDT and Au/BDMT electrodes.

Fig. 4B

We also studied the electron transfer reaction of ferricyanide by varying the immersion time of modified electrodes in the colloidal solution of TOAB-AuNPs. The voltammetric current of ferricyanide increased when the immobilization of AuNPs time increased from 5, 10, 15 min and reached a reversible redox response for ferricyanide after 20 min immobilization (Fig. 4B). In a separate experiment, we immersed Au/BDMT and Au/HDT electrodes into 4 nm C-AuNPs for 20 min, washed with water and then examined the redox behavior of $[\text{Fe}(\text{CN})_6]^{4-/3-}$. We

obtained only a small faradaic response with $\Delta E_p > 350$ mV (Fig. not shown) for $[\text{Fe}(\text{CN})_6]^{4-/3-}$. However, after 12 h immobilization we attained $\Delta E_p = 90$ mV. This fact reveals that immobilization of C-AuNPs on dithiol SAMs takes longer time to attain the coverage of AuNPs giving near-reversible redox response of ferricyanide than the immobilization of TOAB-AuNPs. Now a question may be why immobilization of TOAB-AuNPs onto dithiol SAMs takes shorter time than the immobilization of C-AuNPs? Natan and co-workers studied the kinetic aspects of covalent immobilization of C-AuNPs onto organosilane polymers [34]. They suggested that at short immobilization time, colloidal Au binds to random sites on organosilane coated substrates [34]. However, at longer immobilization times, interparticle repulsion results in a 'saturation' coverage at approximately 30% of a densely packed monolayer [34]. Although the kinetics of immobilization of TOAB-AuNPs were not studied in the past, it has been reported that binding of TOAB ions with AuNPs is labile and can be easily exchanged by other molecules [35,36]. Presumably, the interaction of citrate ions with AuNPs is relatively weaker than the interaction of citrate ions with AuNPs [37]. Thus, immersion of thiol terminated SAMs into TOAB-AuNPs leads to the rapid immobilization of AuNPs. As suggested by Brust and co-workers [25], TOAB ions might be easily replaced upon the attachment of the thiol groups and dissolved into toluene. The observed higher surface coverage of TOAB-AuNPs when compared to C-AuNPs is due to the presence of weak electrostatic repulsion between TOAB capped AuNPs.

Note that the CVs obtained for intermediate immersion time periods (curves b and c in Fig. 4B) are not a sum in shape of curve a for Au/HDT and curve e for reversible response at a macroscopically planar electrode. Most likely, AuNPs first form a number of nano-electrodes and then microelectrodes and islands rather than forming a large densely packed domain of AuNPs from the initial stage. When most of the islands grew to behave as macroscopic planar

electrodes in the experimental time scale, curve d was obtained.

3.4. *Electroreflectance studies*

Fig. 5

Fig. 5 shows the ER spectrum of a Au/BDMT electrode in 0.2 M phosphate buffer solution. It shows a typical ER spectrum expected for an organic monolayer coated Au electrode, being different from the spectrum of a bare polycrystalline Au electrode. The latter shows a negative going broad ER band with a maximum at 500 nm in the real part due to the potential dependent change of the surface free electron density [8,27].

Fig. 6

Fig. 6 illustrates the ER spectra of Au/BDMT/AuNPs and Au/HDT/AuNPs electrodes. They show positive-going strong real part ER signals with a maximum at 554 nm and 584 nm for Au/BDMT/AuNPs (curve a) and Au/HDT/AuNPs (curve b), respectively. The spectrum is assigned to the potential-dependent charging-discharging process of the AuNPs in light of previous reports [8,26,27,38]. When AuNPs are not interacting with each other on the electrode surface, the ER peak due to charging-discharging should appear at slightly shorter wavelength than the plasmon absorption maximum wavelength of the colloidal solution [8]. Therefore, observed 30 nm and 60 nm red shifted peak wavelengths when compared to the colloidal solution of AuNPs (Fig. 1a) clearly indicates that the AuNPs are densely packed and aggregated on the surface of the SAMs. But the aggregation is not at so great extent as to exhibit a strong and broad absorption band around 700-900 nm region. The ER signals of both the electrodes are different from that of a bulk polycrystalline Au electrode, indicating that the individual AuNPs are not fused to form a bulk gold on the SAM surfaces [39]. Similar red shifted plasmon

resonance bands were noticed for the multilayer assemblies of AuNPs on glass and ITO substrates [14,34]. Further, the observed 30 nm more red shift in the ER signal of AuNPs on HDT electrode (curve b) demonstrates that the immobilized AuNPs on Au/HDT electrode may be more extensively aggregated than those on AuNPs immobilized on Au/BDMT electrode (curve a).

Here it is worthwhile to compare the ER bands observed in the present study with the reported ER band for the 2 layers of TOAB-AuNPs on 1,4-benzenedimethanethiol coated Au electrode [21]. It should be emphasized that in the present study, we measured the ER signal for a single layer of AuNPs on Au/BDMT and Au/HDT electrodes. Although a red-shifted plasmon resonance band was observed also in the reported paper [21] as we observed in the present study, the band is negative going in the reported paper. We reported similar positive going band as we observed in Fig. 6 for the C-AuNPs immobilized on 1-mercapto-11-aminoundecane coated Au electrode [11]. The origin of the difference between the reported negative going ER signal [21] and the observed positive going ER signals in Fig. 6 is possibly due to the difference in the definition of the sign of the ER signal. Nevertheless, in addition to the electron transfer reaction of ferricyanide, the appearance of red-shifted strong ER signals confirm that a good electronic communication can be achieved between a single layer of AuNPs and underlying bulk metal. The characteristics of electron transfer reaction of ferricyanide and a red shift of the ER signals clearly suggest that the AuNPs completely cover the surface of dithiol SAMs in a densely packed manner so that the particle layer acts electrochemically as a planar Au electrode but not optically.

3.5. Oxidation of ascorbic acid (AA) at Au/HDT/TOAB-AuNPs and Au/HDT/C-AuNPs electrodes

The advantage of the TOAB-AuNPs modified electrode prepared by 20 min deposition was

demonstrated by studying the oxidation of AA at both TOAB-AuNPs and C-AuNPs modified electrodes in phosphate buffer solution (pH = 7.2). Accurate determination of AA is biologically of paramount importance because its content in biological fluids can be used to access the amount of oxidation stress in human metabolism [40]. Very recently, we reported that C-AuNPs immobilized on HDT modified electrode shows an electrocatalytic activity towards AA [9]. Thus, we have taken AA as a probe to test the electrocatalytic activity of TOAB- and C-AuNPs modified electrodes. Linear sweep voltammograms (LSVs) obtained for 0.5 mM AA in 0.2 M phosphate buffer solution (pH 7.2) at bare Au, Au/HDT, TOAB-AuNPs modified electrodes prepared by 20 min immobilization and C-AuNPs (ca. 4 nm-diameter)-modified electrode prepared by 12 h immobilization are shown in Fig. 7.

Fig. 7

At a bare Au electrode, the oxidation of AA occurs at 0.48 V (curve a) whereas no oxidation peak was observed at Au/HDT electrode (curve b) within the potential region studied. However, at Au/HDT/TOAB-AuNPs electrode, oxidation of AA occurs at 0.23 V, which is nearly 250 mV less positive potential than that at bare Au electrode (curve c). In addition, the current response for AA at this modified electrode is more than twice of that at the bare Au electrode. On the other hand, C-AuNPs modified electrode oxidizes AA at 0.32 V which is 90 mV more positive than that at TOAB-AuNP-modified electrode (curve d). In addition, the oxidation current for AA at C-AuNPs is less than that at TOAB-AuNP-modified electrode. These results indicate that TOAB-AuNP-modified electrode is superior to C-AuNP-modified electrode in two aspects. Firstly, the oxidation of AA was observed at 90 mV less positive potential with higher current at TOAB-AuNP-modified electrode. Secondly, time consumption for the modification of TOAB-AuNP-modified electrode is less than 30 min in contrast to 12 h

for the modification of C-AuNPs electrode.

4. Conclusion

Fabrication of a densely packed single layer of AuNPs on 1,6-hexanedithiol (HDT) and 1,4-benzenedimethanethiol (BDMT) SAMs modified Au electrodes by short duration of time was reported in this paper. The electronic communication between the AuNPs and the underlying bulk Au electrode was demonstrated by cyclic voltammetric studies of solution dissolved species and electroreflectance spectroscopy. Cyclic voltammetric studies indicate that Au/BDMT/AuNPs and Au/HDT/AuNPs electrodes exhibit a reversible redox response for $[\text{Fe}(\text{CN})_6]^{3-/4-}$ and $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ redox species in solution. Electroreflectance studies show a positive going red-shifted strong electroreflectance signals for the immobilized AuNPs on BDMT/Au and HDT/Au electrodes when compared to bulk Au electrode, demonstrating that the immobilized AuNPs are different from that of bulk gold. The immobilized AuNPs are densely packed on the surface of the SAMs of dithiols. Further, the advantage of TOAB-AuNPs prepared by short time immobilization was demonstrated by the observed higher oxidation current for AA with 90 mV less positive potential shift in the oxidation peak when compared to C-AuNPs modified electrode prepared by 12 h immobilization. It is expected that the present AuNPs modified electrode could be used to design new electrodes for the possible applications in electrocatalysis and biosensors.

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Figure Captions

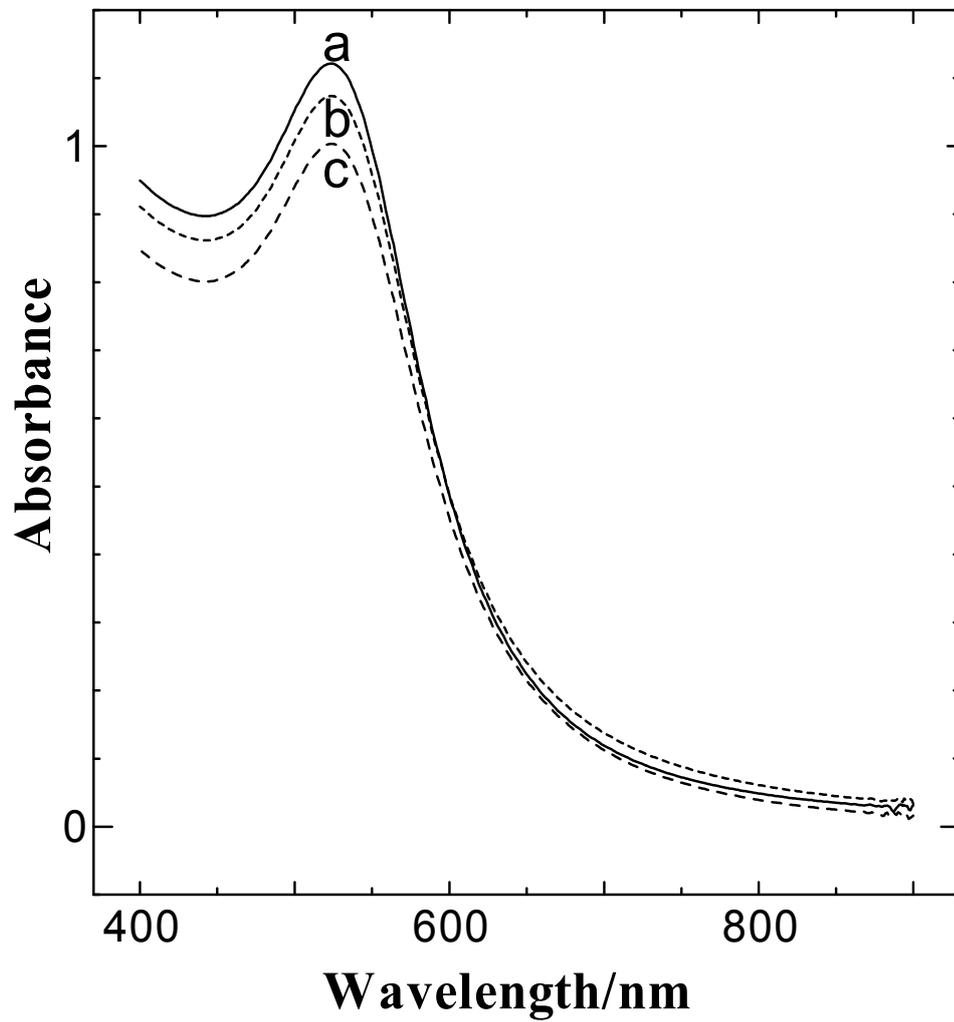


Fig. 1

UV-visible absorption spectra of TOAB-AuNPs in toluene: (a) before immersion of the electrode, (b) after immersion of Au/BDMT for 20 min, and (c) after immersion of Au/HDT electrodes for 20 min.

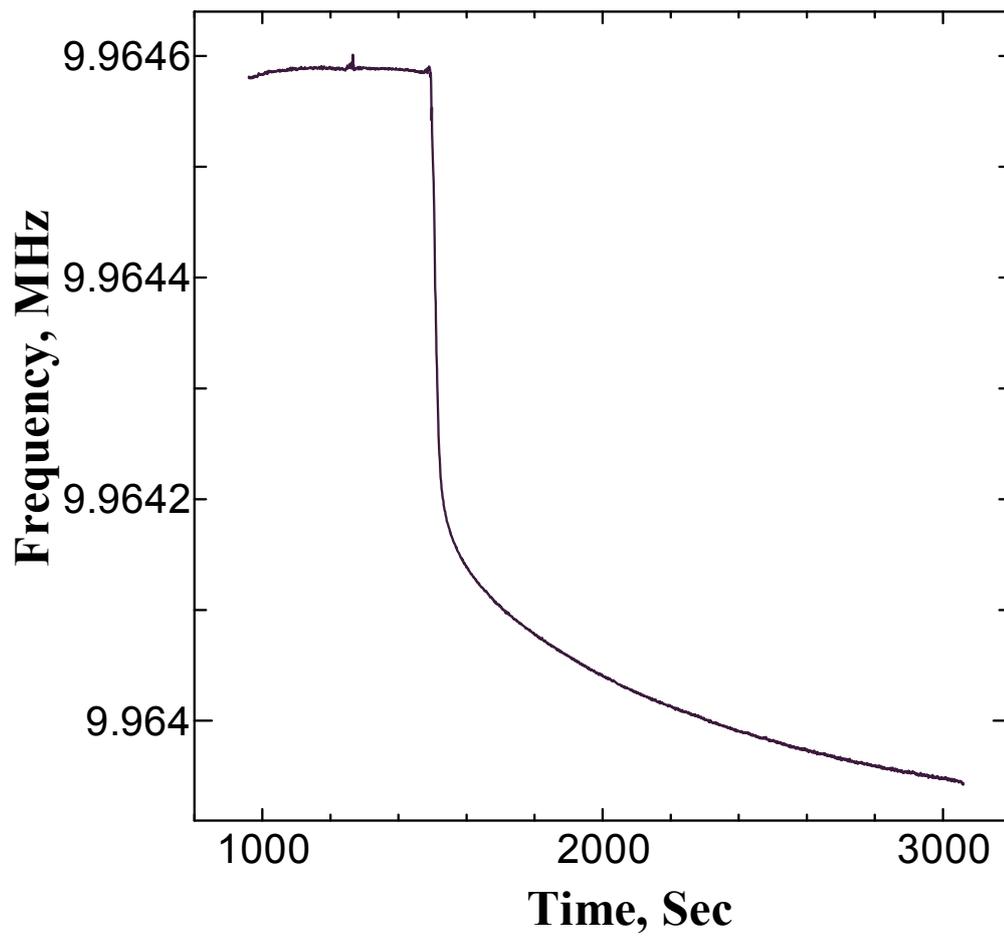


Fig. 2

QCM response obtained for Au/HDT electrode after injection of TOAB-AuNPs into toluene.

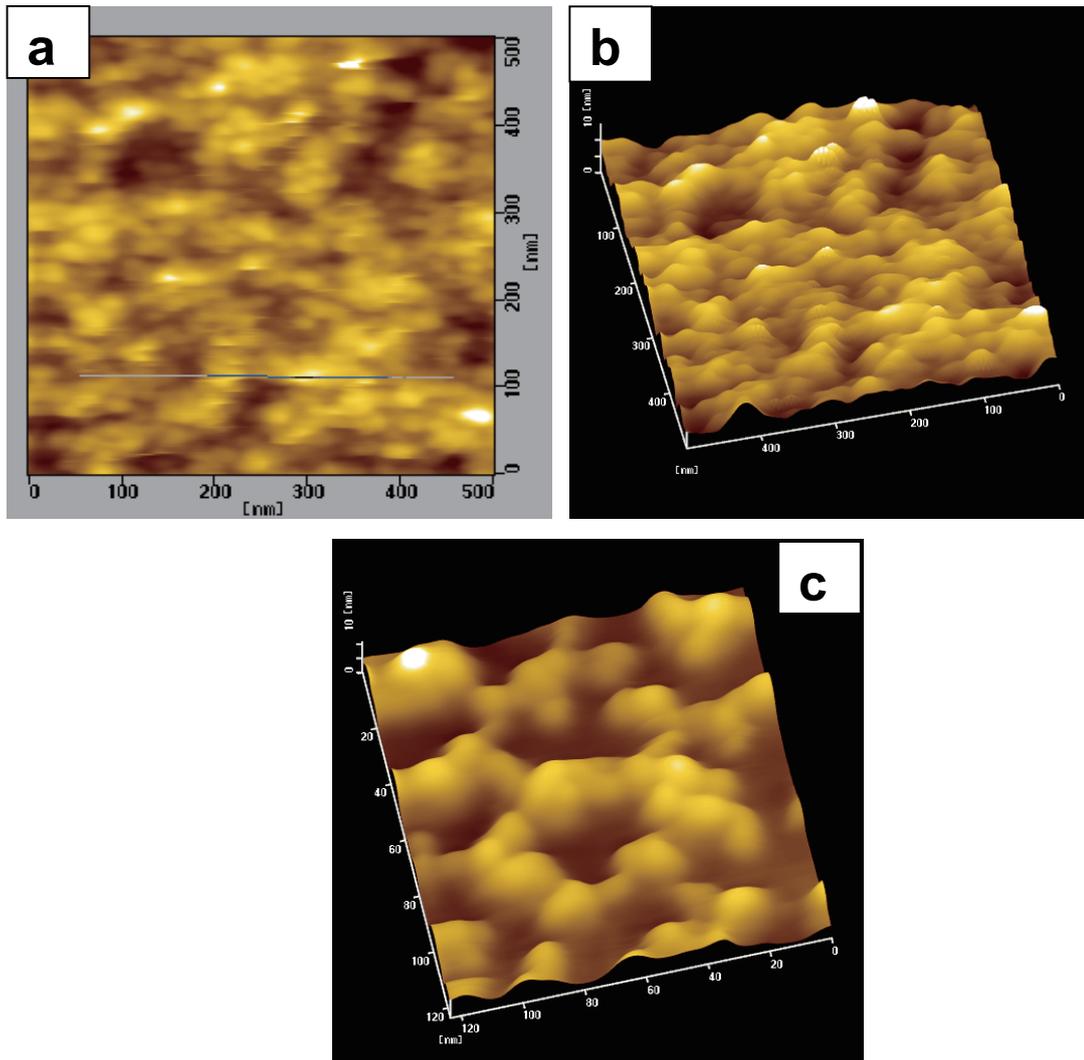


Fig. 3

AFM images of Au/HDT/TOAB-AuNPs: (A) tapping mode, (B) 3-D view and (C) close view of (B).

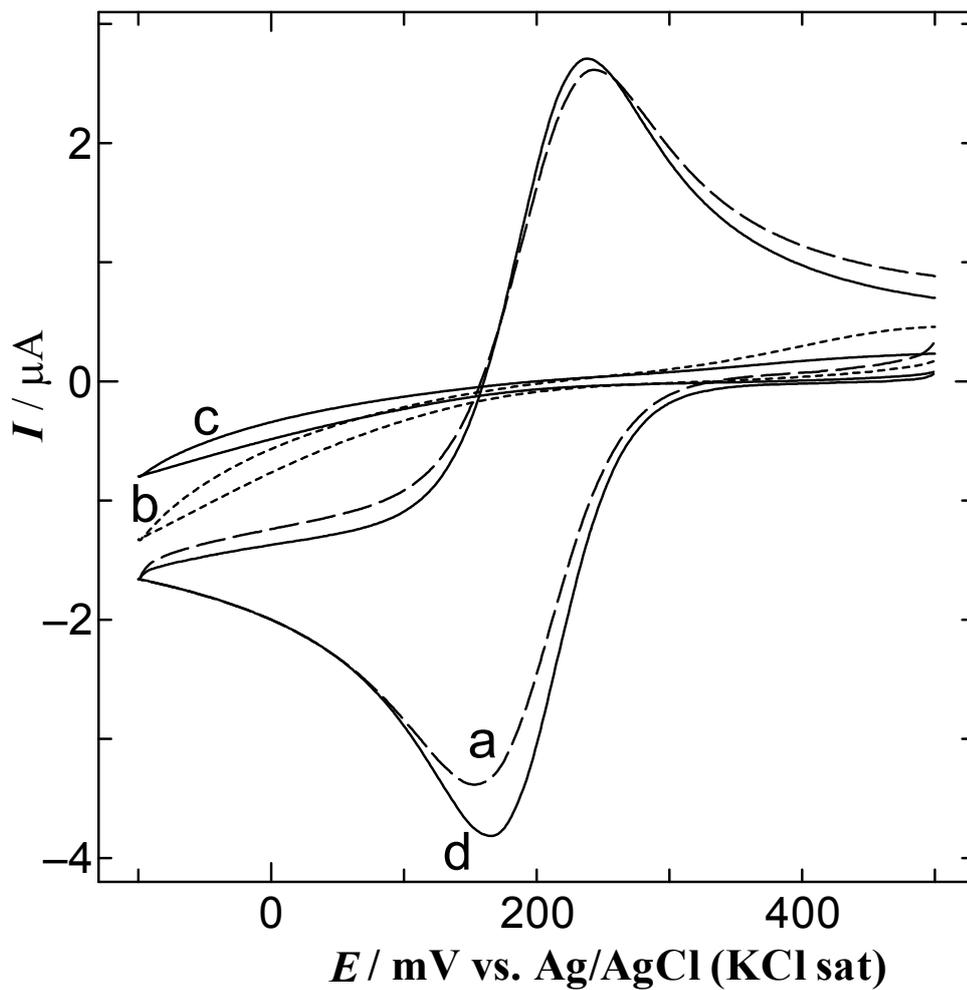


Fig. 4A

CVs obtained for (a) bare Au, Au/BDMT (b) before and (c) after immersed in toluene for 20 min and (d) Au/BDMT/AuNPs electrodes in 0.2 M phosphate buffer solution containing 1 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ at a scan rate of 50 mV s^{-1} .

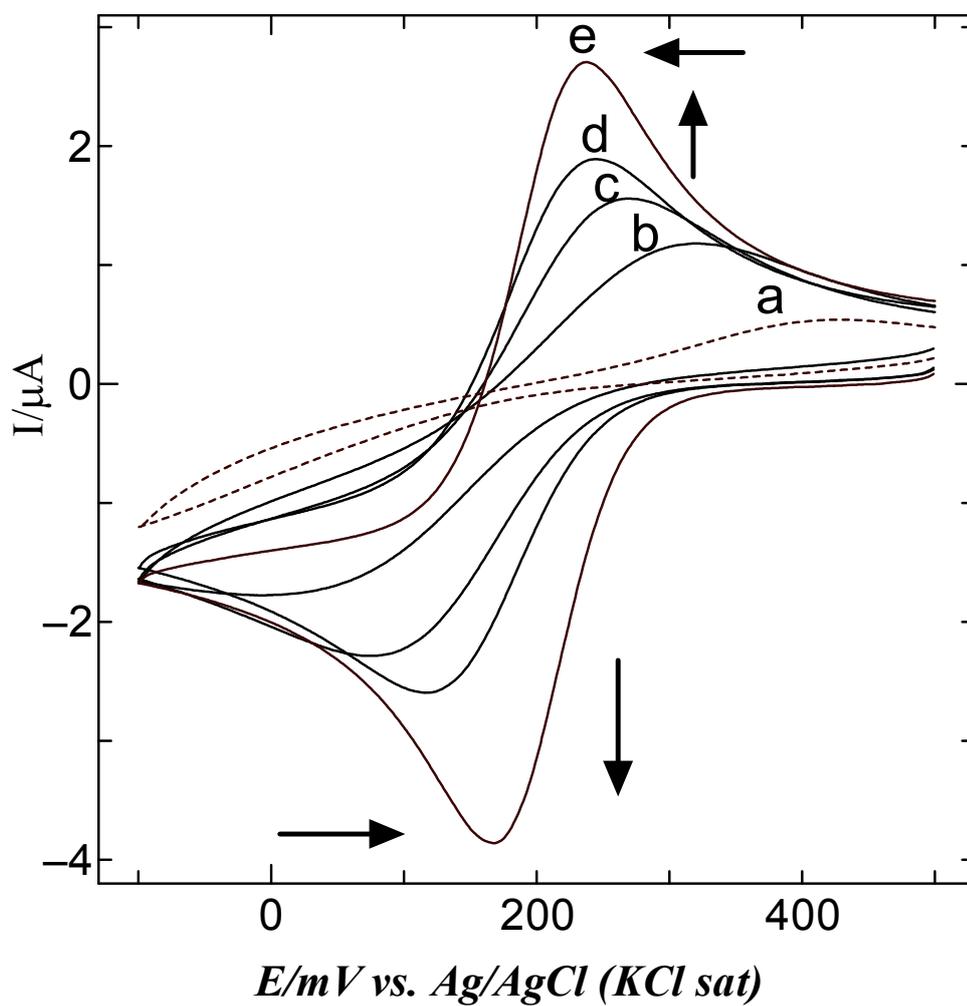


Fig. 4B

CVs obtained for 1 mM $K_3[Fe(CN)_6]$ containing 0.2 M phosphate buffer solution at Au/HDT electrode after immersed (a) 0, (b) 5, (c) 10, (d) 15 and (e) 20 min in TOAB-AuNPs at a scan rate of 50 mV s^{-1} .

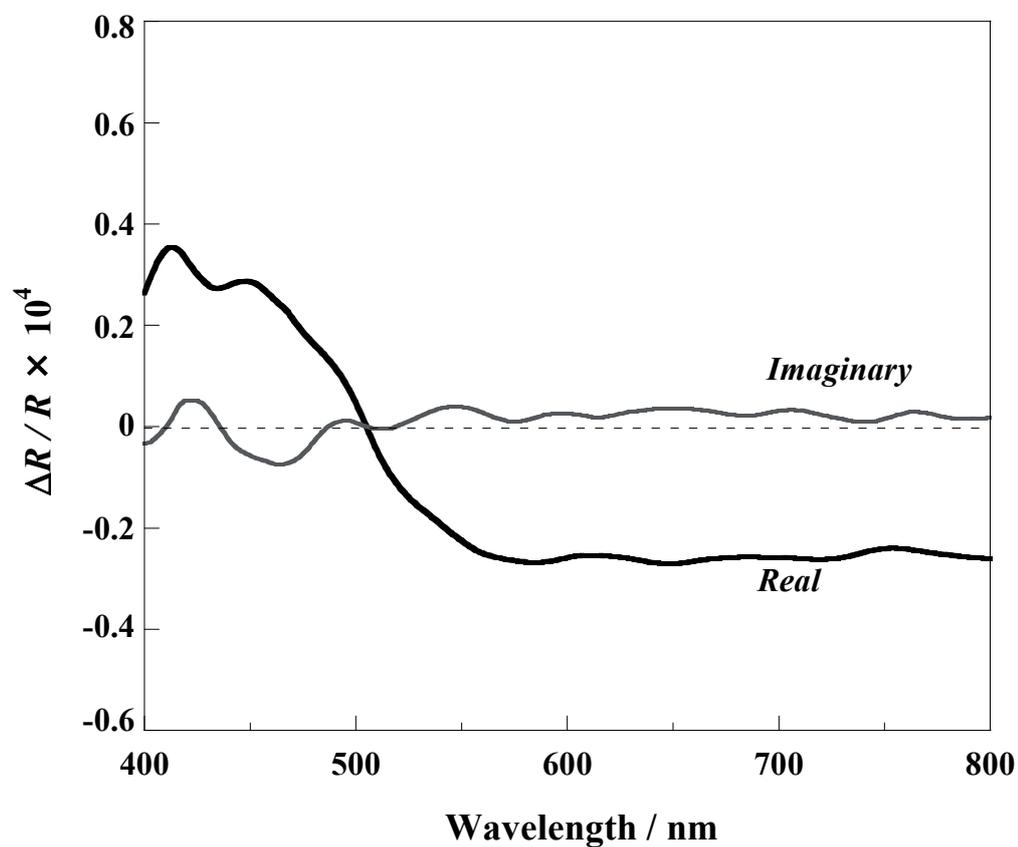


Fig. 5

ER spectrum of real part and imaginary parts of Au/BDMT electrode. The electrolyte solution was 0.2 M phosphate buffer solution, the dc potential (E_{dc}) was 0.0 V, the sine-wave potential modulation zero-to-peak amplitude (ΔE_{ac}) was 99 mV with a frequency (f) of 14 Hz.

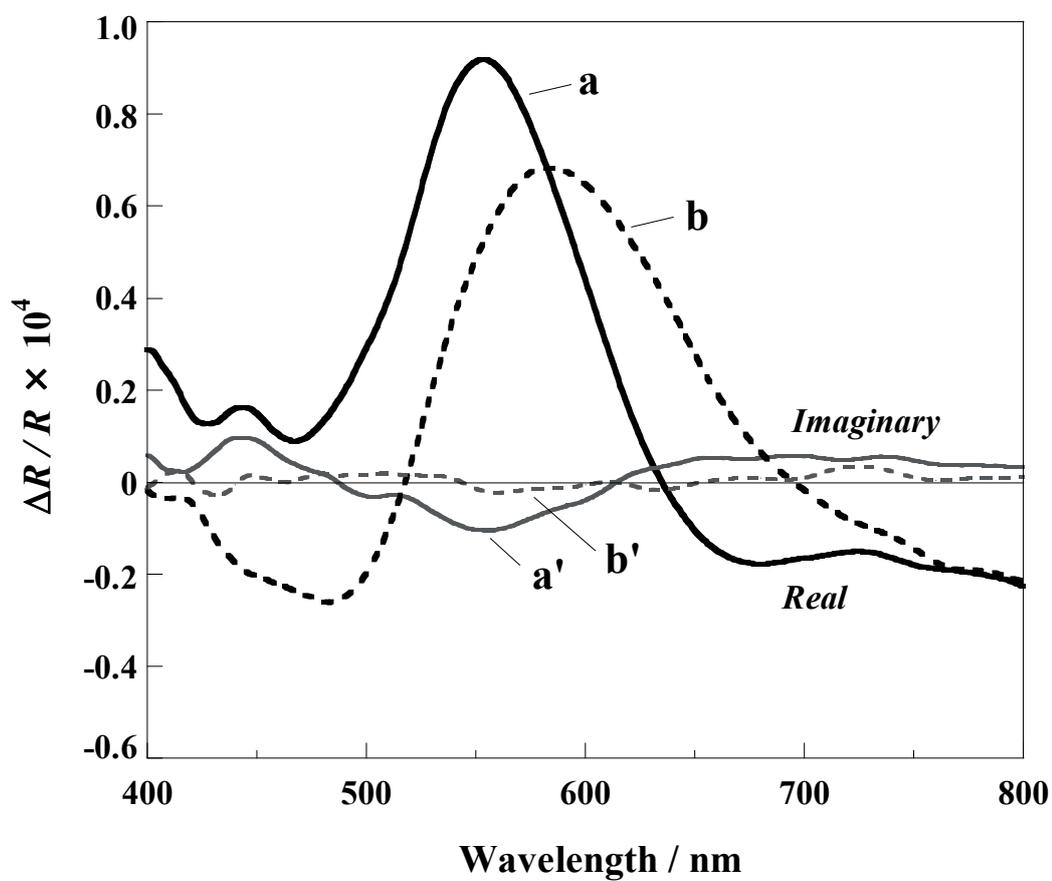


Fig. 6

ER spectra of (real and imaginary parts) Au/BDMT/AuNPs (a and a') and Au/HDT/AuNPs (b and b'). The electrolyte solution was 0.2 M phosphate buffer solution. Conditions of ER measurements were $E_{dc} = 0.0$ V, $\Delta E_{ac} = 99$ mV, $f = 14.0$ Hz.

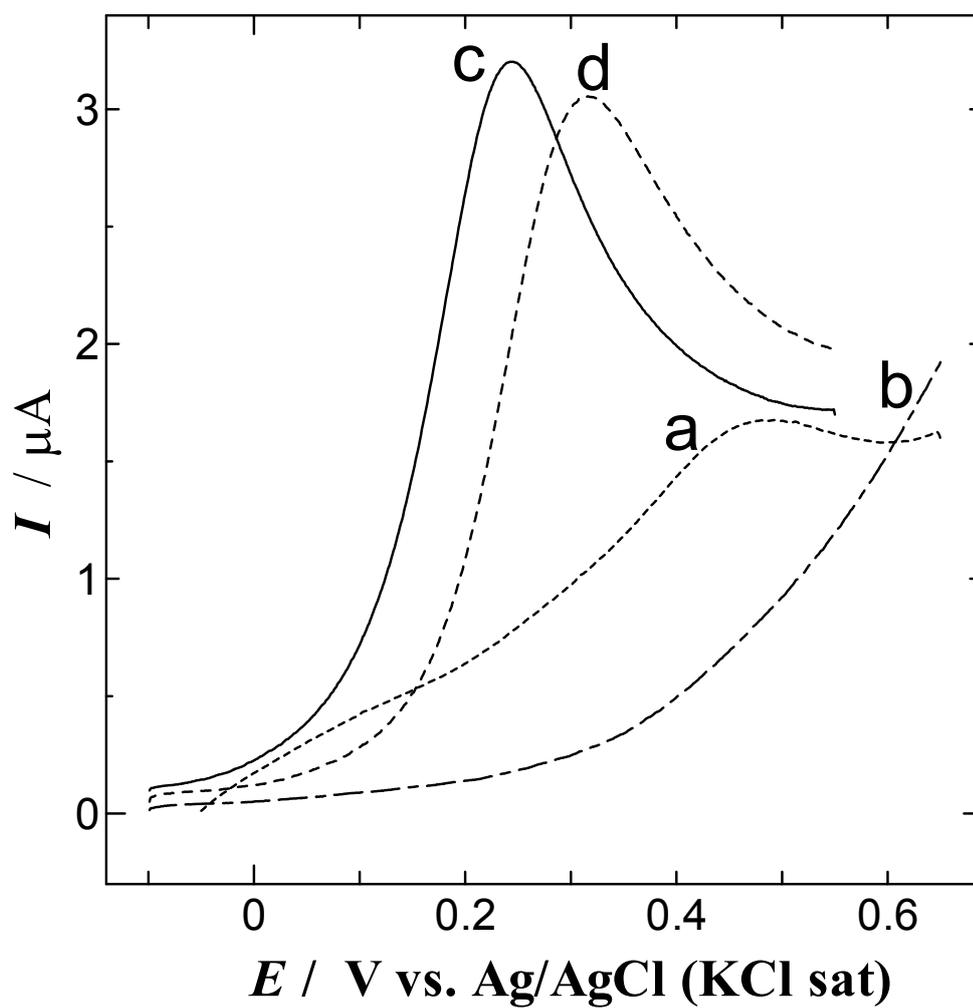


Fig. 7

LSVs obtained for 0.5 mM AA at (a) bare Au, (b) Au/HDT, (c) Au/HDT/TOAB-AuNPs and (d) Au/HDT/C-AuNPs at a scan rate of 50 mV s^{-1} .

Supporting Information

Short-time preparation and electrochemical properties of a single layer of tetraoctylammonium bromide capped Au nanoparticles on dithiol self-assembled monolayer-modified Au electrode

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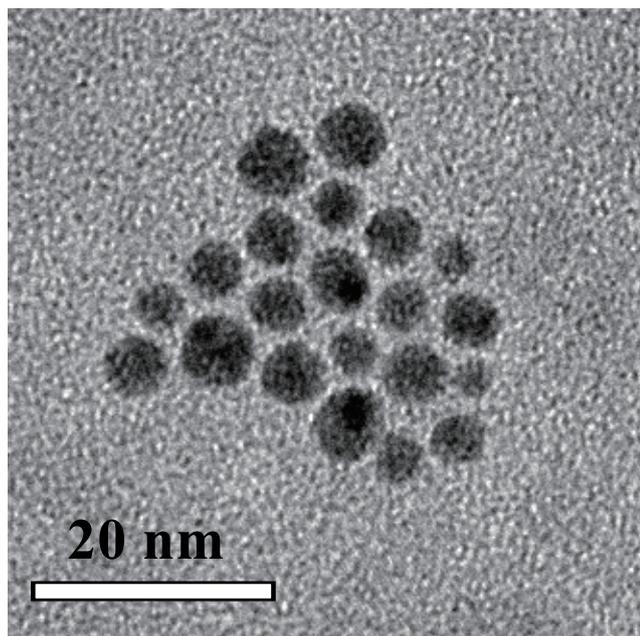


Fig. S1. High-resolution TEM image of TOAB-AuNPs.

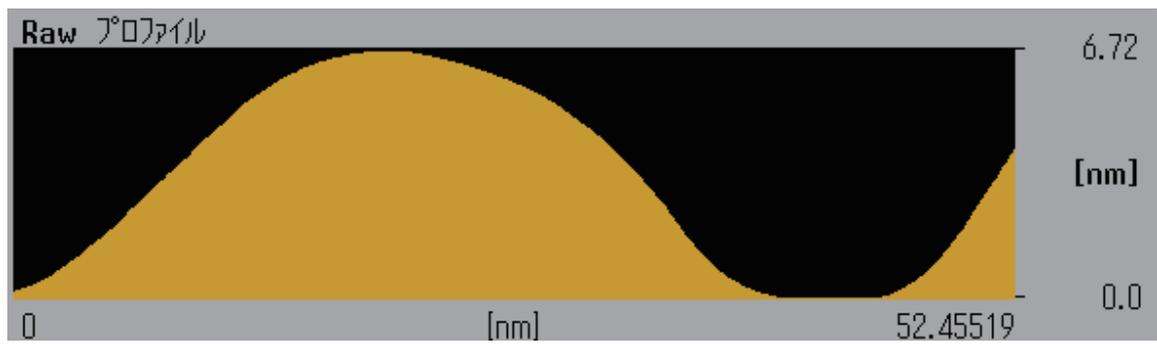
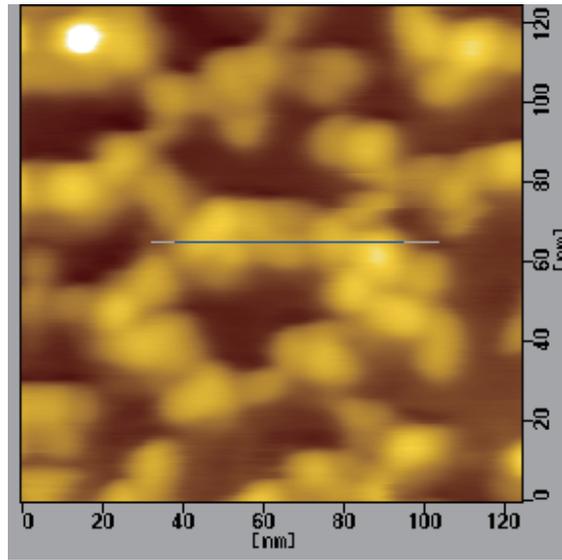


Fig.S2. Close view of Fig.3 and height profile of Au/HDT/TOAB-AuNPs.

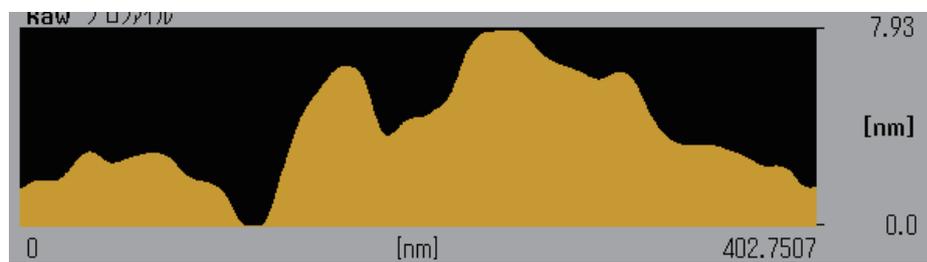


Fig. S2. Close view of Fig. 3 and height profile of Au/HDT/TOAB-AuNPs.