Electrocatalytic Oxidation of Glucose at Carbon Electrodes Modified with Gold and Gold–Platinum Alloy Nanoparticles in an Alkaline Solution

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The electrocatalytic oxidation of glucose in an alkaline solution was examined using gold and gold–platinum alloy nanoparticles as catalysts. In electrolysis, the catalytic activity for oxidation of glucose could be kept much longer time at gold nanoparticle-modified electrode than at a gold plate electrode. Preliminary electrolysis results at 0.3 V indicated that current efficiency for oxalate as 18-electron oxidation product at gold nanoparticle-modified electrode was approximately twice higher than that at gold–platinum alloy nanoparticle-modified electrode.

Metal and semiconductor nanoparticles have been studied extensively because of the design and fabrication of catalysts, the enhancement of catalytic activity or selectivity, and the large surface area-to-volume ratios.[1–9] Recently, interest in the catalytic properties of gold has increased rapidly,[1–6] because the catalytic properties of gold nanoparticles with a few nanometer core could change completely owing to particle phase transitions, i.e., atomic to metallic phase properties change in this size range.

The electrocatalytic oxidation of glucose has been examined extensively because of interest in not only the development of glucose sensors for medical and food industry use, but also for applications in glucose-oxygen fuel cells.[10–14] Gold is an attractive metal for the oxidation of glucose in an alkaline solution.[10–12,14] Recently, the effective electrochemical oxidation of glucose was demonstrated at single crystal gold modified with silver by under-potential deposition (Ag–UPD).[14] In this study, we describe the electrocatalytic oxidation of glucose using gold and gold–platinum alloy nanoparticle-modified electrodes as catalysts. The approach of using gold-based nanoparticle for the electrocatalytic oxidation of glucose will be useful not only for the basic understanding of catalysts, but also for supporting recent interest in fuel cell development based on metallic catalysts and other related systems.

Gold nanoparticles with 2 nm core sizes capped with a decanethiolate monolayer shell (DT–$Au_{2\,nm}$) were synthesized by Schiffrin's two-phase synthesis protocol.[5–8] Gold–platinum alloy (Au–Pt) nanoparticles capped with a DT monolayer shell (DT–(Au–Pt)) were synthesized with and 2:8 feed ratios (Au:Pt) of $HAuCl_4$ and H_2PtCl_6 similar to the synthesis of gold nanoparticles. XPS results showed that content ratios (Au:Pt) of Au and Pt for DT–(Au–Pt) synthesized were evaluated to be Au–Pt (78:22).

Synthetic DT–$Au_{2\,nm}$ and DT–(Au–Pt (78:22)) nanoparticles were characterized by UV–visible (UV–vis) spectroscopy and transmission electron microscopy (TEM). Figure 1 shows the TEM micrographs of nanoparticles and its populations of core sizes. The average core sizes of DT–$Au_{2\,nm}$ and DT–(Au–Pt (78:22)) particles were evaluated to be 2.3 nm (±1.0) and 1.5 (±0.5) nm, respectively. UV–vis spectrum of DT–$Au_{2\,nm}$ in hexane showed a weak peak of surface plasmon (SP) resonance absorption at ca. 520 nm, which was in good agreement with those previously reported for similar particle sizes.[5–8] On the other hand, SP peak for DT–(Au–Pt (78:22)) nanoparticle was not observed, since plasmon oscillation strongly decreased owing to low electron densities in conduction bands.

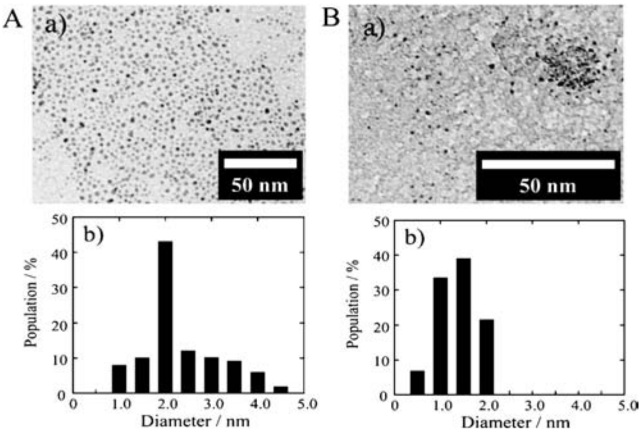

Figure 1. TEM micrographs for DT–$Au_{2\,nm}$ (A(a)) and DT–(Au–Pt (78:22)) (B(a)) nanoparticles and population of core size for DT–$Au_{2\,nm}$ (A(b)) and DT–(Au–Pt (78:22)) (B(b)) nanoparticles.

$Au_{2\,nm}$ and Au–Pt alloy nanoparticle-modified electrodes were prepared as follows: A plastic formed carbon plate (PFC, Mitsubishi Pencil Co., Japan, 2.5 × 2.5 cm) was used as a substrate. For preparation of the electrode for cyclic voltammogram measurements, a 50-µL portion of $Au_{2\,nm}$ (202 µmol dm^{-3}),[15] or DT–(Au–Pt (78:22)) nanoparticles[15,16] in hexane was cast onto a PFC plate (ca. 1 cm^2), and followed by natural evaporation at room temperature. To prepare the electrodes for electrolysis, a 400-µL portion of nanoparticles of interest was cast onto both sides of a PFC plate (ca. 12.5 cm^2). To remove DT monolayer organic encapsulate from particles, nanoparticle-modified PFC electrodes were heated at 300 °C for 2 h. After heat treatment, C–H alkyl stretching absorption peaks for DT chain were no longer present in FT-IR spectra,[17] indicating that the DT encapsulate was completely removed.

Electrochemical measurements were carried out in a conventional three electrode cell with Ag/AgCl (saturated KCl) as a reference electrode and a Pt plate as a counter electrode. All potentials were reported with respect to an Ag/AgCl (saturated KCl) electrode. The electrolyte solution was purged with high purity nitrogen before the measurements. HPLC with UV detector (at 210 nm) was performed to detect electrolysis product.

Figure 2 shows a typical set of cyclic voltammetric curves at

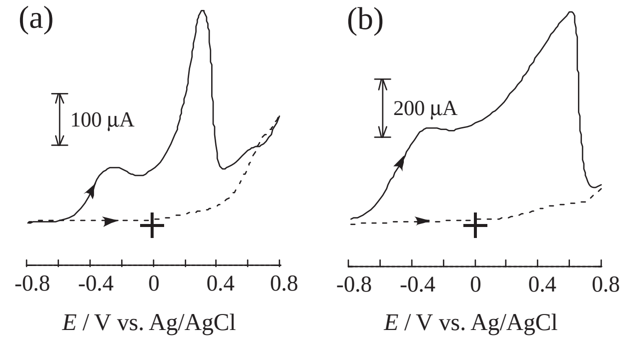

Figure 2. Typical voltammetric curves at PFC electrodes modified with $Au_{2\,nm}$ (a) and Au–Pt (78:22) (b) nanoparticles in a 0.1 mol dm^{-3} NaOH solution in the presence of 5 mmol dm^{-3} glucose (solid line) and in the absence of glucose (broken line). Potential sweep rate: 50 mV s^{-1}. Electrode area: 0.26 cm^2.

PFC electrodes modified with $Au_{2\,nm}$ and Au–Pt (78:22) nanoparticles in a 0.1 mol dm^{-3} NaOH solution in the presence of 5 mmol dm^{-3} glucose. Electrocatalytic oxidation of glucose at the unmodified PFC electrode was not observed over a potential range of −0.8 to 0.8 V. Electrocatalytic oxidation curves of glucose were observed at $Au_{2\,nm}$ and Au–Pt alloy nanoparticle-modified electrodes. Two major oxidation peaks of interest were observed around −0.3 and 0.3 V for $Au_{2\,nm}$ nanoparticle-modified electrode, which were corresponded to the oxidation of glucose and further oxidation of gluconolactone generated at the first oxidation peak (ca. −0.3 V).[14] For Au–Pt alloy nanoparticle-modified electrode, two major oxidation peaks were also observed around −0.3 and 0.6 V, which were corresponded to the oxidation of glucose and oxidation of gluconolactone. The catalytic current at Au–Pt alloy nanoparticle-modified electrode was observed from ca. −0.75 V, which represents a negative potential shift of ca. 0.15 V compared to that at $Au_{2\,nm}$ nanoparticle-modified electrode. On the whole, no significant difference in oxidation reaction was observed between $Au_{2\,nm}$ nanoparticle- and Au–Pt alloy nanoparticle-modified electrodes. These results were in good agreement with those in previous reports using a gold plate and Ag–UPD modified gold electrodes.[11,12,14] However, we found the advantage on the use of $Au_{2\,nm}$ nanoparticle as catalyst. In electrolysis, the current ratios (I/I_i) on initial currents (I_i) and currents (I) during electrolysis at both −0.3 and 0.3 V decreased quickly at a gold plate electrode. On the other hand, at the $Au_{2\,nm}$ nanoparticle-modified electrode the current ratios decreased, but at much slower rate than at a gold plate electrode. These results indicate that the catalytic activity for oxidation of glucose can be kept much longer time at gold nanoparticle-modified electrode than at a gold plate electrode.

Using nanoparticle-modified PFC electrodes, the electrolysis of glucose was performed in a 0.1 mol dm^{-3} NaOH solution containing 10 mmol dm^{-3} glucose at −0.3 and 0.3 V (Table 1). At −0.3 V, both $Au_{2\,nm}$ and Au–Pt (78:22) nanoparticle-modified electrodes gave gluconolactone (or gluconate) as a two-electron oxidation product at a current efficiency of almost 100%.[11,13,14] At 0.3 V both $Au_{2\,nm}$ and Au–Pt (78:22) modified electrodes, oxalate as 18-electron oxidation product was detected in addition to gluconolactone (gluconate) as a main product. However, at an $Au_{2\,nm}$ modified electrode the current efficiency for oxalate was approximately twice higher than at Au–Pt alloy nanoparticle-modified electrodes.

Table 1. Results of glucose oxidation[a]

Electrolytic potential (E/V vs Ag/AgCl)	Nanoparticle modified electrodes	Current efficiencies/%			Charge flow /C
		Oxalate	Gluconolactone	Total	
−0.3	$Au_{2\,nm}$	—	ca. 100	ca. 100	20
	Au–Pt (78:22)	—	ca. 100	ca. 100	15
0.3	$Au_{2\,nm}$	21	61	88	25
	Au–Pt (78:22)	9.8	80	90	15

[a] The electrolysis of glucose was performed in a 0.1 mol dm^{-3} NaOH solution containing 10 mmol dm^{-3} glucose at −0.3 and 0.3 V. Products with a current efficiency less than ca. 3% are shown by crossbar.

To our best knowledge, in the present study the electrocatalytic activities at $Au_{2\,nm}$ and Au–Pt (78:22) nanoparticle-modified electrodes for glucose oxidation were performed, for the first time. Further investigations on electrocatalytic oxidations of glucose using bimetallic nanoparticles based on gold are under way.

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16 The concentration of DT–(Au–Pt (78:22)) nanoparticles in hexane was unknown, however, which was 33 μmol dm^{-3}, when molar absorptivity of 4.4×10^5 mol^{-1} dm^3 cm^{-1} at 520 nm was used.
17 Before heat treatment, for example, bands corresponding to asymmetric and symmetric methylene stretching (2921 and 2852 cm^{-1}), and bands corresponding to asymmetric and symmetric methyl stretching (2956 and 2872 cm^{-1}) were observed for $Au_{2\,nm}$ capped with DT.

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