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Selective deposition of Pt on Au nanoparticles using hydrogen presorbed into Au nanoparticles during $NaBH_4$ treatment

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ABSTRACT

A facile chemical method to prepare a Pt layer selectively on Au nanoparticles is developed. The hydrogen presorbed into Au nanoparticles during $NaBH_4$ treatment leads to the formation of a thin Pt layer on Au nanoparticles. The Pt-coated Au nanoparticles exhibit significantly improved electrocatalytic activity for the electrooxidation of formic acid.

1. Introduction

In recent years, bimetallic Pt-coated Au nanomaterials have generated enormous interest because of their unique catalytic [1–4], electronic [5,6], and optical [7–11] properties compared to their monometallic counterparts. Continuing efforts are being made to develop new synthetic methods that can tailor nanomaterials to have higher activities and lower costs. Au nanoparticles (AuNPs) have been a basic starting material for this tailoring, because Au is relatively cheap and AuNPs can be readily prepared in various sizes and shapes [12–14]. Among noble metals, Pt is attractive because of its superior electrocatalytic and catalytic activities [15,16], but Pt-based applications have been limited by the inherent high consumption of expensive Pt. As an attempt to reduce Pt demands, the formation of a Pt layer on another relatively cheap metal has been widely employed and such Pt layers exhibit better electrocatalytic activity than the bulk metal [4,17–20], and in the case of a Pt (sub)monolayer, every Pt atom can contribute to the electrocatalytic reaction [19].

The formation of a metal layer on a foreign metal has been achieved by (i) spontaneous deposition [21–23], (ii) underpotential deposition (UPD) [11,20,24–28], (iii) metal growth on a foreign seed metal [4,8–10,17–19,29–31], or (iv) reduction of metal ions by presorbed hydrogen [32–37]. Spontaneous deposition is defined as the adsorption of metal ions on a foreign metal followed by their reduction [21–23]. However, nonspecific adsorption of metal ions on other surfaces via electrostatic interaction or complex formation may be problematic. UPD has been commonly employed to prepare a uniform metal (sub)monolayer on a foreign metal. Pt UPD on Au metal being unfavorable, Cu UPD on Au metal followed by Cu redox displacement with Pt is generally used to produce a Pt (sub)monolayer [11,20,24–28]. Metal growth on a foreign seed metal using mild reducing agents such as hydroxylamine is a simple chemical route to form a metal layer [17,18,29,31], however, it is difficult to obtain an uniform thin layer.

Pt and Pd can sorb (adsorb and absorb) a large amount of hydrogen [32–40], and this hydrogen can be used to reduce metal ions. Thus, reduction of metal ions by hydrogen presorbed into metal has been applied to forming an Au layer on Pt nanoparticles [32–34], a Ru layer on Pt nanoparticles [35], and a Pt layer on Pd nanoparticles [36,37]. Unlike Pt and Pd, Au does not sorb hydrogen when the metal is in contact with hydrogen gas [41]. Hence, it has not been feasible to form a Pt layer on Au by using hydrogen presorbed during treatment of hydrogen gas. In our recent study, however, it has been shown that hydrogen is sorbed into AuNPs during $NaBH_4$ treatment [42]. Thus sorbed hydrogen might also be used for reduction of metal ions.

Herein, we present a simple but efficient chemical method to prepare a Pt layer on AuNPs by using hydrogen presorbed into AuNPs during $NaBH_4$ treatment. The formation of a Pt layer was confirmed by cyclic voltammetry and XPS, and the electrocatalytic activities of Pt-coated and uncoated AuNPs for the electrooxidation of formic acid were investigated and compared.

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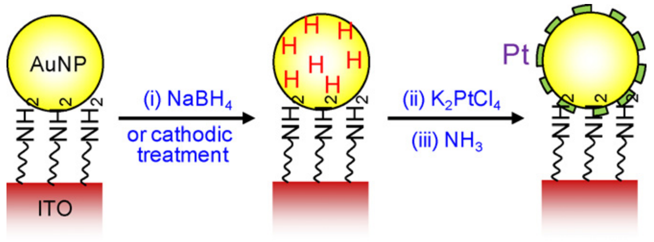

Scheme 1. Schematic representation for the preparation of a Pt layer on AuNPs using sorbed hydrogen.

2. Experimental

Indium-tin oxide (ITO)-coated glasses were obtained from Geomatec (www.geomatec.co.jp). An aqueous solution of citrate-stabilized AuNPs was purchased from Sigma, and the diameter of AuNPs was 20 ± 3 nm. All buffer reagents and other inorganic chemicals were supplied by Sigma, Aldrich, or Fluka. All chemicals were used as received. All aqueous solutions were prepared in doubly distilled water.

A carbonate buffer (pH 10.0) solution consisted of 0.1 M sodium carbonate and sodium bicarbonate. A Tris buffer solution (pH 9.0) consisted of 50 mM tromethamine (Tris) and 7 mM HCl.

ITO electrodes were pretreated according to the reported procedure [42]. (3-aminopropyl)triethoxysilane-modified ITO electrode was prepared by dipping the pretreated ITO into a methanolic solution containing 2% (3-aminopropyl)triethoxysilane (APTES) for 12 h, followed by washing with methanol and dried at 50 °C. AuNP- and APTES-modified ITO (AuNP/APTES/ITO) electrodes were prepared by dropping 100 μL of 20-nm colloidal AuNPs solution on to APTES-modified ITO electrodes for 2 h, followed by washing with water.

The electrochemical experiment was performed using a CHI 708C potentiostat (CH instruments). The electrochemical cell consisted of the modified ITO working electrode, a Pt counter electrode, and an Ag/AgCl reference electrode.

3. Results and discussion

A schematic representation for the formation of a Pt layer on AuNPs is shown in Scheme 1. The AuNP/APTES/ITO electrodes were immersed in a Tris buffer solution (50 mM Tris–HCl, pH 9.0) containing 10 mM $NaBH_4$ for 15 min, or the electrodes were potentiostatically controlled at −0.6 V for 10 min in 0.1 M H_2SO_4 (treatment i of Scheme 1: $NaBH_4$ or cathodic treatment). During the $NaBH_4$ or cathodic treatment, a large amount of hydrogen was sorbed into the AuNPs [42]. Next the hydrogen-sorbed AuNP/APTES/ITO electrodes were washed with water and immersed in an aqueous solution containing 0.1 mM K_2PtCl_4, which formed a Pt layer on the AuNPs (treatment ii of Scheme 1: Pt-ion treatment). Unreduced but adsorbed Pt ions were removed by then immersing the electrodes in an ethanolic solution containing 2 M NH_3 for 10 min (treatment iii of Scheme 1: NH_3 treatment), thusly, producing the Pt/AuNP/APTES/ITO electrodes prepared via $NaBH_4$ or cathodic treatment.

The sorption of hydrogen into AuNPs of AuNP/APTES/ITO electrodes was checked using cyclic voltammetry. In the first anodic scan recorded after $NaBH_4$ treatment of AuNP/APTES/ITO electrodes (curve i of Fig. 1), an anodic peak was observed at 0.2 V vs. Ag/AgCl, which is due to the electrooxidation of the sorbed hydrogen [42]. This peak was not observed in the second anodic scan (curve ii of Fig. 1), which also coincided well with the first scan recorded without $NaBH_4$ treatment (curve iii of Fig. 1). These results indicate that sorbed hydrogen was easily oxidized at low potentials.

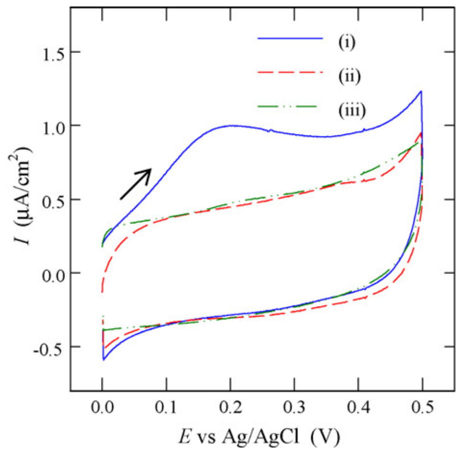

Fig. 1. Cyclic voltammograms of AuNP/APTES/ITO electrodes obtained in a carbonate buffer solution (pH 10) after (i, ii) and before (iii) $NaBH_4$ treatment at a scan rate of 10 mV s^{-1}. Curves (i) and (iii) correspond to the first scan, whereas curve (ii) corresponds to the second scan.

Although the anodic peak potential in curve i of Fig. 1 (ca. 0.2 V) is higher than the standard electrode potential of normal hydrogen electrode (−0.22 V), it is sufficiently lower than the potential required for reducing $[PtCl_4]^{2-}$ ions to elemental Pt (ca. 0.54 V).

Compared to Au electrodes, Pt electrodes require low overpotentials for generating hydrogen cathodically. If a Pt layer is formed on AuNPs, the electrochemical behavior for generating hydrogen cathodically changes substantially. The formation of Pt on AuNPs was verified by a cyclic voltammogram of AuNP/APTES/ITO electrodes obtained in a condition suitable for generating hydrogen cathodically (i.e., in 0.1 M H_2SO_4) after sequential $NaBH_4$, Pt-ion, and NH_3 treatments (curve i of Fig. 2a). Large peaks related to hydrogen generation and oxidation by Pt were observed around −0.3 V, indicating that a Pt layer had formed on the AuNP/APTES/ITO electrodes after the full sequential treatment. However, without the $NaBH_4$ treatment, such peaks were not observed after sequential Pt-ion and NH_3 treatments (curve ii of Fig. 2a). Obviously, the $NaBH_4$ treatment played a crucial role in forming a Pt layer on AuNP/APTES/ITO electrodes, in which hydrogen presorbed during the $NaBH_4$ treatment allowed Pt deposition. Cathodic as well as the $NaBH_4$ treatment allows hydrogen sorption into AuNPs [42]. Hence, a cyclic voltammogram of AuNP/APTES/ITO electrodes obtained after sequential cathodic, Pt-ion, and NH_3 treatments (curve iii of Fig. 2a) also showed Pt-related hydrogen peaks. This result confirms that sorbed hydrogen is involved in forming a Pt layer on the AuNP/APTES/ITO electrodes. Although cathodic treatment can be used for forming a Pt layer, it requires the application of high negative potentials to an electrode, which could damage the electrode and its surface layer. Moreover, cathodic treatment is unfeasible when AuNPs are not in contact with an electrode. Therefore, chemical treatment such as with $NaBH_4$ is more desirable for practical use.

A Pt layer can be formed on AuNPs by the spontaneous deposition in which $[PtCl_4]^{2-}$ ions are adsorbed onto AuNPs and reduced. However, $[PtCl_4]^{2-}$ ions can also be electrostatically adsorbed onto the NH_3^+ groups of APTES/ITO electrodes at neutral pHs [43]. If the adsorbed Pt ions are reduced, small Pt nanoparticles is formed on the APTES layer. Hence, the selective formation of Pt on AuNPs cannot be achieved by spontaneous deposition. To form a Pt layer only on the AuNPs and to reduce Pt ions via only hydrogen presorbed into AuNPs, the Pt ions unreduced but adsorbed on the AuNP/APTES/ITO electrodes should be completely removed. Repetitive water washing cannot remove adsorbed Pt ions from the AuNP/APTES/ITO electrodes, whereas they can be efficiently removed by NH_3 treat-

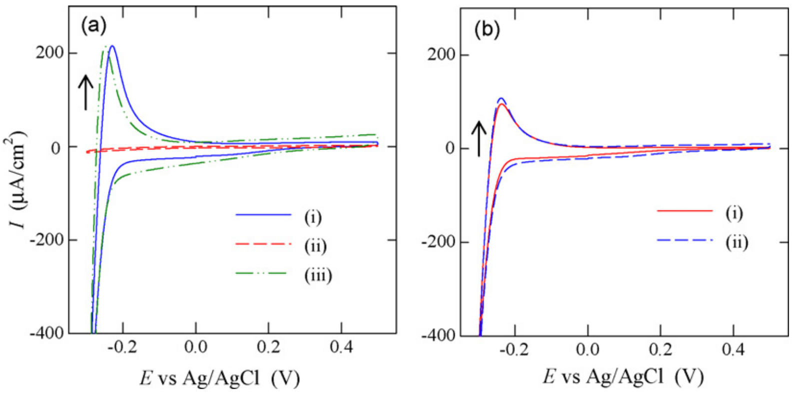

Fig. 2. (a) Cyclic voltammograms of AuNP/APTES/ITO electrodes obtained in deaerated 0.1 M H_2SO_4 at a scan rate of 50 mV s^{-1} after (i) sequential $NaBH_4$, Pt-ion, and NH_3 treatments, (ii) sequential Pt-ion and NH_3 treatments, or (iii) sequential cathodic, Pt-ion, and NH_3 treatments. (b) Cyclic voltammogram of (i) APTES/ITO and (ii) AuNP/APTES/ITO electrodes obtained in deaerated 0.1 M H_2SO_4 at a scan rate of 50 mV s^{-1} after Pt-ion treatment followed by washing with water and reduction of Pt ions. Pt ions were reduced by $NaBH_4$.

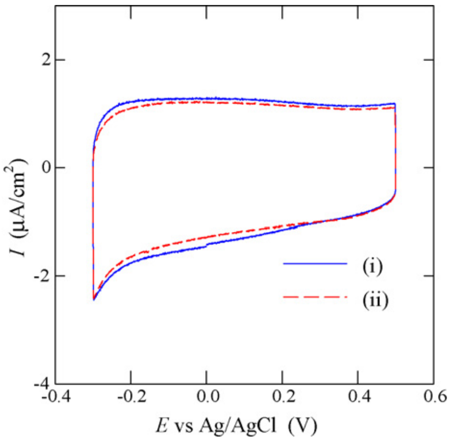

Fig. 3. Cyclic voltammograms of APTES/ITO electrodes obtained in deaerated 0.1 M H_2SO_4 at a scan rate of 50 mV s^{-1} (i) without any treatment or (ii) after sequential $NaBH_4$, Pt-ion, and NH_3 treatments.

ment, possibly facilitated by Pt-ion complexation with NH_3. A cyclic voltammogram of APTES/ITO electrodes obtained in 0.1 M H_2SO_4 after Pt-ion treatment followed by washing with water and reducing Pt ions (curve i of Fig. 2b) was similar to that of AuNP/APTES/ITO electrodes (curve ii of Fig. 2b). Even in the absence of AuNPs, Pt-related peaks were observed, clearly showing that Pt ions were adsorbed on the APTES layer as well as the AuNPs and, thus, it was essential to remove adsorbed Pt ions for the selective formation of Pt on AuNPs. Notably, curve ii of Fig. 2a shows no Pt-related hydrogen peaks, indicating complete removal of adsorbed Pt ions from the electrodes by NH_3 treatment. A cyclic voltammogram of APTES/ITO electrodes recorded after sequential $NaBH_4$, Pt-ion, and NH_3 treatments (curve ii of Fig. 3) showed no Pt-related peaks, reconfirming removal of Pt ions from the electrodes by NH_3 treatment and also showing that the hydrogen was sorbed only into AuNPs during the $NaBH_4$ treatment. Therefore, a thin Pt layer was formed only on hydrogen-sorbed AuNPs.

The presence of Pt on AuNPs was further confirmed by X-ray photoelectron spectroscopy (XPS) (Fig. 4). The peaks at 86.8 and 83.2 eV in spectra of AuNP/APTES/ITO electrodes (curve i of Fig. 4a) are associated with Au $4f_{5/2}$ and Au $4f_{7/2}$ core levels, respectively [25]. Spectra of Pt/AuNP/APTES/ITO electrodes prepared via $NaBH_4$ treatment (curve ii of Fig. 4b) contained two additional peaks corresponding to Pt $4f_{5/2}$ and Pt $4f_{7/2}$ at 75.1 and 71.6 eV, respectively, indicating the presence of Pt^0 states on the AuNPs [44]. The intensity of Pt signals was much lower than that of Au, which implied that the amount of Pt was quite small compared to that of Au [19].

Pt-coated AuNPs are very active in the electrooxidation of formic acid [17,18]. The electrocatalytic activities of Pt/AuNP/APTES/ITO and as-prepared AuNP/APTES/ITO electrodes for the electrooxidation of formic acid were compared by their cyclic voltammograms obtained in 0.1 M H_2SO_4 containing 1.0 M HCOOH. The activities of the AuNP/APTES/ITO electrodes were quite low (curve i of Fig. 5a), but after $NaBH_4$ treatment, the activities of these electrodes increased significantly (curve ii of Fig. 5a). $NaBH_4$ treatment does enhance the electrocatalytic activity of AuNPs [42], however, the improved activities of AuNP/APTES/ITO electrodes were significantly lower than the activities of Pt/AuNP/APTES/ITO electrodes prepared via $NaBH_4$ treatment (curve iii of Fig. 5b).

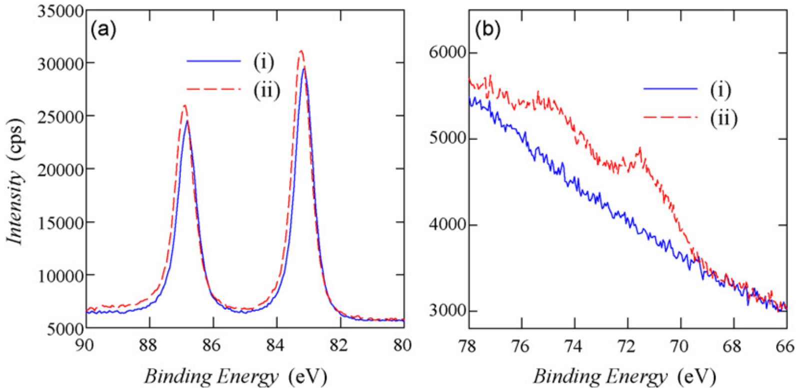

Fig. 4. (a) Au and (b) Pt XPS spectra of (i) AuNP/APTES/ITO electrodes and (ii) Pt/AuNP/APTES/ITO electrodes.

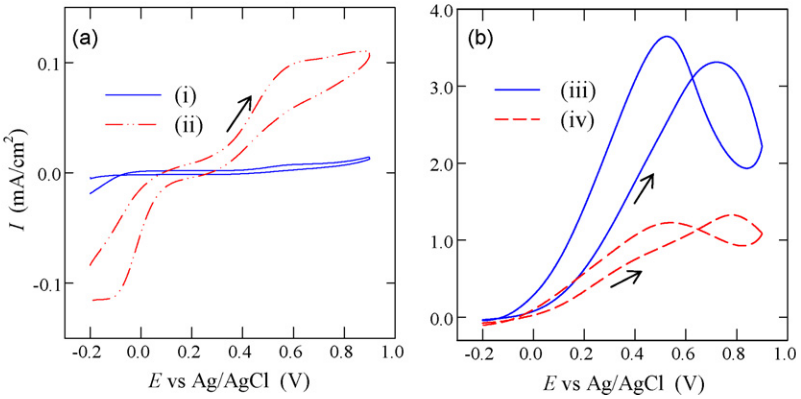

Fig. 5. Cyclic voltammograms obtained in 0.1 M H_2SO_4 and 1.0 M HCOOH at a scan rate of 50 mV s^{-1} on (a) AuNP/APTES/ITO electrodes (i) before and (ii) after $NaBH_4$ treatment and on (b) Pt/AuNP/APTES/ITO electrodes prepared via (iii) $NaBH_4$ treatment and (iv) spontaneous deposition.

During HCOOH electrooxidation on Pt electrodes, CO-poisoning effect due to HCOOH dehydration could be a serious problem [17,45–47]. In this case, anodic current in the forward scan is much lower than that in the reverse scan [17]. Cyclic voltammogram for HCOOH electrooxidation on Pt/AuNP/APTES/ITO electrodes showed one peak at 0.7 V in the forward scan and one peak at 0.56 V in the reverse scan (curve iii of Fig. 5b). Two peak currents are not significantly different. It indicates that CO-poisoning effect is not serious on this electrode.

The amount of Pt loading was varied by changing the time of $NaBH_4$ treatment (Fig. S2 in Supplementary Materials). It has been found that the peak current for HCOOH electrooxidation increased with increasing the treatment time. However, the cyclic voltammogram on Pt/AuNP/APTES/ITO electrodes obtained after 15-min treatment (curve iii of Fig. 5b) is similar to that after 30-min treatment (curve iii of Fig. S2 in Supplementary Materials). It shows that there was no significant change in the peak current after $NaBH_4$ treatment for more than 15 min. It seems that the hydrogen sorption was saturated after 15-min $NaBH_4$ treatment.

It is interesting to note that the electrocatalytic activities of Pt/AuNP/APTES/ITO electrodes prepared via spontaneous deposition (curve iv of Fig. 5b) were lower than those of Pt/AuNP/APTES/ITO electrodes prepared via $NaBH_4$ treatment (curve iii of Fig. 5b). Moreover, the anodic peak current associated with hydrogen oxidation in the case of spontaneous deposition was smaller than that of $NaBH_4$ treatment (curve i of Fig. 2a), possibly resulting from the effect that the amount of Pt formed via $NaBH_4$ treatment was higher than that formed via spontaneous deposition.

4. Conclusions

In conclusion, we have developed a facile chemical method to prepare a Pt layer selectively on the AuNPs of AuNP/APTES/ITO electrodes. Hydrogen presorbed into AuNPs during $NaBH_4$ treatment led to the formation of a thin Pt layer on the AuNPs. NH_3 treatment facilitated the removal of Pt ions unreduced but absorbed on the AuNPs and the APTES layer. The Pt-coated AuNPs exhibited significantly improved electrocatalytic activity for the electrooxidation of formic acid. The formation of other metal-coated AuNPs via $NaBH_4$ treatment could be possible, and the formation of other metal layers on Pt or Pd nanoparticles might be possible without using explosive hydrogen gas. Therefore, $NaBH_4$ treatment is practically appealing for the preparation of a metal layer on foreign metals.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.electacta.2009.01.022.

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