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Electrocatalytic Oxidation of Glucose at Gold-Silver Alloy, Silver and Gold Nanoparticles in an Alkaline Solution

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Abstract

Gold, silver and gold-silver alloy nanoparticles capped with decanethiolate monolayer shells (DT-Au, DT-Ag and DT-Au/Ag) were synthesized, with core sizes 2.3 (± 1.0), 3.3 (± 1.0) and 2.0 (± 1.0) nm, respectively. To activate the synthesized nanoparticles for the electrocatalytic oxidation of glucose, nanoparticles were treated at 300 °C for 2 hours. Heat-treated nanoparticles surfaces were characterized by FT-IR, X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and cyclic voltammetry (CV). The elimination of C-H alkyl chains and thiolates from DT capped Au and Au/Ag nanoparticles was evident post heat-treatment by TGA, FT-IR and XPS investigations. In DT-Ag nanoparticles, C-H chains from DT were eliminated by heat-treatment, though thiolate was still present on nanoparticle surfaces. However, the thiolate from DT was eventually removed by further oxidation and reduction cycle treatments in an alkaline solution. After heat-treatment at 300 °C for 2 hours, the surface content ratio of Au and Ag changed from Au:Ag(84:16) to Au:Ag(73:27). This tendency to increase the surface content ratio of Ag after heat-treatment was also observed in other Au-Ag alloy nanoparticle content ratios. Results from cyclic voltammograms at Au/Ag nanoparticles modified PFC electrodes in H₂SO₄ and NaOH solutions indicated that the distribution of Au and Ag atoms of Au/Ag nanoparticles on nanocrystal surfaces is homogeneous.

Electrocatalytic peaks for glucose oxidation in a 0.1 mol dm⁻³ NaOH solution were observed around -0.4 and 0.4 V (vs. Ag/AgCl) at heat-treated Au nanoparticle modified carbon electrode and around -0.4 and 0.6 V at heat-treated Au/Ag nanoparticle modified electrode, which correspond to the oxidation of glucose and further oxidation of gluconolactone generated by the first oxidation peak (-0.4 V), respectively. It is interesting to note that the catalytic current at Au/Ag nanoparticle modified electrodes was observed from ca. -0.75 V, which represents a negative potential shift of ca.
0.1 V compared to that at Au nanoparticle modified electrodes. This result indicates that Au-Ag alloy nanoparticles are effective catalysts for the electrocatalytic oxidation of glucose. At both Au and Au/Ag nanoparticles, aldose-type monosaccharides showed catalytic oxidation peaks in an alkaline solution, however ketose-type monosaccharides did not show any catalytic peaks in the potential region of -0.8 ~ 0.8 V.

After the controlled-potential electrolysis at a potential of -0.3 V, gluconolactone (or gluconate, a two-electron oxidation product) was only detected at a current efficiency of 100 % at Au and Au/Ag nanoparticles modified carbon electrodes. In the case at 0.3 V, oxalate (an 18-electron oxidation product) and gluconolactone as the main product were detected at Au nanoparticle modified electrodes, and formate (a 12-electron oxidation product) in addition to oxalate and gluconolactone as the main products were detected at both Au/Ag and Ag nanoparticles modified electrodes. These results indicate that the catalytic selectivity at a potential of 0.3 V would be strongly governed by silver atoms containing Au/Ag nanoparticles surfaces.

**Keywords**

Electrochemistry, oxidation, glucose, nanoparticle, alloy, gold, silver
1. Introduction

The electrocatalytic oxidation of glucose is an attractive research field for applications in glucose-oxygen fuel cells and for the development of glucose sensors for medical and food industries [1-5]. Gold is an attractive metal for the oxidation of glucose. The electrocatalytic oxidation of glucose has been examined extensively [1-3]. Recently, a single crystal gold modified with catalytically active metals (such as Ru, Ag, Cu, Pt, Pd and Cd) by under potential deposition (UPD) was studied for the oxidation of sugar. The effective electrochemical oxidation of glucose was demonstrated at Ag-UPD single crystal gold electrodes [5,6]. These previous reports suggest that multi component surface compositions are expected to produce synergistic effects to achieve high activity and selectivity.

Recently, gold nanoparticles have been studied extensively for the design and fabrication of catalysts, an enhancement of catalytic activity or selectivity, and the large surface area-to-volume ratios [7-23], because the catalytic properties of gold nanoparticles with a few nanometer cores could change completely due to particle phase transitions i.e. atomic to metallic phase property changes over this size range [7-10,13,14,16,20-22]. In a previous investigation, we found that the catalytic activity on the controlled-potential electrolysis of glucose was improved by use of carbon electrodes modified with ~2 nm core sized gold nanoparticles as catalysts, and electrolysis products were determined along with current efficiencies [24,25]. To our best knowledge, however, the glucose oxidation has not been previously investigated by use of gold-based bimetallic nanoparticles as catalysts. Nanoparticles with multi component surface compositions would be expected to produce synergistic effects, which in the case of catalysts would provide high activities and selectivity for the electrocatalytic oxidation of glucose.
In the present study, Au, Ag and Au-Ag alloy nanoparticles capped with decanethiol monolayer shells were synthesized. We selected Ag for gold-based alloy nanoparticles, because Ag atom modified gold electrodes by UPD showed the effective electrochemical oxidation of glucose [5,6]. To activate the synthesized nanoparticles prior to the examination of the electrocatalytic oxidation of glucose, nanoparticles were treated at 300 °C for 2 hours. Nanoparticles surfaces after heat-treatment were characterized by FT-IR, X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and cyclic voltammetry (CV). Electrocatalytic activities and electrolysis product selectivities were investigated by using heat-activated nanoparticles. The results obtained indicate that Au-Ag alloy nanoparticles are also effective catalysts for the electrocatalytic oxidation of glucose. Furthermore, a strong metal composition dependence of nanoparticles on electrolysis oxidation products was observed at Au and Au/Ag nanoparticles at electrolysis potential of 0.3 V, which indicate that catalytic selectivity would be strongly governed by Ag atoms containing Au/Ag nanoparticle surfaces. Our preliminary results suggest the design and preparation of catalysts with bifunctional properties are important in achieving high activities and selectivities in the electrocatalytic oxidation of glucose, and for applications using glucose-oxygen fuel cells, and for the development of glucose sensors for the medical and food industries.

2. Experimental Section

2.1. Chemicals

Hydrogen tetrachloroaurate (III) trihydrate (HAuCl₄·3H₂O, 99.9+ %), sodium borohydride (NaBH₄, 99.995 %) and decanethiol (DT, 96 %) were purchased from Aldrich and used as receive. Tetraoctylammonium bromide (TOAB, 98 %) and silver nitrate (AgNO₃, 99.8 %) were obtained
from Lancaster and Nacalai Tesque (Japan), respectively, and used as receive. Water was purified with a Millipore Milli-Q water system. Other chemical reagents used were of analytical grade.

2.2. Preparation of Monometallic Gold and Silver Nanoparticles and Gold-Silver Alloy Nanoparticles

The synthesis of gold nanoparticles with ~2 nm cores capped with decanethiolate monolayer shells (DT-Au nanoparticles) were synthesized by Schiffrin’s two-phase synthesis protocol [11,12]. Briefly, for the synthesis of DT-Au, 0.75 mmol HAuCl₄ was dissolved in 25 mL of a purified water solution. To transform AuCl₄⁻ from aqueous phase to toluene phase, an HAuCl₄ aqueous solution was added to an 80 mL toluene solution containing tetraoctylammonium bromide (TOAB, 3.0 mmol) as a phase transfer reagent. Then, DT as a capping agent was added to the toluene phase at a 2:1 DT/Au ratio. An aqueous solution (25 mL) of 20 mmol NaBH₄ as a reducing agent was slowly added (dropwise) to the solution. The reaction proceeded with stirring at ambient temperature for 2 hours. Synthesized DT-Au nanoparticles were then purified by multiple wash steps using ethanol. Nanoparticles were dried and dissolved in hexane.

The synthesis of silver nanoparticles with ~3 nm cores capped with decanethiolate monolayer shells (DT-Ag nanoparticles) followed a previously reported procedure [17-19]. Briefly, 0.75 mmol AgNO₃ was dissolved into a 25 mL purified water solution, which was added to a toluene solution containing 3.0 mmol TOAB. DT was then added to this solution at a 2:1 DT/Ag ratio followed by the addition of an excess (20 mmol) of NaBH₄. Synthesized DT-Ag nanoparticles were purified by multiple wash steps using ethanol.

The synthesis of DT-capped Au/Ag alloy (DT-Au/Ag) nanoparticles with ~ 2 nm cores were synthesized similar to the synthesis of gold and silver nanoparticles as described above [17-19].
Mixed aqueous solutions with 90:10 feed molar ratios HAuCl₄ to AgNO₃ were transferred to a toluene solution containing 3.0 mmol dm⁻³ TOAB. Excess DT was added to the solution. Excess NaBH₄ was slowly added to the solution as an aqueous reducing agent. The reaction proceeded with stirring at ambient temperature for 2 hours. Synthesized DT-Au/Ag nanoparticles were then purified by multiple cleaning procedures.

Synthesized DT-Au, DT-Ag and DT-Au/Ag nanoparticles were characterized by X-ray photoelectron spectroscopy (XPS), UV-visible (UV-Vis) spectroscopy, transmission electron microscopy (TEM), and thermogravimetric analyses (TGA).

2.3. Preparation of Carbon Electrodes Modified with DT-Au, DT-Ag and DT-Au/Ag Nanoparticles

DT-Au, DT-Ag and DT-Au/Ag nanoparticle-modified electrodes were prepared as follows [24,25]: A plastic-formed carbon plate (PFC, Mitsubishi Pencil Co., Japan, 2.5 cm x 2.5 cm) was used as a substrate electrode. For the preparation of electrodes for cyclic voltammogram measurements, a 50 µL aliquot of DT-Au (5-10 mg ml⁻¹), DT-Ag (6-10 mg ml⁻¹) and DT-Au/Ag (8-12 mg ml⁻¹) nanoparticles in hexane was cast onto a PFC plate (surface area of ca. 1 cm²), and followed by natural evaporation at room temperature. For the preparation of electrodes for electrolysis, a 200 µL aliquot of nanoparticles was cast onto both sides of a PFC plate (surface area of ca. 13 cm²). To remove the DT monolayer organic encapsulate from nanoparticles, PFC electrodes modified with DT-Au, DT-Ag and DT-Au/Ag nanoparticles were heated from room temperature to 300 °C at a rate of 10 °C min⁻¹, and the temperature was kept at 300 °C for 2 h under an air atmosphere using a muffle furnace. The temperature was controlled to within ± 10 °C.
After heat-treatment, nanoparticles on electrodes were characterized by XPS, TG, IR, SEM and CV as described in the results and discussion sections.

2.4. Analysis and Characterization of Nanoparticles

Synthesized nanoparticles were characterized using XPS, TEM, UV-Vis, TGA, IR, CV. TEM characterization was performed on a JEOL-2000FX electron microscope with an acceleration voltage of 200 kV. Nanoparticle samples dissolved in hexane were cast onto a carbon-coated copper grid sample holder followed by natural evaporation at room temperature.

XPS measurements were carried out using a Thermo VG Scientific, Sigma Probe HA6000II. The instrument uses a focused monochromatic Al Kα X-ray (1486.68 eV) source for excitation and a spherical section analyzer, and a 6-element multichannel detection system. The X-ray beam was incident normal to the sample and the detector was 37° away from the normal. The percentage of individual elements detected was determined from the relative composition analysis of peak band areas. The Mo substrate was used for XPS analysis.

TGA was performed with a Seiko SSC5020 thermal analysis system and a Seiko TG-300 thermogravimetric analysis. Nanoparaticle samples were cast onto an aluminum sample pan (Seiko, in 5 mm diameter) and then evaporated hexane. Samples weighing ~5 mg were heated at a rate of 5 °C min⁻¹ under an atmosphere. Aluminum oxide was used as a reference sample.

UV-Vis measurements were carried out with a Shimadzu, UV-3100 spectrophotometer. Spectra were collected over a range of 300-800 nm using a quartz cell with a 1 cm path length.

FTIR reflection spectra were obtained using a Bio-Rad FTS-6000 spectrometer, which was purged with dry-nitrogen gas. The spectrometer was equipped with a liquid nitrogen-cooled
HgCdTe detector. Nanoparticles (hexane solution) were cast onto Si wafers and then evaporated hexane. IR spectra were collected over 700 – 4000 cm\(^{-1}\).

SEM images were observed to characterize surface morphology of nanoparticles modified electrode using a JEOL JSM-6060L. For preparation of SEM sample, a 10 µL portion of nanoparticle (hexane solution) was cast on a PFC or high oriented pyrolytic graphite (HOPG) plate (ca. 0.32 cm\(^2\)).

### 2.5. Electrochemical measurement instrumentation

Cyclic voltammetric measurement and controlled-potential electrolysis were performed with an electrochemical analyzer (ALS/Chi, Model 600A) in a conventional three electrode cell with Ag/AgCl (saturated KCl) as the reference electrode and a Pt plate as the counter electrode. For the electrolysis study, working and counter electrodes were separated by a glass filter. All potentials were reported with respect to the Ag/AgCl (saturated KCl) electrode. The electrolyte solution was purged with high purity nitrogen before taking measurements. HPLC (PU-2080 Plus, JASCO, Japan) combined with packed columns (Shodex KC-G+KC-811, Showa Denko, Japan) and a UV detector (UV-2075 Plus, JASCO, at 210 nm) was employed to detect products generated by electrolysis. A phosphate solution (0.1 %) was used as an eluent for HPLC.

### 3. Results and Discussion

#### 3.1. Characterization of Nanoparticles

Before heat-treatment, surface content ratios (Au:Ag) of DT-Au/Ag nanoparticles were evaluated to be 84:16 by XPS. Fig. 1 shows TEM micrographs of DT-Au, DT-Ag and DT-Au/Ag nanoparticles and their population core sizes. The average core size of DT-Au, DT-Ag and DT-
Au/Ag nanoparticles was evaluated to be 2.3 (± 1.0), 3.3 (± 1.0) and 2.0 (± 1.0) nm, respectively. Fig. 2 shows UV-Vis spectra of DT-Au, DT-Ag and DT-Au/Ag nanoparticles in hexane. Gold and silver nanoparticles are known to have surface plasmon (SP) resonance absorption bands in the visible region [26-28]. DT-Au nanoparticles showed a weak SP resonance absorption at ca. 520 nm, which is in good agreement with that previously reported for similar particle sizes [10-13]. For DT-Ag and DT-Au/Ag nanoparticles, SP resonance absorption were observed at ca. 435 and 520 nm, respectively. DT-Ag nanoparticles showed well-defined SP resonance peak, which might be due to core sizes larger than DT-Au and DT-Au/Ag. The wavelength and intensity of the SP resonance absorption are strongly dependent on alloy composition and particle core size [15,18,19].

3.2. Heat-Treatment for Nanoparticles

Fig. 3 shows representative of TGA data for DT-Au, DT-Ag and DT-Au/Ag nanoparticles. The mass decrease at ca. 140 °C and a transition at ca. 210 °C were observed. Overall mass loss percentages were ca. 22, 25 and 23 % for DT-Au, DT-Ag and DT-Au/Ag nanoparticles, respectively. Compared to expected values of 21 % for 2 nm particles, respectively, based on model calculations with the percentage of organic decanethiolate shells [11]. Results obtained for DT-Au, DT-Ag and DT-Au/Ag nanoparticles were in good agreement with expected results. TGA data indicated that DT monolayer organic encapsulates were eliminated from nanoparticles by heat-treatment at 300 °C for 2 hours under an air atmosphere as described in the experimental section.

On FT-IR reflection spectra for DT-Au as shown in Fig. 4a), before heat-treatment, bands corresponding to asymmetric and symmetric methylene stretching, $\nu_{as,s}(\text{CH}_2)$ (2921 and 2852 cm$^{-1}$, respectively), and bands corresponding to asymmetric and symmetric methyl stretching, $\nu_{as,s}(\text{CH}_3)$ (2956 and 2872 cm$^{-1}$, respectively) were observed [13,18,23,26,28]. The Si wafer itself does not
show any spectral change upon heat-treatment in this frequency region. Bands corresponding to diagnostic C-H bending, wagging and C-C stretching modes for DT-Au were also observed in the low-frequency region 1150–1400 cm\(^{-1}\) (not shown) \[13,18,23,26,28\]. After heat-treatment, C-H alkyl chains representing absorption bands for DT in DT-Au nanoparticles in both the high-frequency region of 2800 - 3000 cm\(^{-1}\) and the low-frequency region of 1150-1400 cm\(^{-1}\) almost disappeared in the FT-IR reflection spectra (Fig. 4b). These results clearly indicate that at least the DT alkyl chain for not only DT-Au but also DT-Ag and DT-Au/Ag nanoparticles had been removed.

Surface species of DT-Au, DT-Ag and DT-Au/Ag nanoparticles before and after heat-treatment were examined by XPS. Fig. 5A(a) shows XPS data for DT-Au nanoparticles deposited on planer Mo substrates before heat-treatment, which shows peaks corresponding to S(2p) bands observed at 162.5 and 163.5 eV. The S(2p) band was characterized by a doublet arising from spin-orbit coupling, 2p\(_{3/2}\) and 2p\(_{1/2}\). The 2p\(_{3/2}\) peak arose ~1 eV lower compared to the 2p\(_{1/2}\) band because sulfur species interact strongly with the surface of gold \[29,30\]. After heat-treatment at 300 \(^\circ\)C for 2 hours, the S(2p) band was no longer present at least below the detection limit. The oxidation of thiolate would produce the sulfonate species(-SO\(_3^-\)), which shows a XPS peak around 167 eV \[31\]. After heat-treatment for DT-Au, almost no observation for peaks corresponding to sulfonate species were obtained. These XPS results together with results from TGA and FT-IR indicate that organic decanethiolate shells encapsulating DT-Au were completely removed from gold nanoparticles by heat-treatment at 300 \(^\circ\)C for 2 hours.

Results for DT-Au/Ag by heat-treatment were almost similar to those for DT-Au. Before heat-treatment, the doublet band corresponding to S(2p) of DT-Au/Ag was observed at 162.4 and 163.6 eV (Figure 5C(a)). After heat-treatment at 300 \(^\circ\)C for 2 hours, the S(2p) band was completely absent. Also, sulfonate species derived from oxidation of thiolate were not detected. These results
indicate that decanethiolate shells from DT-Au/Ag were completely eliminated. Results obtained from TGA and FT-IR, as described above, also supported the complete elimination of decanethiolate shells from Au-Ag alloy nanoparticles.

Fig. 5B(a,b) shows XPS data for DT-Ag in the S(2p) region before and after heat-treatment. The obtained results after heat-treatment were different from the results for DT-Au and DT-Au/Ag. Before heat-treatment the peak observed at 162.0 eV was assigned to S(2p) of the thiolate species. After heat-treatment at 300 °C for 2 hours, peaks corresponding to S(2p) were still observed at 162.0 and 163.2 eV. Both before and after heat treatment, sulfur species derived from oxidation of thiolate were detected around 167 eV [31]. TGA and FT-IR results together with this result clearly indicate that the DT C-H alkyl chain for DT-Au/Ag was completely removed, however, the DT thiolate was still present. As described in the cyclic voltammetric characterization, the thiolate could not be completely eliminated by oxidation and reduction cycles of heat-treated Ag nanoparticles modified electrodes in an alkaline aqueous solution.

Furthermore, it was noted that surface content ratios (Au:Ag) for DT-Au/Ag nanoparticles changed before and after heat-treatment at 300 °C for 2 hours. Before heat-treatment surface content ratios (Au:Ag) were evaluated to be 84:16 by XPS, as described above. However, after heat-treatment surface content ratios were evaluated to be 73:27, indicating that the surface content ratio of Ag increased after heat-treatment. A similar tendency was also observed at Au-Ag alloy nanoparticles with various content ratios. For example, Au-Ag nanoparticles with surface content ratios Au:Ag(91:9) and Au:Ag(54:56) changed to Au:Ag(83:17) and Au:Ag(36:65) by heat-treatment at 250 °C for 30 min. XPS probes had relatively more surface composition than the composition in layers under the surface. These results would indicate that surfaces of Au-Ag alloy
nanoparticles prepared herein are enriched with Ag atoms compared with the inner parts of alloy nanoparticles.

Fig. 6A shows cyclic voltammograms at PFC electrodes modified with Au, Ag and Au/Ag nanoparticles in a 0.1 mol dm$^{-3}$ H$_2$SO$_4$ solution, where nanoparticles modified PFC electrodes were prepared by heat-treatment at 300 °C for 2 hours. Typical redox responses corresponding to the oxidation and reduction of Au were observed at Au nanoparticles modified electrodes at a potential range of 0.6-1.5 V, as shown in Fig. 6A(a). This voltammetric behavior was similar to a polycrystalline Au electrode. For Ag nanoparticles modified electrodes (Fig. 6A(b)), oxidation and reduction responses for Ag nanoparticles were obtained at 0-1.0 V. Large oxidation and reduction peaks of Ag nanoparticles were observed around 0.7 and 0.3 V, respectively. Fig. 6A(c) shows the cyclic voltammogram at Au/Ag nanoparticles modified electrodes. It is interesting to note that the voltammogram shape was very similar to the Au nanoparticle modified electrode, and there was no redox peak representing an Ag surface even when nanoparticles contained 27 % Ag atoms on their surface. This result provides strong evidence that Au-Ag alloy nanoparticles are composed by atomically mixed Ag and Au atoms, not composed by Ag and Au metal domains. In a 0.1 mol dm$^{-3}$ NaOH solution, redox waves of Au/Ag nanoparticles modified electrodes were similar to those of Au nanoparticles modified electrodes (Fig. 6B), which also supports the distribution of Au and Ag atoms of Au/Ag nanoparticles on nanocrystal surfaces as being relatively homogeneous.

It is known that the electrochemical oxidative desorption of self-assembled alkanethiolate monolayers on planar gold surfaces occurs in alkaline solutions [32]. By three cycles of oxidation and reduction in a region of -0.8~0.8 V at heat-treated Ag nanoparticles modified electrodes in a 0.1 mol dm$^{-3}$ NaOH solution, the significant decrease of XPS peaks for the remaining thiolate species on nanoparticles was observed as shown in Fig. 5B(c). Therefore, prior to using Ag nanoparticle
modified electrodes for electrochemical measurements, the electrodes were carried through three cycles of oxidation and reduction in an alkaline solution.

Fig. 7 shows typical surface morphology for a bare PFC surface and DT-Au nanoparticles modified PFC electrode before and after heat-treatment at 300 °C for 2 hours. The surface morphological change in the Au nanoparticle film on PFC was observed after heat-treatment. To investigate nanometer scale size, TEM measurements were carried out. The TEM image was obtained after heat-treatment at 300 °C for 2 hours for DT-Au nanoparticles cast on a carbon-coated grid sample holder. The results of TEM image indicated that Au nanoparticles aggregated, however nanoparticles retained their shapes. The similar results were obtained, when DT-Ag and DT-Au/Ag nanoparticles were used. When a HOPG substrate was used, surface morphological changes induced by heat-treatment were almost the same as results obtained using PFC.

3.3. Voltammetric Studies on the Electrocatalytic Oxidation of Glucose

Before heat-treatment, no electrocatalytic oxidation of glucose was observed at PFC electrodes modified with Au, Ag and Au/Ag nanoparticles. This behavior can be understood to mean that organic DT shells of nanoparticles block the reaction of glucose at the metal surface of nanoparticles. 

Fig. 8a-c shows a typical voltammetric curve at PFC electrodes modified with Au, Ag and Au/Ag nanoparticles in a 0.1 mol dm⁻³ NaOH aqueous solution in the presence of 5 mmol dm⁻³ glucose. The electrocatalytic oxidation of glucose at PFC electrodes was not observed over a potential range of –0.8 to 0.8 V. At PFC electrodes modified with Au nanoparticles (Fig. 8a), two large oxidation peaks of interest were observed around –0.4 and 0.4 V, which correspond to the oxidation of glucose and the further oxidation of gluconolactone (as shown in Fig. 8d) generated by
the first oxidation peak (ca. -0.4 V), respectively [2,3,5]. For Au/Ag nanoparticles modified electrodes, two major oxidation peaks were also observed around -0.4 and 0.6 V (Fig. 8c), which correspond to the oxidation of glucose and the further oxidation of gluconolactone (Fig. 8f). It is interesting to note that the catalytic current at Au/Ag nanoparticle modified electrodes were observed from ca. -0.75 V, which represent a negative potential shift of ca. 0.1 V compared to that at Au nanoparticle modified electrodes. This result indicates that Au-Ag alloy nanoparticles are effective catalysts for the electrocatalytic oxidation of glucose. This observed effect of silver on the electrocatalytic oxidation of glucose was in good agreement with previous investigations using single crystal gold modified with silver by under-potential deposition [5,6].

Aldose-type monosaccharides such as mannose, galactose and xylose showed well-defined catalytic oxidation peaks around -0.4 and 0.4~0.6 V at the Au and Au/Ag nanoparticles modified electrodes in a 0.1 mol dm$^{-3}$ NaOH aqueous solution similar to the same aldose-type monosaccharide, glucose. While ketose-type monosaccharides such as fructose and sorbose did not show any catalytic oxidation peak in the potential region of -0.8~0.8 at Au and Au/Ag nanoparticle modified electrodes.

At Ag nanoparticle modified electrodes, typical voltammetric curves displayed an oxidation wave at ca. 0.35 V extending to the potential limit in the absence of glucose. This oxidation peak is attributed to the oxidation of silver(0) to silver (I) [33]. In the presence of glucose, the catalytic oxidation current was observed at ca. 0.5 V, which peak potential was ~ 0.15 V positive compared to that in the absence of glucose (Fig. 8b). The result obtained was similar to the behavior observed at silver electrodes [33]. These results indicate that glucose was oxidized catalytically at Ag nanoparticles. Although, a linear relationship between the oxidation peak current did not increase with glucose concentration. Further investigation is under way.
3.4. Controlled-Potential Electrolysis of Glucose

As previously reported, we have already noted advantages in using nanoparticles for the controlled-potential electrolysis of glucose [24,25]. In this study, Au, Ag and Au/Ag nanoparticles modified electrodes in a 0.1 mol dm\(^{-3}\) NaOH solution, experienced current decreases was also much slower than that at gold plate electrodes. Therefore, a sufficient current flow to detect electrolysis products was performed at Au, Ag and Au/Ag nanoparticles.

The controlled-potential electrolysis of glucose was performed in a 0.1 mol dm\(^{-3}\) NaOH solution containing 10 mmol dm\(^{-3}\) glucose at potentials at -0.3 and 0.3 V using PFC electrodes modified with Au, Ag and Au/Ag nanoparticles. Table 1 shows a summary of controlled-potential electrolysis results. After electrolysis at a potential of −0.3 V using Au nanoparticle modified electrodes, gluconolactone (or gluconate) was only detected by HPLC at a current efficiency of 100 %, which results in good agreement with previous papers [24,25]. At Au/Ag nanoparticle modified electrodes, gluconolactone was also detected at a current efficiency of 100 % after electrolysis at -0.3 V. These electrolysis results for Au and Au/Ag nanoparticles indicate that a two-electron oxidation for glucose occurred at nanoparticles-modified electrodes at -0.3 V [2,4,5].

At electrolysis potential of 0.3 V, a strong metal composition dependence of nanoparticles on electrolysis oxidation products was obtained. For Au nanoparticle modified electrodes, oxalate (18-electron oxidation product) and gluconolactone (or gluconate) were detected as main products, indicating that the electrocatalytic oxidation was promoted at more positive electrolysis potentials compared to the electrolysis at -0.3 V. For Au/Ag nanoparticles modified electrodes, formate (12-electron oxidation product) was detected as an electrolysis product in addition to oxalate and gluconolactone as main products. The remarkable difference between Au and Au/Ag nanoparticles
modified electrodes was evident on electrolysis products. First, the current efficiency for gluconolactone at Au/Ag nanoparticles was much smaller than that at Au nanoparticles. Secondly, formate, a 12-electron oxidation product, was one of the main products at Au/Ag nanoparticle modified electrodes, whereas formate was not detected at Au nanoparticles. This result would indicate that the formation of surface oxygenated species plays an important role in catalytic selectivity. Thirdly, it is interesting to note that the current efficiency for electrolysis products at Au/Ag nanoparticles modified electrodes was similar to that at Ag nanoparticle modified electrodes. These results indicate that catalytic selectivity at potential of 0.3 V would be governed by ca. 30 % silver atoms containing Au/Ag nanoparticles surfaces even if the other ca. 70 % gold atoms are contained, and Au/Ag nanoparticles shows electrolysis results similar to Ag nanoparticles.

4. Conclusions

In conclusion, Au, Ag and Au-Ag alloy nanoparticles capped with decanethiolate monolayer shells (DT-Au, DT-Ag and DT-Au/Ag) were synthesized by a two-phase synthesis protocol. Average core sizes for DT-Au, DT-Ag and DT-Au/Ag were evaluated by TEM to be 2.3 (± 1.0), 3.3 (± 1.0) and 2.0 (± 1.0) nm, respectively. Heat-treatments were performed at 300 °C for 2 hours to remove DT organic shells from nanoparticles. Results from TGA, FT-IR and XPS clearly indicated that C-H alkyl chains and thiolates from DT caps on Au and Au/Ag nanoparticles were completely eliminated after heat-treatment. In DT-Ag nanoparticles, elimination of DT C-H chains by heat-treatment was evident by TGA and FT-IR results, however XPS results indicated that DT thiolates were still present on Ag nanoparticle surfaces. Eventually, the remaining thiolate on Ag nanoparticles was almost removed by oxidation and reduction cycles in an alkaline solution. The surface content ratio of Au and Ag was evaluated to be Au:Ag(84:16) by XPS measurements before.
heat-treatment. After heat-treatment at 300 °C for 2 hours, the surface content ratio changed to Au:Ag(73:27). The increasing surface content ratio of Ag after heat-treatment was also observed with other content ratios of Au-Ag alloy nanoparticles. Results in cyclic voltammograms at Au/Ag nanoparticles modified PFC electrodes in H₂SO₄ and NaOH solutions were similar to those at Au nanoparticle modified electrodes, unlike those at Ag nanoparticle modified electrodes, which indicate the distribution of Au and Ag atoms of Au/Ag nanoparticles on nanocrystal surfaces is homogeneous.

Using heat-treated activated nanoparticles, the electrocatalytic oxidation of glucose was examined in a NaOH solution. Catalytic oxidation peaks for glucose around -0.4 and 0.4 V at Au nanoparticle modified electrodes and around -0.4 and 0.6 V at Au/Ag nanoparticles modified electrodes were observed, which correspond to the oxidation of glucose and the further oxidation of gluconolactone generated by the first oxidation peak (-0.4 V), respectively. It is interesting to note that the catalytic current at Au/Ag nanoparticles modified electrodes was observed from ca. -0.75 V, which represents a negative potential shift of ca. 0.1 V compared to that at Au nanoparticle modified electrodes. This result indicates that Au-Ag alloy nanoparticles are effective catalysts for the electrocatalytic oxidation of glucose. At both Au and Au/Ag nanoparticles, aldose-type monosaccharides showed catalytic oxidation peaks in an alkaline solution, however ketose-type monosaccharides did not show any catalytic peaks in the potential region of -0.8 ~ 0.8 V.

The controlled-potential electrolysis of glucose was performed in a 0.1 mol dm⁻³ NaOH solution. After electrolysis at a potential of -0.3 V, gluconolactone (or gluconate, two-electron oxidation product) was only detected at a current efficiency of 100 % at Au and Au/Ag nanoparticle modified electrodes. In the case of 0.3 V, oxalate (18-electron oxidation product) and gluconolactone were detected as the main product at Au nanoparticle modified electrodes. For
Au/Ag nanoparticle modified electrodes, formate (12-electron oxidation product) was detected in addition to oxalate and gluconolactone as main products, which is a similar result with Ag nanoparticle modified electrodes. These results would indicate that the catalytic selectivity at a potential of 0.3 V is governed by ca 30 % silver atoms containing Au/Ag nanoparticles surfaces. XPS measurements were carried out to reconfirm the surface metal composition ratio after electrolysis. The content ratio of Au:Ag(73:27) was observed, which was exactly the same surface metal composition ratio before electrolysis. Further investigations into the effect of content ratios of Au and Ag on electrolysis products are under way to gain insight into catalytic selectivity.

Acknowledgement

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References


Figure Captions

Fig. 1. TEM micrographs for DT-Au (a), DT-Ag (b) and DT-Au/Ag (c) nanoparticles, and the distribution of its core size.
Fig. 2. UV-Vis spectra for DT-Au (a), DT-Ag (b) and DT-Au/Ag (c) nanoparticles in a hexane.

Fig. 3. TG analysis curves for DT-Au (a), DT-Ag (b) and DT-Au/Ag (c) nanoparticles. Samples were heated at a rate of 5 °C min⁻¹ under an atmosphere. Aluminum oxide was used as a reference sample.

Fig. 4. FT-IR spectra for DT-Au nanoparticles before (a) and after (b) the heat-treatment at 300 °C for 2 hours.

Fig. 5. XPS spectra in the S(2p) region for DT-Au (A), DT-Ag (B) and DT-Au/Ag (C) nanoparticles before (A(a), B(a) and C(a), respectively) and after heat-treatment at 300 °C for 2 hours (A(b), B(b) and C(b), respectively), and for heat-treated DT-Ag nanoparticles followed by three cycles of oxidation and reduction in a region of -0.8 ~ 0.8 V in a 0.1 mol dm⁻³ NaOH solution (B(c)).

Fig. 6. Typical cyclic voltammograms at PFC electrodes modified with Au, Ag and Au/Ag nanoparticles obtained in a 0.1 mol dm⁻³ H₂SO₄ solution (A(a), A(b) and A(c), respectively) and NaOH solution (B(a), B(b) and B(c), respectively).

Fig. 7. Typical SEM images for a PFC substrate surface (a) and DT-Au nanoparticle-modified PFC surfaces before (b) and after (c) heat-treatment at 300 °C for 2 hours.

Fig. 8. Typical voltammetric curves at Au, Ag and Au/Ag nanoparticle modified electrodes in a 0.1 mol dm⁻³ NaOH solution in the presence of 5 mmol dm⁻³ glucose (a, b and c, respectively) and
Table 1. Results from the controlled-potential electrolysis of glucose.

The controlled-potential electrolysis was performed at PFC electrodes modified with Au, Ag and Au/Ag nanoparticles in a 0.1 mol dm$^{-3}$ NaOH solution (20 ml) in the presence of 10 m mol dm$^{-3}$ glucose at -0.3 and 0.3 V. Electrode area: ca. 10 cm$^2$. 

Gluconolactone (d, e and f, respectively), and in the absence of glucose and gluconolactone (broken line). Potential sweep rate: 50 mV s$^{-1}$. Electrode area: 0.26 cm$^2$. 

Table 1. Results from the controlled-potential electrolysis of glucose.
Fig. 1

Click here to download high resolution image
Fig. 2
Figure 3

Fig. 3
Figure 4

Fig. 4
Figure 5
Click here to download high resolution image
A) $\text{H}_2\text{SO}_4$

a) Au

b) Ag

c) Au/Ag

E / V vs Ag/AgCl (sat.KCl)

Fig 6A
B) 0.1M NaOH

a) Au

b) Ag

c) Au/Ag

E / V vs Ag/AgCl (sat.KCl)

Fig. 6B
Figure 8

E / V vs. Ag / AgCl (sat. KCl)
Table 1. Results of controlled-potential electrolysis of glucose.

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<th>glycolate 6e-</th>
<th>glucarate 6e-</th>
<th>gluconolactone 2e-</th>
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