

In Situ Chemical Reductive Growth of Platinum Nanoparticles on Indium Tin Oxide Surfaces and Their Electrochemical Applications

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Platinum nanoparticles directly attached to indium tin oxide (PtNP/ITO) were successfully fabricated by using an in situ chemical reductive growth method. In this method, PtNPs could be grown on the ITO surface via the one-step immersion into the growth solution containing PtCl_4^{2-} and ascorbic acid. The attached and grown PtNPs were spherical having an agglomerated nanostructure composed of small nanoclusters. From the morphological changes depending on the growth time, which were observed with an FE-SEM, PtNPs were found to be grown via the progressive nucleation mechanism. As the characteristics of the PtNP/ITO were those of a working electrode, it was found that the charge transfer resistivity was significantly lowered due to the grown PtNPs. Hence, for a typical redox system of $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$, the PtNP/ITO electrode exhibited the electrochemical responses similar to those of the bulk Pt electrode. Furthermore, it was clarified that the PtNP/ITO electrode had significant electrocatalytic properties for the oxygen reduction and methanol oxidation. The present PtNPs that had the agglomerated nanostructure may be promising for a new type of electrode material.

Introduction

Metal nanoparticle-attached surfaces have been attracting active attention in recent years because the unique properties of metal nanoparticles, such as optical, electronic, magnetic, and catalytic properties, can be added onto the characteristics of the attached surfaces. Various attachment methods of metal nanoparticles are available nowadays, including physical and chemical methods, such as casting, metal evaporation, electrochemical deposition, chemical impregnation reduction, the use of bridging reagents, etc. For example, the preparation methods of Pt nanoparticles on solid supports have been well summarized in the papers by Dong and co-workers.^{1,2}

Although a suitable method has been adopted to attach metal nanoparticles depending on the research purposes and/or the characteristics of the substrate surfaces, the colloid-based nanoparticle synthesis combined with bridging reagents would be a better method with respect to the uniformity of the nanoparticles. On glass surfaces, Au or Ag nanoparticles can be attached with the bridging reagents, such as 3-mercaptopropyltrimethoxysilane or 3-aminopropyltrimethoxysilane utilizing the affinity of the $-\text{SH}$ or the $-\text{NH}_2$ group toward Au or Ag.^{3–5} The same method is effective for the attachment on the indium tin oxide (ITO) surfaces, which is conductive and optically transparent. The electrochemical characteristics of Au nanoparticle-attached ITO have been studied for the application as nanoelectrode ensembles.^{6,7}

Although many papers have been devoted to the modification of Pt nanoparticles (PtNPs) on carbon, platinum, and gold

electrode substrates,^{8–13} reports of the attachment of PtNPs on ITO are very scarce in comparison with the works on Au or Ag nanoparticle-attached ITO. This is probably due to the smaller affinity of Pt toward the functional groups, such as $-\text{SH}$ or $-\text{NH}_2$. Up to now, only the layer-by-layer assembly method has been applied to the modification of PtNPs on ITO.^{2,14} As another approach, ultrathin Pt-coated Au nanoparticle-attached ITO has been reported with the electrochemical characteristics.¹⁵

Despite the scarceness of the studies, if we can attach PtNPs on ITO, in particular with keeping a moderate dispersion in a monolayer, like the cases of Au and Ag,^{3–5} some interesting applications may be permitted. One possibility is the application for optical devices, because PtNPs are also known to be effective for surface-enhanced Raman and IR spectroscopy.^{16–18} Another application is for electrochemistry. Although the high-conducting substrates (C, Pt, Au) have been mainly utilized for the electrochemical measurements with PtNPs,^{8–13} the combination with the less-conducting ITO may permit us to evaluate the electrochemical characteristics of PtNPs themselves by separating the responses of PtNPs from those of conducting substrates. Thus, in the present work, we adopted the attachment of PtNPs on ITO as a new target in a series of our studies on metal nanoparticle-attached ITO.^{19–22}

In the previous papers, we reported the attachment of Au or Ag nanoparticles on ITO without using bridging reagents.^{19–22} By applying the seed-mediated growth approach, which was originally developed for the formation of Au or Ag nanorods in solution,^{23,24} to the surface modification of ITO, we have succeeded in attaching the Au nanosphere particles and nanorods^{19,20,22} and the Ag nanoparticles and nanowires²¹ on ITO surfaces.

However, in our preliminary trial, the seed-mediated growth approach was found to be difficult to apply to the fabrication of PtNP-attached ITO. This is because brown precipitates

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appeared in the growth solution prepared in the same process, i.e., containing K_2PtCl_4 , cetyltrimethylammonium bromide (CTAB), and ascorbic acid, even when the seed-attached ITO was not immersed. Despite this difficulty, after several trials, we have found that the attachment of PtNPs on ITO is possible by a rather simple method, i.e., the one-step in situ chemical reduction of PtCl_4^{2-} by ascorbic acid without using CTAB. In the present paper, the attachment and the structural growth of PtNPs on ITO are described at first. Then, the PtNPs directly attached ITO (PtNP/ITO) are applied for some electrochemical measurements, and the results are compared with those of our AuNP/ITO and AgNP/ITO electrodes.^{19,20,22}

Experimental Section

Materials. $\text{K}_3[\text{Fe}(\text{CN})_6]$, $\text{K}_4[\text{Fe}(\text{CN})_6]$, ascorbic acid, and K_2PtCl_4 were obtained from Wako Pure Chemicals, Ltd. Glass plates on which ITO film was coated were purchased from CBC Ings Optics Ltd. (resistance ca. $50 \Omega/\square$, size $18 \text{ mm} \times 18 \text{ mm}$). A piece of the ITO glass was cut into four pieces, and used after washing in acetone, ethanol, and pure water with sonication and drying with nitrogen gas. The conventional bulk Pt electrode (Pt disk; $\phi = 1.6 \text{ mm}$) was purchased from BAS Inc. It was polished to a mirrorlike finish with a diamond suspension (250 nm) and washed carefully by the same method used for ITO pieces. In all the procedures and the preparation of solution, we used pure water prepared using Millipore Autopure WR600A (Millipore, Ltd., resistivity $> 18 \text{ M}\Omega$).

Apparatus. The surface morphology of the PtNPs attached to the ITO surfaces was characterized with a field-emission scanning electron microscopy (FE-SEM, JSM-7400F, JEOL, Japan). The electrochemical measurements were performed with an EG&G M263A potentiostat/galvanostat (Princeton Applied Research (PAR), U.S.A.) and a 5210 lock-in amplifier (PAR) controlled by a computer with M270 and M398 programs (PAR). The UV-vis pattern was measured on the P400-2-UV-vis system (BAS, Inc.).

In Situ Chemical Reductive Growth Procedures. Typical procedures to attach PtNPs on ITO eventually adopted in the present work are as follows: First, 0.5 mL of 10 mM K_2PtCl_4 solution was added into 18 mL of pure water. Then, a carefully cleaned piece of ITO was immersed into the solution. After that, 1.0 mL of 0.10 M ascorbic acid was added into the solution containing the ITO piece and the solution was left for a constant time (4, 8, 12, and 24 h.) at room temperature. The PtNPs that directly attached ITO (PtNP/ITO) were removed from the solution, and rinsed with pure water several times, then dried with nitrogen gas for the FE-SEM characterization and the electrochemical measurements.

If the ITO was immersed after the addition of ascorbic acid or during the PtNPs formation process, the attachment of PtNPs was possible. However, the attached density became lower in such cases. Thus, we show the results prepared in the above conditions.

Fabrication of the PtNP/ITO Electrode. To evaluate the electrochemical properties of PtNP/ITO, a handmade PtNP/ITO working electrode was fabricated as follows: At first, a piece of ITO on which PtNPs was attached was connected to a strip of copper adhesive tape (3M Copper Tape 1181, $50 \text{ mm} \times 6 \text{ mm}$) and then molded into a piece of scotch tape (3M Filament Tape 898, $50 \text{ mm} \times 18 \text{ mm}$) that was made to have a 2-mm-diameter hole. For the electrochemical measurements, the exposed area of $\phi = 2.0 \text{ mm}$ was the working surface to contact with the solution.

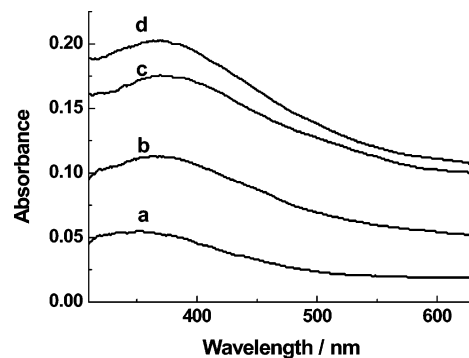


Figure 1. UV-visible absorbance spectra of the PtNP/ITOs fabricated with different growth times: (a) 4, (b) 8, (c) 12, and (d) 24 h.

Results and Discussion

Absorption Spectra of PtNP/ITO. During the in situ chemical reductive growth process, the color of the solution gradually turned from pale yellowish-brown to darkish, confirming the formation of Pt colloids in the aqueous phase. Accompanying this transformation, the color of the ITO was also observed to change from transparent to pale yellowish-brown and finally pale darkish brown. Thus, it is expected that the attachment and growth of PtNPs proceeded on the surface of the ITO, though the PtNPs were concurrently formed in the solution during the present reduction process.

Figure 1 shows the absorption spectra of the PtNP/ITO samples fabricated with different immersing times (4, 8, 12, and 24 h) in the growth solution. The absorbance around 350 nm increased with an increase of the growth period, accompanying a slight red-shift of the absorption maximum. This implies that the attachment and/or growth of PtNPs proceeded with an increase in the reduction time. However, compared with the increase until 12 h, the absorption observed after 24 h of growth did not exhibit a significance increase. Thus, the attachment and growth processes may be saturated before 24 h.

In the formation process of the Pt colloid from PtCl_6^{2-} , it is known that the UV-vis absorption transforms from that with a peak of PtCl_6^{2-} at 258 nm to the featureless one, in which the absorption merely increases with the decrease of wavelength.^{25,26} However, the absorption of PtNPs grown over several tens of nanometers is not well known. Thus, for recognizing the exact grown-up structures of PtNPs on ITO, we observed the FE-SEM images of each ITO surface.

FE-SEM Observation of PtNP/ITO Surface. Figure 2 shows the typical FE-SEM images of the surface of PtNP/ITO that was prepared by immersion into the growth solution for 24 h. As shown in the low-magnification image (Figure 2A), it was found that the PtNPs, which were recognized as bright dots, grew on the ITO surface with keeping a moderate dispersion. The shape of PtNPs was almost spherical, but the size dispersion was not very regular; i.e., the diameters of the spherical PtNPs ranged from ca. 5 to 100 nm. From this irregularity, it is inferred that each particle grew randomly on the ITO surface until a certain size of ca. 100 nm.

In addition, each spherically grown PtNP did not exhibit single crystal-like appearance as in the case of AuNPs,²⁰ but looked as if it were composed of some small nanoclusters. Figure 2B shows the high-magnification FE-SEM image of the surface of PtNP/ITO. It can be recognized that each PtNP is not a single crystal but has an agglomerated nanostructure. As the result of the literature survey for the PtNPs on various formed surfaces, it was found that quite similar nanostructured

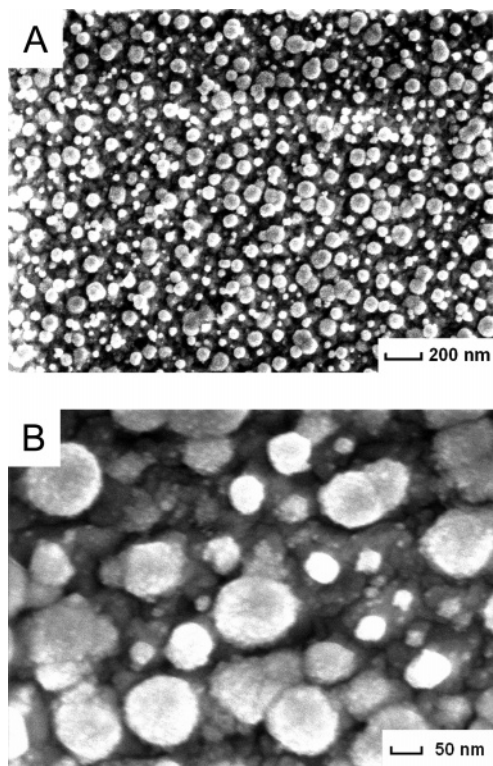


Figure 2. Typical FE-SEM images of the Pt nanoparticle-attached ITO surface: (A) low-magnification image and (B) high-magnification image for the same area. The ITO substrate was immersed in the growth solution containing 0.25 mM K_2PtCl_4 and 5 mM ascorbic acid for 24 h.

PtNPs were reported to be formed on boron-doped diamond (BDD) electrode surfaces.²⁷ In this work, it was clarified that the electrodeposition of PtNPs on the BDD proceeded via the progressive nucleation mechanism, and that the 3D spherical nanostructured PtNPs were favorably formed due to the small binding energy between Pt adatom and the BDD support, which is much weaker than that of the Pt adatoms themselves.²⁷ Because the appearance of PtNPs formed on the ITO surface (Figure 2) is very similar to that on BDD with electrochemical deposition, we can expect that the interaction between ITO and PtNP is also weak, and that the progressive nucleation has made the spherical 3D nanostructured PtNPs also in the present in situ chemical reduction on the ITO surface. The size irregularly observed in Figure 2A also implies that the PtNPs proceeded via the progressive nucleation where the nucleation rate is low and nuclei are continuously formed during the chemical deposition processes.

Effect of Reduction Time on the Surface Morphology of PtNP/ITO. To elucidate the in situ chemical reductive growth in more detail, we observed the FE-SEM images of the PtNP/ITO samples prepared with the different reduction times (4, 8, and 12 h). Figure 3 shows the typical FE-SEM images.

After 4 h of reduction (Figure 3A), PtNPs were observed to attach sparsely on the ITO surface. The sizes of the PtNPs were between 5 and 30 nm. After 8 h of reduction (Figure 3B), the density of PtNPs was apparently increased in comparison with that in Figure 3A, with the size distribution between 5 and 80 nm. The average diameter was increased after 12 h of reduction as shown in Figure 3C. However, the small PtNPs of ca. 5 nm could be observed on the surface also in this case. Thus, the morphological changes in the FE-SEM images with the reduction time also support the progressive nucleation mechanism.

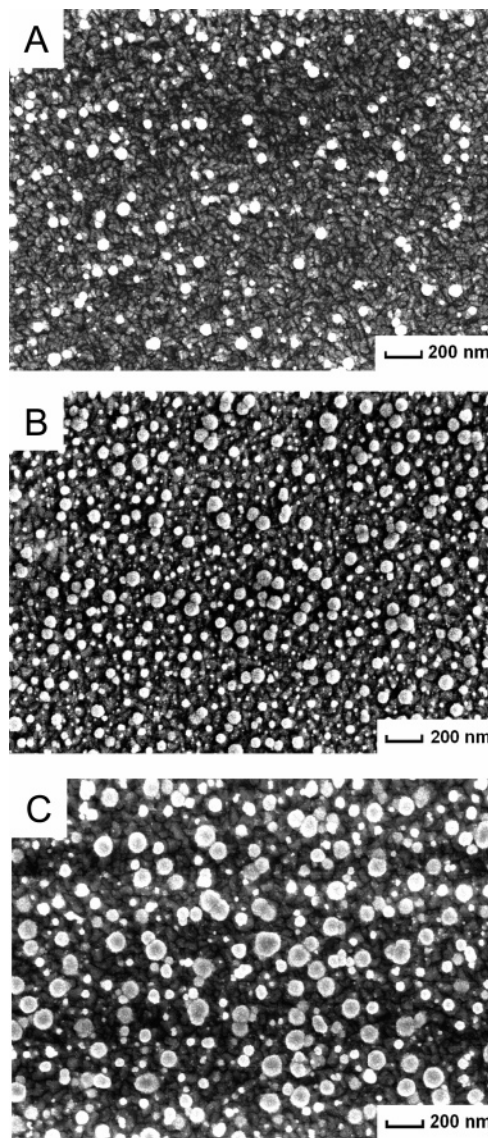


Figure 3. FE-SEM image of the PtNP/ITO samples prepared with different reduction times: (A) 4, (B) 8, and (C) 12 h.

In a comparison between Figure 2A (24 h) and Figure 3C (12 h), while the attached density of PtNPs increased with time, the maximum size of grown PtNPs was not very different. This is in contrast with Figure 3A–C, where the size increase was observed with the increase in the reduction time. Thus, we can assume that the present chemical reductive growth or nucleation was saturated before 24 h of reduction. Actually, we cannot find the distinct difference between the FE-SEM images of the reduction of 36 and 24 h (data are not shown). This conclusion agrees with the changes of the UV–visible spectrum in Figure 1, of course, because the absorption is the reflection of the attached density and sizes of PtNPs.

Applicability of PtNP/ITO for Electrochemical Measurements. On the basis of the above FE-SEM observation, it is expected that we can control the dispersion and size of PtNPs directly attached to ITO by changing the reduction time. In addition, due to the progressive nucleation to form the agglomerated nanostructure of PtNP, which is quite different from the previous cases of AgNP/ITO and AuNP/ITO, it should be interesting to observe the electrochemical characteristics of the PtNP/ITO. Thus, we applied the PtNP/ITO as a working electrode for several electrochemical measurements.

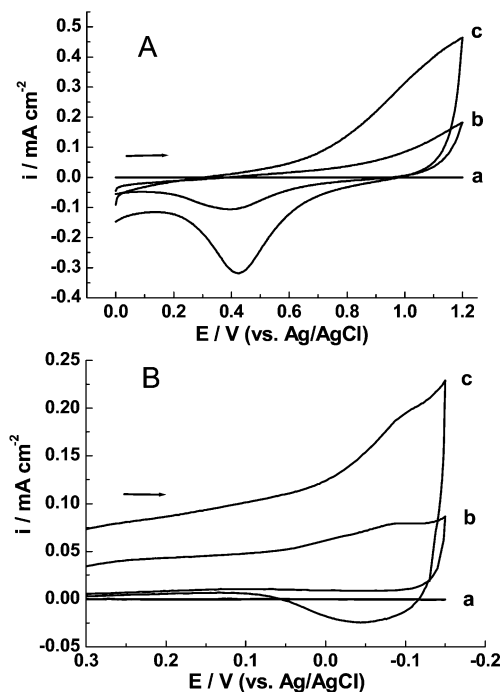


Figure 4. Cyclic voltammograms recorded with the PtNP/ITO electrode in the solution containing H₂SO₄. (A) Oxidative scan in 0.05 M H₂SO₄ solution and (B) reductive scan in the 1.0 M H₂SO₄ solution. Working electrode: (a) a bare ITO electrode, (b, c) the PtNP/ITO electrodes prepared via (b) 4 and (c) 24 h of growth. Scan rate: 50 mV s⁻¹. Geometric electrode area: (a–c) 0.031 cm².

Before describing the results, we would like to mention the robustness of the attachment of PtNPs on ITO. As described in the Experimental Section, the surface of PtNP/ITO was washed by flushing with water several times and drying before the FE-SEM measurement. However, the FE-SEM images clearly showed the PtNPs attached to ITO. In addition, though we observed the FE-SEM images after treating the PtNP/ITO in hot water with sonication for 20 min, no distinct removal of PtNPs was observed. So, in the present *in situ* chemical reductive growth method, we are sure that PtNPs adhered to the ITO surface strong enough for practical uses, e.g., as a working electrode. We expect that this firm binding comes from the initial adhesion of small nuclei particles on the ITO surface followed by the gathering growth. While the present approach is one-step reduction, the adhesion ability of grown nanoparticles is similar to those of AuNPs and AgNPs formed on ITO via the seed-mediated growth approach.^{19–21}

Electrochemical Characterizations of the PtNP/ITO Electrode. To evaluate the electrochemical properties of the PtNP/ITO, several electrochemical measurements were carried out with the PtNP/ITO working electrode. Figure 4 shows the redox properties recorded with the PtNP/ITO working electrode for the aqueous solutions containing H₂SO₄. As shown in this figure, the redox properties that come from Pt were clearly observed for the PtNP/ITO electrodes in the oxidative scan for the Pt oxidation and the Pt oxide reduction (Figure 4A) and in the reductive scan for the hydrogen redox region (Figure 4B). Reflecting the difference of the crystal growth of PtNPs on the ITO surface (Figures 2 and 3), the redox current reasonably increased in comparison between the 4 and 24 h of growth. In addition, it was also noticed that the background current increased with the growth of PtNPs. Although the potential was cycled several times from -0.2 to 1.5 V with the PtNP/ITO electrode, the redox behaviors of Pt showed good reproduc-

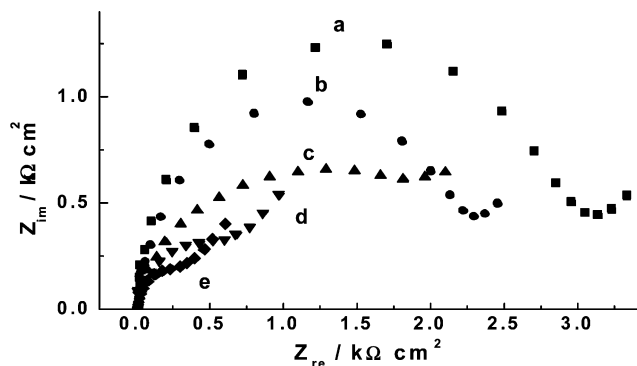


Figure 5. Electrochemical impedance spectra recorded at 0.22 V in 0.1 M phosphate buffer solution (pH 7.0) containing 0.5 mM [Fe(CN)₆]³⁻ and 0.5 mM [Fe(CN)₆]⁴⁻ with use of (a) a bare ITO electrode and (b–e) PtNP/ITO electrodes prepared via (b) 4, (c) 8, (d) 12, and (e) 24 h of growth. Geometric electrode area: (a–c) 0.031 cm².

ibility. This indicates that the PtNPs on the ITO surface were stable in the cyclic potential scans.

Next, the electrochemical impedance of the PtNP/ITO electrode was measured to evaluate the effect of PtNPs on the electron-transfer reactions. To compare with the results of the AuNP/ITO^{19,22} and AgNP/ITO²¹ electrodes, the Cole–Cole plots were recorded for the sample solution containing both [Fe(CN)₆]³⁻ and [Fe(CN)₆]⁴⁻ in the PBS solution (pH 7.0). The results are shown in Figure 5. The decrease in the charge-transfer resistivity (*R*_{ct}) was clearly observed for the PtNP/ITO electrodes, along with the increase of the growth time of PtNPs, compared with that of the bare ITO electrode. The *R*_{ct} values were determined to be 3.05 kΩ cm⁻² for the bare ITO electrode and 2.36, 1.54, 0.74 and 0.44 kΩ cm⁻² for the PtNP/ITO electrodes prepared with the growth time of 4, 8, 12, and 24 h, respectively.

In comparison with the cases of AuNP/ITO and AgNP/ITO electrodes, the decrease in *R*_{ct} of the PtNP/ITO electrode prepared with 24 h of growth was much larger. That is, the *R*_{ct} of the PtNP/ITO electrode was ca. 15% of that of the bare ITO electrode, while the decreased degree was ca. 27% for the AuNP/ITO electrode¹⁹ and ca. 44% for the AgNP/ITO electrode.²¹ In addition, it was characteristic that the plots for the PtNP/ITO electrodes prepared with 12 and 24 h of growth exhibited the straight line responses at higher frequency, which means that the effect of the charge-transfer resistivity is smaller than the effect of the diffusion control. Thus, compared with the AuNP/ITO and AgNP/ITO electrodes, the PtNP/ITO electrode prepared with 12 or 24 h of growth is inferred to have superior characteristics with respect to the charge-transfer resistivity. The tendency of the decrease in *R*_{ct} with the growth time roughly coincides with the growth of PtNPs observed in the FE-SEM images.

As an example for the observation of typical redox systems, the cyclic voltammetry for the oxidation of [Fe(CN)₆]⁴⁻ in 1.0 M KCl and 0.1 M phosphate buffer solutions was recorded with the PtNP/ITO electrode prepared by the 24 h of growth. The results are shown in Figure 6, together with those obtained by using the bare ITO electrode and the bulk Pt electrode. The current values were normalized by dividing the electrode geometric surface area, i.e., in the present case, the area of $\phi = 2.0$ mm exposed to the solution. As recognized from Figure 6, the electrochemical responses observed with the PtNP/ITO electrode were similar to those observed with the bulk Pt electrode, and were much improved in comparison with those obtained with the bare ITO electrode.

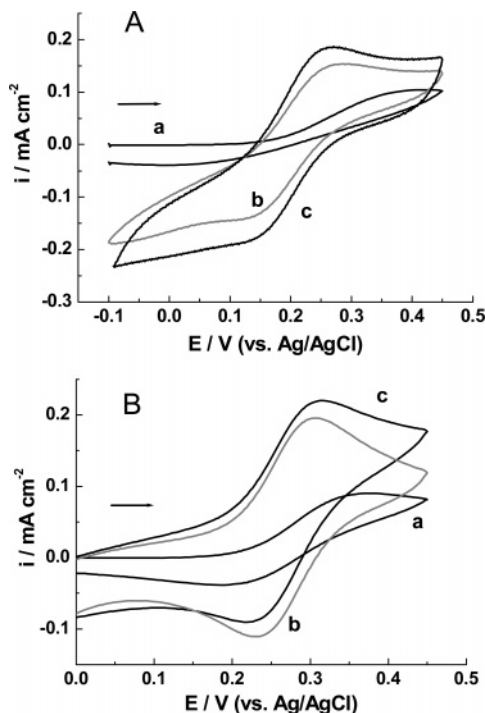


Figure 6. Cyclic voltammograms of 1.0 mM $[\text{Fe}(\text{CN})_6]^{4-}$ in (A) 0.1 M phosphate buffer solution (pH 7.0) and (B) 1.0 M KCl solution recorded with (a) a bare ITO electrode, (b) a bulk Pt electrode, and (c) the PtNP/ITO electrode prepared via 24 h of growth. Scan rate: 50 mV s^{-1} . Geometric electrode area: (a, c) 0.031 and (b) 0.020 cm^2 . The current axis was normalized by dividing the surface areas.

As shown in Figure 2, not all the ITO surface was covered by PtNPs. However, the redox current recorded with the PtNP/ITO electrode was similar, or rather larger than those observed with the Pt electrode. Thus, it is inferred that the coverage of PtNPs as in Figure 2 is sufficient to form a diffusion layer similar to the case of the planer bulk Pt electrode. As a remarkable function of PtNPs, it is expected that they reduced the electron-transfer resistivity as in Figure 5, and presented the enhanced electrochemical response, in particular for the case of the low conductive 0.1 M phosphate buffer solution (Figure 6A).

Electrocatalytic Properties of the PtNP/ITO Electrode for the Reduction of Oxygen and the Oxidation of Methanol. Although it was found that the PtNP/ITO electrode was utilized to obtain the redox behaviors similar to those obtained with the bulk Pt electrode, judging from the surface images in nanoscale, in particular, from the agglomerated nanostructure of PtNPs (Figure 2B), it was expected the specific electrochemical responses might be observed with the present PtNP/ITO electrode. To realize this assumption, we observed the electrochemical responses of the oxygen reduction and the methanol oxidation.

Figure 7 shows the cyclic voltammograms obtained for the oxygen reduction with the PtNP/ITO electrode (Figure 7a) and the Pt bulk electrode (Figure 7c) in the air-saturated 0.5 M sulfuric solution, together with that recorded with the PtNP/ITO electrode in the N_2 -saturated 0.5 M H_2SO_4 solution (Figure 7b). As is easily recognized from Figure 7, the significantly enhanced catalytic response was observed with the PtNP/ITO electrode for the reduction of oxygen. The peak current was more than three times that recorded with the bulk Pt electrode.

In the recent work by Dong and co-workers,² tunable electrocatalytic characteristics for the dioxygen reduction have been reported by constructing layer-by-layer assembly of PtNPs

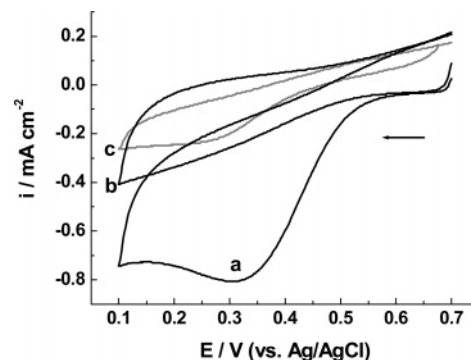


Figure 7. Cyclic voltammograms recorded with (a, b) the PtNP/ITO electrode prepared via 24 h of growth for (a) air-saturated and (b) N_2 -saturated 0.5 M H_2SO_4 solutions and (c) a Pt bulk electrode for the air-saturated 0.5 M H_2SO_4 solution. Scan rate: 50 mV s^{-1} . Geometric electrode area: (a, b) 0.031 and (c) 0.020 cm^2 . The current axis was normalized by dividing the surface areas.

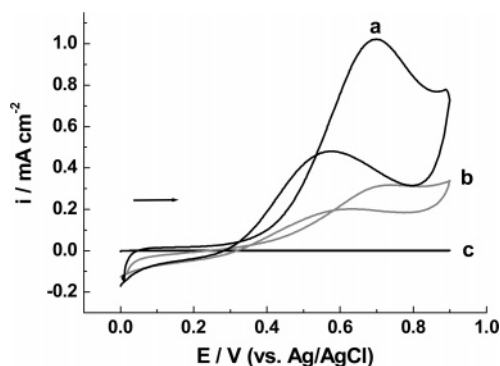


Figure 8. Cyclic voltammograms obtained for 0.1 M methanol oxidation in the N_2 -saturated 0.5 M sulfuric solution recorded with (a) the PtNP/ITO electrode prepared via 24 h of growth, (b) a Pt bulk electrode, and (c) a bare ITO electrode. Scan rate: 50 mV s^{-1} . Geometric electrode area: (a, c) 0.031 and (b) 0.020 cm^2 . The current axis was normalized by dividing the surface areas.

and [tetrakis(*N*-methylpyridyl)porphyrinato]cobalt. By modifying a glassy carbon electrode via 4-aminobenzoic acid with the layer-by-layer structure, the increase of the electrocatalytic property has been beautifully reported with the increase in the layers. However, the enhanced peak current observed with 14 layers of PtNPs, which was the maximum, was ca. -0.3 mA cm^{-2} . Thus, in comparison with this previous data, the present PtNPs attached and grown on the ITO are inferred to have an excellent electrocatalytic property for the oxygen reduction. As a explanation of this feature, while the PtNPs have grown up to 100 nm on the ITO surface in the present preparation, it is expected that each nanocluster of the agglomerated structure has sufficient electrocatalytic ability.

Figure 8a shows the cyclic voltammogram for the oxidation of 0.1 M methanol in the N_2 -saturated 0.5 M H_2SO_4 solution recorded with the PtNP/ITO electrode, which was prepared with 24 h of growth. A typical response for the electrocatalytic oxidation of methanol was observed with the PtNP/ITO electrode, indicating the electrocatalytic function of the present PtNPs. Compared with the response obtained with the bulk Pt electrode (Figure 8b), the oxidation peak current increased over three times. This enhancement also supports the assumption that each nanocluster of the agglomerated structure has sufficient electrocatalytic ability for the methanol oxidation. Interestingly, compared with the PtNPs formed on the BDD electrode that had a similar nanostructure,²⁷ the electrocatalytic current value normalized by the geometrical surface was almost the same.

For both the oxygen reduction and the methanol oxidation, the electrocatalytic characteristics of the PtNP/ITO electrode prepared with 24 h of growth could be confirmed. In the preparation method we are proposing in this work, each PtNP has grown up to 100 nm. However, if the state of the surface of grown PtNPs merely reached that of the bulk Pt as the result of the crystal growth, such catalytic behaviors would not be observed. Thus, we believe that the present PtNPs attached and grown on the ITO surface are promising as electrode materials having electrocatalytic functions due to the agglomerated nanostructures. It is quite advantageous that the preparation method is rather simple for fabricating the present PtNP/ITO.

Conclusions

In the present work, we successfully fabricated the PtNP/ITO by the in situ chemical reduction growth of PtNP on the ITO surface, from PtCl_4^{2-} using ascorbic acid as the reductant. Compared with our previous AuNP/ITO^{19,21,22} and AgNP/ITO,²¹ which was fabricated using the seed-mediated growth approach, the present approach was quite simple and convenient because the crystal growth was completed in the one step, i.e., only immersing into the growth solution. In addition, the crystal morphologies of PtNPs grown and formed on the ITO surfaces were quite different from those of previous AuNPs and AgNPs: while crystal-like appearances were formed in the case of AuNP,²⁰ the present PtNPs exhibited the agglomerated nanostructures as if small nanoclusters were gathered to form the spherical structure. This crystal growth was similar to the reported result on the BDD electrode,²⁷ which indicated the crystal growth of PtNPs proceeded via the progressive nucleation mechanism. It was clarified that the amount of attached PtNPs could be tuned by changing the growth time, though it was difficult to obtain the monodispersed PtNPs due to the nature of this growth process.

In the electrochemical applications of the PtNP/ITO as a working electrode, at first, the presence of PtNPs on the ITO substrate was confirmed from the electrochemical responses coming from Pt. In addition, the function of PtNPs to lower the R_{ct} was confirmed by observing the changes in R_{ct} depending on the growth time to prepare PtNPs, i.e., the number of PtNPs attached to ITO. The decreased degree of R_{ct} from bare ITO was significant for the PtNP/ITO electrode prepared with 12 or 24 h of growth in comparison with those of our previous AuNP/ITO and AgNP/ITO electrodes. This would be a reflection of the excellent characteristics of Pt as electrode material, but the structural differences of NPs might have some effects on the electron-transfer reactions. Thus, we observed cyclic voltammograms of $[\text{Fe}(\text{CN})_6]^{4-}$, oxygen, and methanol. While the PtNPs gave fewer effects on the redox properties of $[\text{Fe}(\text{CN})_6]^{4-}$ compared with those of the bulk Pt electrode, the significant electrocatalytic properties of PtNPs were confirmed for the oxygen reduction and methanol oxidation.

Up to now, such electrocatalytic function has been believed to be peculiar to small (several nanometers or larger) and

independent (not gathered) PtNPs. However, the present result showed that the agglomerated PtNPs gathered by small nanoclusters are also effective for electrocatalytic reactions. Along with the ease of preparation, such nanostructured PtNPs may be promising for a new type of electrode material. Thus, we are now studying the modification of PtNPs on carbon materials.

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