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Composition-Activity Relationships of Carbon Electrode-Supported Bimetallic Gold-Silver Nanoparticles in Electrocatalytic Oxidation of Glucose

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Abstract

Composition-activity relationships are important when developing synergistic properties in multimetallic nanoparticles in catalytic reactions. This paper reports findings regarding correlations between catalytic activities and bimetallic compositions of carbon electrode-supported AuAg nanoparticles in the electrocatalytic oxidation of glucose in alkaline solutions. Electrocatalytic activities were characterized using voltammetric and electrolytic techniques, and were also compared with those obtained with gold and silver nanoparticle catalysts under the same conditions. Results from cyclic voltammograms at bimetallic Au$_m$Ag$_{100-m}$ ($m$: atomic %) nanoparticle modified-electrodes in H$_2$SO$_4$ solutions suggested that synthesized Au$_{82}$Ag$_{18}$ and Au$_{73}$Ag$_{27}$ nanoparticles were composed by atomically mixed Ag and Au atoms, and not composed of Ag and Au metal domains, in other words, they were homogeneous. On the other hand, Au$_{40}$Ag$_{60}$ and Au$_{17}$Ag$_{83}$ nanoparticles were heterogeneous, composed of Ag and Au metal domains. Homogeneously bimetallic Au$_m$Ag$_{100-m}$ nanoparticles showed improvements in electrocatalytic activity for glucose, and heterogeneous bimetallic nanoparticles did not show any improvements. The electrolytic product was strongly dependant on the composition ratio of Ag, regardless of whether nanoparticles were homogeneous or heterogeneous. Au$_m$Ag$_{100-m}$ ($100-m = ca. 30$) nanoparticles showed synergistic catalytic activities with both characteristic properties of Au$_{nano}$ and Ag$_{nano}$ nanoparticles.

Keywords

Electrocatalytic reaction, oxidation, glucose, nanoparticle, alloy, gold, silver
1. Introduction

The electrocatalytic oxidation of glucose has been extensively studied for applications in glucose-oxygen fuel cells and for the development of glucose sensors for medical and food industries [1-11]. Electrocatalytic behaviors of glucose oxidation in alkaline media were investigated using Cu, Ni, Fe, Pt and Au electrodes. At Cu, Ni and Fe electrodes, glucose oxidation reactions occur when positive potentials exceed ca. 0.6 to 0.7 V (vs. Ag/AgCl), which produce formic acid (a 12-electron oxidation product) as a main product [12-17]. At Pt electrodes, reactions occur from -0.3 V, and glycolic acid (a 6-electron oxidation product) is obtained as the main product [18]. When gold electrodes are used, oxidation reactions occur from ca. -0.6 V, and gluconolactone (a 2-electron oxidation product) is obtained with a current efficiency of 100 % at an electrode potential of -0.3 V [8-10]. The oxidation potential at gold is more negative in comparison to Cu, Ni, Fe, Pt electrodes. Therefore, gold is an attractive metal when oxidizing glucose, and the electrocatalytic oxidation of glucose has been examined extensively [1-11]. Furthermore, the effective electrochemical oxidation of glucose was demonstrated at a single crystal gold electrode modified with Ag under potential deposition (Ag-UPD) in comparison to other metals (such as Ru, Ag, Cu, Pt, Pd and Cd) -UPD gold electrodes [6,7]. Previous reports suggest that multi component surface compositions should produce synergistic effects to achieve high activities and selectivities.

Generally, gold, in bulk state, is an inert metal in comparison to transition metals. On the other hand, gold shows high catalytic activities in nanocale revels [19-22]. Recently, we found that the catalytic activity on the controlled-potential electrolysis of glucose was improved by using carbon electrodes modified with ~2 nm core sized gold nanoparticles as catalysts, and electrolytic products were determined along with current efficiencies [8,9]. Furthermore, we reported the
electrocatalytic oxidation of glucose at carbon electrode-supported bimetallic gold-silver nanoparticles [9]. Preliminary results from electrolyses at Au:Ag(73:27, atomic %) nanoparticle-modified electrodes suggest that the design and preparation of catalysts with bifunctional properties are important in achieving high activities and selectivities for the electrocatalytic oxidation of glucose. This paper reports findings regarding correlations between catalytic activities and bimetallic compositions of carbon electrode-supported AuAg nanoparticles in the electrocatalytic oxidation of glucose in alkaline solutions. Our results suggest suitable bimetallic compositions of \( \text{Au}_m\text{Ag}_{100-m} \) (\( m \): atomic %) for glucose oxidation reactions. These findings provide synergistic catalytic activity insights for the design of gold-based bimetallic nanoparticle catalysts to achieve high activities and selectivities for the electrocatalytic oxidation of glucose, and applications using glucose-oxygen fuel cells, and for the development of glucose sensors for medical and food industries.

2. Experimental Section

2.1. Chemicals

Hydrogen tetrachloroaurate (III) trihydrate (HAuCl\(_4\) \(3\)H\(_2\)O, 99.9+ %), sodium borohydride (NaBH\(_4\), 99.995 %) and decanethiol (DT, 96 %) were purchased from Aldrich and used as received. Tetraoctylammonium bromide (TOAB, 98 %) and silver nitrate (AgNO\(_3\), 99.8 %) were obtained from Lancaster and Nacalai Tesque (Japan), respectively, and used as received. Water was purified with a Millipore Milli-Q water system. Other chemical reagents were of analytical grade and used without further purification.
2.2. Preparation of Monometallic Gold and Silver Nanoparticles and Gold-Silver Alloy Nanoparticles

Gold nanoparticles with ~2 nm cores capped with decanethiolate monolayer shells (DT-Au\textsubscript{nano}) were synthesized by Schiffrin’s two-phase synthesis protocol [23-25]. Silver nanoparticles capped with decanethiolate monolayer shells (DT-Ag\textsubscript{nano}) were synthesized via a previously reported procedure [26-28]. Briefly, 0.75 mmol AgNO\textsubscript{3} 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 NaBH\textsubscript{4}. Synthesized DT-Ag nanoparticles were purified by multiple washing steps using ethanol. DT-capped Au\textsubscript{m}Ag\textsubscript{100-m} alloy (DT-Au\textsubscript{m}Ag\textsubscript{100-m}) nanoparticles with ~ 2 nm cores were synthesized similar to the synthesis of gold and silver nanoparticles [26-28]. Mixed aqueous solutions with various feed molar ratios of HAuCl\textsubscript{4} to AgNO\textsubscript{3} were transferred to a toluene solution containing 3.0 mmol dm\textsuperscript{-3} TOAB. Excess DT was added to the solution and excess NaBH\textsubscript{4} 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\textsubscript{m}Ag\textsubscript{100-m} nanoparticles were then purified by multiple cleaning procedures.

Synthesized nanoparticles were characterized by X-ray photoelectron spectroscopy (XPS), UV-visible (UV-vis) spectroscopy, transmission electron microscopy (TEM), scanning electron microscopy (SEM) and thermogravimetric analyses (TGA).

2.3. Preparation of Carbon Electrodes Modified with Nanoparticles
DT-Au$_m$Ag$_{100-m}$ nanoparticle-modified electrodes were prepared as follows [8-11]: 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$_m$Ag$_{100-m}$ (5-10 mg ml$^{-1}$) nanoparticles in hexane was cast onto a PFC plate (surface area of ca. 1 cm$^2$), 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 cm$^2$). To remove the DT monolayer organic encapsulate from nanoparticles, PFC electrodes modified with DT-Au$_m$Ag$_{100-m}$ 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. Characterization of Nanoparticles

Synthesized bimetallic DT-Au$_m$Ag$_{100-m}$ nanoparticles were characterized using XPS, TEM, SEM, UV-vis, TGA, IR and CV. TEM characterizations were 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. SEMs were carried out using a JEOL JSM-6060LV.

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 percentage of
individual elements detected was determined from the relative composition analysis of peak band areas.

TGA was performed with a Seiko SSC5020 thermal analysis system and a Seiko TG-300 thermogravimetric analysis. Nanoparticle 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 air 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.

FT-IR 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 (in hexane solution) were cast onto Si wafers and then evaporated hexane.

2.5. Electrochemical measurement instrumentation

Cyclic voltammetric measurements and controlled-potential electrolyses 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 electrolytic studies, 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 the eluent for HPLC.

3. Results and Discussion

3.1. Characterization of DT-Au\textsubscript{m}Ag\textsubscript{100-m} Nanoparticles

Before heat-treatment, surface atom content ratios of DT-Au\textsubscript{m}Ag\textsubscript{100-m} nanoparticles were evaluated by XPS. Fig. 1 shows the plot of the relationship between Ag ratios in synthetic feeding and Ag composition ratios in the synthesized nanoparticles. Ag composition ratios in DT-Au\textsubscript{m}Ag\textsubscript{100-m} nanoparticles were not linear in relationship to Ag feed ratios. A tendency towards a slight increase in the Ag composition ratio against the Ag feed ratio was observed. Fig. 2 shows TEM micrographs of DT-Au\textsubscript{nano}, DT-Au\textsubscript{92}Ag\textsubscript{8}, DT-Au\textsubscript{84}Ag\textsubscript{16}, DT-Au\textsubscript{54}Ag\textsubscript{46}, DT-Au\textsubscript{27}Ag\textsubscript{73}, and DT-Ag\textsubscript{nano} nanoparticles and their population core sizes. The average core size of the nanoparticles is summarized in Table 1. A tendency towards an increase in core size with increasing Ag composition ratios in nanoparticles was obtained.

Gold and silver nanoparticles have surface plasmon (SP) resonance absorption bands in the visible region [29-31]. SP resonance bands are strongly dependant on the size, shape, composition, and dielectric properties of nanoparticles and their local environment. Fig. 3a shows UV-vis spectra from DT-Au\textsubscript{nano}, DT-Au\textsubscript{m}Ag\textsubscript{100-m} and DT-Ag\textsubscript{nano} in hexane. DT-Au\textsubscript{nano} has a weak SP resonance absorption at ca. 520, which is in good agreement with that previously reported for similar particle sizes [23,24,32,33]. DT-Au\textsubscript{54}Ag\textsubscript{46}, DT-Au\textsubscript{27}Ag\textsubscript{73}, and DT-Ag\textsubscript{nano} have well-defined SP resonance peaks, which would be due to core sizes larger than DT-Au\textsubscript{nano}, DT-Au\textsubscript{92}Ag\textsubscript{8}, DT-Au\textsubscript{84}Ag\textsubscript{16}, as shown in Table 1. The peak position in SP resonance adsorption of DT-Au\textsubscript{m}Ag\textsubscript{100-m
depends on the composition ratio of Ag in nanoparticles. The peak position of DT-Au$_{92}$Ag$_8$ and DT-Au$_{84}$Ag$_{16}$ was almost the same as that of DT-Au$_{\text{nano}}$ (Fig. 3b). On the other hand, for higher Ag containing nanoparticles of DT-Au$_{54}$Ag$_{46}$ and DT-Au$_{27}$Ag$_{73}$, peak positions showed significant shifts to shorter wavelengths. K. Kim and coworkers reported that SP band peak position from AuAg alloy nanoparticles showed linear red shifts with increasing Ag nanoparticle content ratios and they concluded that synthesized AuAg alloy nanoparticles were composed of homogeneously mixed Au and Ag atoms [27]. Compared to this previous report, the higher Ag containing nanoparticles of DT-Au$_{54}$Ag$_{46}$ and DT-Au$_{27}$Ag$_{73}$ synthesized in this study could be heterogeneous, in other words, these bimetallic nanoparticles could be composed of Au and Ag metal domains. This presumption was implied by the voltammetric behavior of Au$_{54}$Ag$_{46}$ and Au$_{27}$Ag$_{73}$ modified-electrodes as described in the section below.

3.2. Heat-Treatment for Nanoparticles and Voltammetric Characterization

To remove the DT monolayer organic encapsulate from DT-Au$_{\text{nano}}$, DT-Au$_m$Ag$_{100-m}$ and DT-Ag$_{\text{nano}}$ nanoparticles, nanoparticle-modified PFC electrodes 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. There are two important pieces of evidence supporting the effective removal of DT capping molecules from nanoparticles via heat-treatment. First, the removal of vibrational bands characteristic of DT was confirmed by FT-IR reflection measurement. Bands corresponding to asymmetric and symmetric methylene stretching, ($\nu$as(CH$_2$): 2921 and $\nu$s(CH$_2$): 2852 cm$^{-1}$, respectively), and methyl stretching, ($\nu$as(CH$_3$): 2956 and $\nu$s(CH$_3$): 2872 cm$^{-1}$) [27,29,31,33,34], were observed before heat-treatment, which practically disappeared after heat-treatment. Second,
the removal of capping molecules was detected by TGA. Mass decreases at ca. 140 °C and transitions at ca. 230 °C were observed in DT-Au_{nano}, DT-Au_{m}Ag_{100-m} and DT-Ag_{nano} nanoparticles. Overall mass loss percentages were evaluated to be 22-25 %. Compared to expected values of 21 % for 2 nm particles, respectively, based on model calculations with the percentage of organic decanethiolate shells [23,24]. The obtained results are in good agreement with the expected results. FT-IR and TGA results indicate that DT monolayer organic encapsulates were eliminated from nanoparticles by heat-treatment at 300 °C for 2 hours under an air atmosphere.

Surface species of DT-Au_{nano}, DT-Au_{m}Ag_{100-m} and DT-Ag_{nano} nanoparticles before and after heat-treatment were examined by XPS. Before heat-treatment, peaks corresponding to S(2p) bands were observed at ca. 162.4 and ca. 163.6 eV [35-37]. After heat-treatment at 300 °C for 2 hours, for DT-Au_{nano}, DT-Au_{92}Ag_{8} and DT-Au_{84}Ag_{16} nanoparticles, the S(2p) band was no longer present or was below the detection limit. For DT-Au_{54}Ag_{46}, DT-Au_{27}Ag_{73} and DT-Ag_{nano} nanoparticles, peaks corresponding to S(2p) were still observed after heat-treatment. TGA and FT-IR results together with this result clearly indicate that alkyl chains in DT-Au_{54}Ag_{46}, DT-Au_{27}Ag_{73} and DT-Ag_{nano} capping molecules were completely removed, however, a DT thiolate species was still present. The thiolate species for DT-Au_{54}Ag_{46}, DT-Au_{27}Ag_{73} and DT-Ag_{nano} nanoparticles could be almost completely eliminated by three cycles of oxidation and reduction cycles in a region of -0.8~0.8 V at heat-treated nanoparticle-modified electrodes in a 0.1 mol dm^{-3} NaOH solution.

It should be noted that surface atom content ratios of DT-Au_{m}Ag_{100-m} changed before and after heat-treatment, as shown in Fig. 1. The surface content ratio of Ag increased after heat-treatment: DT-Au_{92}Ag_{8}, DT-Au_{84}Ag_{16}, DT-Au_{54}Ag_{46}, DT-Au_{27}Ag_{73} changed to Au_{82}Ag_{18}, Au_{73}Ag_{27}, Au_{40}Ag_{60} and Au_{17}Ag_{83}, respectively. XPS probes detect relatively more surface composition than
the composition in layers under the surface. These results would indicate that surfaces of bimetallic 
AuAg nanoparticles are enriched with Ag atoms compared with the inner parts of alloy 
nanoparticles.

Fig. 4 shows cyclic voltammograms at PFC electrodes modified with Au\textsubscript{nano}, Au\textsubscript{m}Ag\textsubscript{100-m} and 
Ag\textsubscript{nano} nanoparticles in 0.1 mol dm\textsuperscript{-3} H\textsubscript{2}SO\textsubscript{4} solution, where nanoparticle-modified PFC electrodes 
were prepared by heat-treatment at 300 °C for 2 hours. Au\textsubscript{nano} nanoparticle-modified electrodes 
showed typical redox responses corresponding to the oxidation and reduction of Au at a potential 
range of 0.6-1.5 V, which was similar to a polycrystalline Au electrode. Large oxidation and 
reduction peaks of Ag\textsubscript{nano} nanoparticles were observed around 0.7 and 0.3 V, respectively. In terms 
of voltammetric responses on Au\textsubscript{m}Ag\textsubscript{100-m} nanoparticle-modified electrodes, it is interesting to note 
that the voltammetric shape for Au\textsubscript{82}Ag\textsubscript{18} and Au\textsubscript{73}Ag\textsubscript{27} was very similar to the Au\textsubscript{nano} nanoparticle-
modified electrode. This result provides strong evidence that Au\textsubscript{82}Ag\textsubscript{18} and Au\textsubscript{73}Ag\textsubscript{27} nanoparticles 
were composed by atomically mixed Ag and Au atoms, and not composed by Ag and Au metal 
domains. On the other hand, the voltammetric shape for Au\textsubscript{40}Ag\textsubscript{60} and Au\textsubscript{17}Ag\textsubscript{83} was composed 
from individual oxidation and reduction peaks corresponding of Au and Ag electrodes, indicating 
that Au\textsubscript{40}Ag\textsubscript{60} and Au\textsubscript{17}Ag\textsubscript{83} nanoparticles were composed by Ag and Au metal domains.

Fig. 5 shows the typical surface morphology for a bare PFC surface and an electrode modified 
with Au\textsubscript{nano}, Au\textsubscript{73}Ag\textsubscript{27} and Ag\textsubscript{nano} nanoparticles before and after heat-treatment at 300 °C for 2 hours. 
TEM measurements were carried out to investigate the nanometer scale. The TEM images were 
obtained, as shown in Fig. 6, after heat-treatment at 300 °C for 2 hours for DT-Au\textsubscript{nano} nanoparticles 
cast on carbon-coated grid sample holders. After heat-treatment, the surface morphological change 
in the Au\textsubscript{nano} nanoparticle film on PFC was observed by SEM results, and aggregated Au\textsubscript{nano}
nanoparticles were observed by TEM, however it was concluded that nanoparticles retained their nanoscale shapes with 3-20 nm size in a diameter. Similar results were obtained, when other nanoparticles were used.

3.3. Voltammetric Studies on the Electrocatalytic Oxidation of Glucose

Fig. 7 shows typical voltammetric curves at PFC electrodes modified with Au\textsubscript{nano}, Au\textsubscript{m}Ag\textsubscript{100-m} and Ag\textsubscript{nano} nanoparticles in a 0.1 mol dm\textsuperscript{-3} NaOH aqueous solution in the presence of 5 mmol dm\textsuperscript{-3} glucose. Two interesting large oxidation peaks were observed around –0.4 and 0.4 V, which correspond to the oxidation of glucose and the further oxidation of gluconolactone generated by the first oxidation peak (ca. -0.4 V), respectively [1,3,6]. No catalytic current was observed at a PFC electrode over a potential range of -0.8 to 0.8 V. It is interesting to note that the catalytic current at Au\textsubscript{82}Ag\textsubscript{18} and Au\textsubscript{73}Ag\textsubscript{27} 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 an Au\textsubscript{nano} nanoparticle-modified electrode. On the other hand, at Au\textsubscript{40}Ag\textsubscript{60} nanoparticle-modified electrodes, the catalytic reaction occurs from ca. -0.65, which is a similar potential to an Au\textsubscript{nano} nanoparticle-modified electrode. For an Au\textsubscript{17}Ag\textsubscript{83} nanoparticle-modified electrode, the catalytic activity was less than that from an Au\textsubscript{nano} nanoparticle-modified electrode, because the reaction occurred from ca. -0.5 V.

These results indicate that bimetallic Au\textsubscript{m}Ag\textsubscript{100-m} nanoparticles, where 100-m is 20 ~ 30, are effective catalysts for the electrocatalytic oxidation of glucose. However, upon bimetallic Au\textsubscript{m}Ag\textsubscript{100-m} nanoparticles with higher Ag containing ratios (100-m > ca. 30) such as Au\textsubscript{40}Ag\textsubscript{60} and Au\textsubscript{17}Ag\textsubscript{83}, improvements in electrocatalytic reactions are not seen. This tendency correlates with voltammetric characterization results from Au\textsubscript{m}Ag\textsubscript{100-m} nanoparticles as described in a section above.
Thus, we conclude that the observed activity-composition correlation of bimetallic AuAg nanoparticles in the electrocatalytic oxidation of glucose would be due to the surface homogeneity of Au and Ag atoms on alloy nanoparticles. For example, from their voltammetric behavior in H$_2$SO$_4$ solution, it is thought that Au$_{82}$Ag$_{18}$ and Au$_{73}$Ag$_{27}$ nanoparticles are homogeneous at the atomic level. Such homogeneously bimetallic Au$_m$Ag$_{100-m}$ nanoparticles would show improvements in their electrocatalytic activity for glucose, because a potential of zero charge at the electrode surface would shift negatively by the homogeneous surface of Ag and Au atoms to allow the formation of AuOH sites as active sites for oxidation of glucose on the electrode surface at positive potential [7]. On the other hand, heterogeneous bimetallic Au$_m$Ag$_{100-m}$ nanoparticles such as Au$_{40}$Ag$_{60}$ and Au$_{17}$Ag$_{83}$ do not show improvements in electrocatalytic activity, because the electrocatalytic behavior for Ag atom domain surfaces on nanoparticles would be similar to Ag$_{\text{nano}}$ nanoparticle-modified and Ag electrodes. No effective electrocatalytic reactions were observed at Ag$_{\text{nano}}$ nanoparticle-modified and Ag electrodes, as described in a previous report [9].

3.4. Controlled-Potential Electrolysis of Glucose

The controlled-potential electrolysis of glucose was performed in a 0.1 mol dm$^{-3}$ NaOH solution (20 ml) containing 10 mmol dm$^{-3}$ glucose at potentials at -0.3 and 0.3 V using PFC electrodes modified with Au$_{\text{nano}}$, Au$_m$Ag$_{100-m}$ and Ag$_{\text{nano}}$ nanoparticles. Table 2 shows a summary of controlled-potential electrolysis results. The electrolysis of glucose at a potential of –0.3 V using Au$_{\text{nano}}$ and Au$_m$Ag$_{100-m}$ nanoparticle-modified electrodes, yielded gluconolactone (or gluconate) at a current efficiency of 100 %, which was independent of the composition ratio of Ag within nanoparticles. These electrolytic results indicate that a two-electron oxidation for glucose occurs at
Au_{nano} and Au_{m}Ag_{100-m} nanoparticle-modified electrodes at -0.3 V [2,5,6,8,9], and correlations between composition ratios of Ag and electrolytic oxidation products were not observed. On the other hand, at an electrolytic potential of 0.3 V, a remarkable difference in a strong metal composition dependence of nanoparticles was evident on electrolysis products. For Au_{nano} 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. Using Au_{m}Ag_{100-m} nanoparticle-modified electrodes, in particular for Au_{73}Ag_{27}, Au_{40}Ag_{60} and Au_{17}Ag_{83}, formate (a 12-electron oxidation product) was detected as a main electrolysis product in addition to oxalate and gluconolactone, which were similar to results obtained at Ag_{nano} nanoparticle-modified electrodes. The Au_{82}Ag_{18} nanoparticle-modified electrode showed tendencies towards those seen with Au_{nano} and Ag_{nano} particle-modified electrodes.

The results presented herein indicate that the formation of surface oxygenated species would play an important role in catalytic selectivity. The electrolytic product strongly depends on the composition ratio of Ag, even though Ag atom domain surfaces are present in Au_{m}Ag_{100-m} nanoparticles with higher Ag containing ratios (100-m > ca. 30) such as Au_{40}Ag_{60} and Au_{17}Ag_{83}, which do not show improvements in electrocatalytic reactions. We conclude that Au_{m}Ag_{100-m} (100-m = ca. 30) nanoparticles have synergistic catalytic activities in both characteristic properties of Au_{nano} and Ag_{nano} nanoparticles.

4. Conclusions
In conclusion, DT-Au\textsubscript{nano}, DT-Au\textsubscript{92}Ag\textsubscript{8}, DT-Au\textsubscript{84}Ag\textsubscript{16}, DT-Au\textsubscript{54}Ag\textsubscript{46}, DT-Au\textsubscript{27}Ag\textsubscript{73}, and DT-Ag\textsubscript{nano} nanoparticles were synthesized by a two-phase synthesis protocol. DT organic shells were completely eliminated from DT-Au\textsubscript{nano}, DT-Au\textsubscript{92}Ag\textsubscript{8} and DT-Au\textsubscript{84}Ag\textsubscript{16} nanoparticles by heat-treatment at 300 °C for 2 hours, which was confirmed by TGA, FT-IR and XPS measurements. For DT-Au\textsubscript{54}Ag\textsubscript{46}, DT-Au\textsubscript{27}Ag\textsubscript{73} and DT-Ag\textsubscript{nano} nanoparticles, DT organic shells could be almost completely eliminated by heat-treatment, followed by three cycles of oxidation and reduction at -0.8~0.8 V in 0.1 mol dm\textsuperscript{-3} NaOH solution. The surface content ratio of Ag increased after heat-treatment: DT-Au\textsubscript{92}Ag\textsubscript{8}, DT-Au\textsubscript{84}Ag\textsubscript{16}, DT-Au\textsubscript{54}Ag\textsubscript{46}, DT-Au\textsubscript{27}Ag\textsubscript{73} changed to Au\textsubscript{82}Ag\textsubscript{18}, Au\textsubscript{73}Ag\textsubscript{27}, Au\textsubscript{40}Ag\textsubscript{60} and Au\textsubscript{17}Ag\textsubscript{83}, respectively. Results from cyclic voltammograms at Au\textsubscript{nano}, Au\textsubscript{m}Ag\textsubscript{100-m} and Ag\textsubscript{nano} modified-PFC electrodes in H\textsubscript{2}SO\textsubscript{4} solutions suggested that Au\textsubscript{82}Ag\textsubscript{18} and Au\textsubscript{73}Ag\textsubscript{27} nanoparticles were homogeneous at the atomic level, and Au\textsubscript{40}Ag\textsubscript{60} and Au\textsubscript{17}Ag\textsubscript{83} were heterogeneous, that is, nanoparticles were composed of Ag and Au metal domains.

Compared to investigations with the electrocatalytic oxidation of glucose at Au\textsubscript{m}Ag\textsubscript{100-m} nanoparticle-modified electrodes, homogeneously bimetallic Au\textsubscript{m}Ag\textsubscript{100-m} nanoparticles would show improvements in their electrocatalytic activity for glucose. On the other hand, heterogeneously bimetallic nanoparticles did not show any improvements. The electrolytic product strongly depended on the composition ratio of Ag, regardless of whether nanoparticles were homogeneous or heterogeneous. Au\textsubscript{m}Ag\textsubscript{100-m} (100-m = ca. 30) nanoparticles showed synergistic catalytic activities with both characteristic properties of Au\textsubscript{nano} and Ag\textsubscript{nano} nanoparticles. These findings provide new synergistic catalytic activity insights for the design of gold based bimetallic nanoparticle catalysts to achieve high activities and selectivities.
References


Figure and Table Captions

Fig. 1. Plot of the relationship between Ag ratios in synthetic feeds and Ag composition ratios in synthesized nanoparticles.

Fig. 2. TEM micrographs for DT-Au$_{nano}$ (a), DT-Au$_{92}$Ag$_{8}$ (b), DT-Au$_{84}$Ag$_{16}$ (c), DT-Au$_{54}$Ag$_{46}$ (d), DT-Au$_{27}$Ag$_{73}$ (e) and DT-Agnano (f) nanoparticles, and the distribution of their core sizes.

Fig. 3. UV-vis spectra for DT-Au$_{nano}$ (a), DT-Au$_{92}$Ag$_{8}$ (b), DT-Au$_{84}$Ag$_{16}$ (c), DT-Au$_{54}$Ag$_{46}$ (d), DT-Au$_{27}$Ag$_{73}$ (e) and DT-Agnano (f) nanoparticles in hexane (A). Plot of SP peak position vs. Ag composition ratio in nanoparticles (B).

Fig. 4. Typical cyclic voltammograms at PFC electrodes modified with DT-Au$_{nano}$ (a), Au$_{82}$Ag$_{18}$ (b), Au$_{73}$Ag$_{27}$ (c), Au$_{40}$Ag$_{60}$ (d) and Au$_{17}$Ag$_{83}$ (e) and DT-Agnano (f) nanoparticles obtained in a 0.1 mol dm$^{-3}$ H$_2$SO$_4$ solution. Potential sweep rate: 50 mV s$^{-1}$. Electrode area: 0.26 cm$^2$.

Fig. 5. Typical SEM images for DT-Au$_{nano}$ (a, b), DT-Au$_{84}$Ag$_{16}$ (c, d) and DT-Agnano (e, f) nanoparticle-modified PFC substrate surfaces and a bare PFC surface (g) before (a, c, e) and after (b, d, f) heat-treatment at 300 °C for 2 hours.

Fig. 6. TEM images for DT-Au$_{nano}$ nanoparticles before (a) and after (b) heat-treatment at 300 °C for 2 hours.
Fig. 7. Typical voltammetric curves at PFC electrodes modified with $\text{Au}_{\text{nano}}$ (a), $\text{Au}_{82}\text{Ag}_{18}$ (b), $\text{Au}_{73}\text{Ag}_{27}$ (c), $\text{Au}_{40}\text{Ag}_{60}$ (d) and $\text{Au}_{17}\text{Ag}_{83}$ (e) nanoparticles in 0.1 mol dm$^{-3}$ NaOH solution in the presence of 5 mmol dm$^{-3}$ glucose, and in the absence of glucose (broken lines). Potential sweep rate: 50 mV s$^{-1}$. Electrode area: 0.26 cm$^2$.

Table 1. The average particle diameter size of nanoparticles.

Table 2. Results from the controlled-potential electrolysis of glucose.

The controlled-potential electrolysis was performed at PFC electrodes modified with $\text{Au}_{\text{nano}}$, $\text{Au}_{m}\text{Ag}_{100-m}$ and $\text{Ag}_{\text{nano}}$ nanoparticles in a 0.1 mol dm$^{-3}$ NaOH solution (20 ml) in the presence of 10 mmol dm$^{-3}$ glucose at -0.3 and 0.3 V. Electrode area: $ca.$ 10 cm$^2$. 
Figure 1
Fig. 2
Figure 3

A

Absorbance / a.u.

Wavelength / nm

B

Peak position / nm

Ag ratio / %

Fig. 3
Figure 4

a) $\text{Au}_{\text{nano}}$

b) $\text{Au}_{82}\text{Ag}_{18}$

c) $\text{Au}_{73}\text{Ag}_{27}$

d) $\text{Au}_{40}\text{Ag}_{60}$

e) $\text{Au}_{17}\text{Ag}_{83}$

f) $\text{Ag}_{\text{nano}}$

---

$E / V$ vs. $\text{Ag}/\text{AgCl}$ (sat. $\text{KCl}$)

$100 \mu A$

$500 \mu A$
Figure 5

(a) 

(b) 

(c) 

(d) 

(e) 

(f) 

(g) 

Fig. 5
Figure 6

(a) Image with a scale bar of 20 nm
(b) Image with a scale bar of 50 nm

Distribution of Particle Diameter (nm)

---

Fig. 6
Figure 7

a) $\text{Au}_{\text{nano}}$

b) $\text{Au}_{82}\text{Ag}_{18}$

c) $\text{Au}_{73}\text{Ag}_{27}$

d) $\text{Au}_{40}\text{Ag}_{60}$

e) $\text{Au}_{17}\text{Ag}_{83}$

E / V vs. Ag / AgCl (sat. KCl)
<table>
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<tr>
<th>Nanoparticles</th>
<th>DT-Au$_{nano}$</th>
<th>DT-Au$<em>{92}$Ag$</em>{8}$</th>
<th>DT-Au$<em>{84}$Ag$</em>{16}$</th>
<th>DT-Au$<em>{54}$Ag$</em>{46}$</th>
<th>DT-Au$<em>{27}$Ag$</em>{73}$</th>
<th>DT-Ag$_{nano}$</th>
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<td>Average of core size</td>
<td>1.9 (± 1.0)</td>
<td>2.1 (± 0.9)</td>
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<td>2.8 (± 1.1)</td>
<td>2.4 (± 2.0)</td>
<td>3.3 (± 0.7)</td>
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Table 1
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<th>Total</th>
<th>Charge flow [C]</th>
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Table 2