Seed-Mediated Growth of Palladium Nanocrystals on Indium Tin Oxide Surfaces and Their Applicability as Modified Electrodes

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Palladium nanoparticles (PdNPs) were successfully attached and grown on an indium tin oxide (ITO) surface using a seed-mediated growth method, i.e., via a simple two-step immersion of the ITO substrate into the seed and growth solutions. After the growth treatment for 24 h, PdNPs grew up to 60–80 nm, exhibiting crystal-like appearances and accompanying the formation of short rodlike nanocrystals as a minor product. Thus prepared PdNPs tend to stick each other, so that the dense gathering of PdNPs was observed on the ITO surfaces. Due to the dense attachment, the PdNPs directly attached to the ITO (PdNP/ITO) electrode had a significantly lowered charge-transfer resistivity compared with that of a bare ITO, and the redox reaction of $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ was observed as reversible in 0.1 M phosphate buffer solution. The electrocatalytic property of PdNPs was confirmed for the reduction of oxygen. In addition, some typical responses were observed in 0.5 M H₂SO₄ with the PdNP/ITO electrode, reflecting both the characteristics of NPs and the thin layer in nanoscale. The present preparation method of PdNP-attached surfaces would be promising for catalytic applications as well as electrochemical uses.

Introduction

Along with the increasing interests in the size- and shapedependent properties of metal nanoparticles (NPs) [e.g., see the review on gold NPs (AuNPs)],¹ modification of the electrode surfaces with metal NPs has been extensively carried out nowadays. While the electrochemical reductive deposition of noble metal ions is a typical approach to prepare metal NPs on conducting surfaces,^{2–4} the use of linker molecules, which have bonding groups for both metal NPs and the substrate,⁵ have been a popular method in recent years to attach metal NPs on electrode surfaces via pure chemical treatments. Assuming the attached metal NPs as a nanoelectrode ensemble, the fine-tuning is possible by controlling the conditions for the chemical preperations.^{6,7}

As a novel approach to prepare metal NP-attached electrodes with wet chemical treatments, our group is proposing a seed-mediated growth method for surface modification,^{8–13} which is an alteration of the original seed-mediated method for preparing metal nanorods in solution.^{14,15} In actual, the nanoseed particles are attached on the surface by just immersing a piece of conducting substrate, such as indium tin oxide (ITO), into a seed solution containing metal NPs of ca. 4 nm. Then, by immersing the nanoseed-particle-attached substrate into the growth solution, which contained metal ions, ascorbic acid as reductant, and cetyltrimethylammonium bromide (CTAB), the crystal growth of metal NPs on the substrate's surface is possible. While the second process is chemical reductive growth, the first process is physisorption of small nanoseed particles, which is known as a precursor method in the field of catalysis.¹⁶

This method was successfully applied to the attachment of AuNPs⁸ and AgNPs⁹ on the ITO surfaces, and the electrochemi-

cal characteristics were observed.^{9–11} The advantageous characteristic of thus formed AuNPs directly attached to the ITO (AuNP/ITO) surface or the AgNP/ITO surface is that the electron-transfer resistivities are lower than those of the metal NP-modified electrodes prepared using linker molecules.^{10,11} In addition, the weakly capped surface of AuNPs is suitable for the further modification, e.g. hemeproteins.^{12,13}

In the present work, as a series of our trials to fabricate metal-NP-attached electrodes, the attachment and growth of palladium NPs (PdNPs) on ITO surfaces are investigated using the same seed-mediated growth method.

PdNPs are useful for catalytic purposes,¹⁷⁻¹⁹ so that active researches have been devoted to the preparation methods of PdNPs in solution phase.^{20–23} In addition, shape-controlled wet synthesis of unique PdNPs, i.e., nanocubes and nanoplates, has been reported.^{24,25} However, in contrast to the synthesis in solution, research works using the PdNP-modified electrodes are not numerous. The electrochemical deposition was utilized for the preparations of PdNPs on glassy carbon² and gold³ electrodes by Wang and Dong's group. Also, Dong and co-workers proposed a simple preparation method of multilayer polymer films containing PdNPs on a 4-aminobenzoic acid-modified GC electrode.²⁶ Gómez et al. reported the surface-enhanced Raman spectroscopic results on nanostructured electrode prepared by depositing PdNPs on either gold or platinum electrodes.²⁷ However, compared with the cases of AuNPs and AgNPs, in general, the attachment method of PdNPs on the electrode surfaces are very limited, which is presumably because linker molecules suitable for PdNPs are not established.

Despite of this scarceness of PdNP-modified electrodes, the Pd nanostructured films are electrochemically interesting objectives because they can be used for the detection of combustible gases²⁸ and nitrous oxide,²⁹ surface enhanced Raman measurements,³⁰ and elucidating the hydrogen adsorption and absorption processes.³¹ Thus, if we can form the nanostructured ensembles

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of PdNPs without using strong binders or linker molecules, the potential applicability of the formed Pd nanomaterials would be significant including the uses as catalysts.

The first aim of the present paper is to show what kind of nanostructured particles are formed in the case of Pd using the seed-mediated growth method. While this method brought the successes in attaching and growing AuNPs and AgNPs on ITO,^{8,9} it was not valid for the case of platinum NPs (PtNPs), so that we reported a different approach for fabricating the PtNP/ ITO electrode.³² However, in the case of Pd, the seed-mediated growth has found to be applicable to allow the crystal growth of Pd. Because the grown nanostructure of Pd was different from those of AuNPs and AgNPs,^{8,9} the structural differences are described on the basis of the SEM images.

The second aim of the present work is to investigate the properties of Pd nanocrystals grown on the ITO surfaces through the electrochemical measurements. By using a thus prepared PdNP/ITO electrode as the working electrode, the electrochemical characteristics and applicability are explored.

Experimental Section

Materials. Cetyltrimethylammonium bromide (CTAB) and K₂PdCl₆ (99.998%) were purchased from Aldrich Co., Ltd. NaH₂PO₄ and Na₂HPO₄ from Wako Pure Chemicals, Ltd. were used to prepare phosphate buffer solutions. Other reagents were obtained from Wako Pure Chemicals. Glass plates on which ITO film was coated were purchased from CBC Ings Ltd. (sheet resistance ca. 50 Ω sqr., size 18 mm \times 18 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. A conventional Pd bulk electrode (Pd disk; the diameter, 0.16 cm) was purchased from BAS Inc. It was polished to be mirrorlike, finished by a diamond suspension (250 nm), and washed carefully by the same method as for ITO. The reference electrode used was Ag/AgCl in 3 M NaCl purchased from BAS Inc. In all the procedures and the preparation of solution, we used pure water prepared using Millipore Autopure WR600A (Millipore, Ltd., resistivity > 18 M Ω cm).

Apparatus. The surface morphology of the PdNPs attached on the ITO surfaces was observed with a field-emission scanning electron microscopy (FE-SEM, JSM-7400F, JEOL). The electrochemical measurements were performed using an EG&G M263A potentiostat/galvanostat (Princeton Applied Research (PAR)) and a 5210 lock-in amplifier (PAR) controlled by a computer with M270 and M398 programs (PAR). All the electrochemical measurements were carried out at room temperature, ca. 25 °C.

Procedures. Typical procedures of seed-mediated growth method are as follows. First, the seed solution of ca. 4 nm Pd colloid was prepared by adding 0.5 mL of ice-cold solution of 0.01 M NaBH₄ into 18 mL of aqueous solution containing 0.25 mM K₂PdCl₆ and 0.25 mM trisodium citrate. A piece of the ITO substrate was then immersed into the seed solution and left for 2 h in order to attach the Pd nanoseed particles on the surface. Then, ITO substrate with Pd nanoseeds attached was immersed in the growth solution and left for 4, 12, or 24 h. The growth solution was prepared by mixing the aqueous solutions of 0.5 mL of 10 mM K₂PdCl₆, 18 mL of 0.10 M CTAB solution, 0.1 mL of 1.0 M NaOH solution, and 0.1 mL of 0.1 M ascorbic acid. Thus ITO fabricated with Pd nanocrystals attached was removed from the growth solution, rinsed with pure water several times, and then dried with nitrogen gas for the FE-SEM characterizations and the electrochemical measurements. All the wet chemical treatments were carried out at room temperature, ca. 25 °C.



Figure 1. Typical FE-SEM images of Pd nanocrystals attached and grown on the ITO surfaces observed after (A) immersing only into the seed solution for 2 h and immersing into the seed solution for 2 h and then into the growth solution for (B) 4 h and (C) 12 h.

Fabrication of PdNP/ITO Electrodes. To evaluate the electrochemical properties of the PdNPs directly attached to ITO (PdNP/ITO), a handmade PdNP/ITO working electrode was fabricated as follows. At first, a piece of ITO on which PdNPs were attached was connected to a strip of copper adhesive tape (3M copper tape 1181, 50 mm \times 6 mm) and then molded into a piece of tape (3M filament tape 898, 50 mm \times 18 mm) that was made to have a 0.2-cm-diameter hole. For the electrochemical measurements, the exposed area of the diameter of 0.20 cm was the working surface to contact with the sample solution.

Results and Discussion

FE-SEM Observation of PdNP/ITO Surfaces. First, we would like to show how the surface morphology changed in the seed-mediated growth treatments, in particular, depending on the immersion time into the growth solution. A typical FE-SEM image observed just after immersing into the seed solution is shown in Figure 1A. In this image, bright dots correspond to the Pd nanoseed particles attached on the ITO surface, while the background structure is that of ITO crystals. Although the nanoseed particles were difficult to recognize in the case of AuNPs and AgNPs on the ITO surfaces due to the resolution of the FE-SEM,^{8,9} some of the Pd nanoseed particles were observable, as shown in this image.



Figure 2. Typical FE-SEM images of Pd nanocrystals attached and grown on the ITO surfaces observed after immersing into the seed solution for 2 h and then into the growth solution for 24 h. The images are shown in three different scales.

Parts B and C of Figure 1 show typical FE-SEM images recorded after treating the Pd-nanoseed-particle-attached ITO substrates in the growth solution for 4 and 12 h, respectively. As apparent from the figures, the crystal growth of PdNPs from Pd nanoseeds on the ITO crystals was observed with the increase in the immersion time into the growth solution. While the size of grown Pd nanocrystals was around 15 nm after 4 h of growth, the size after 12 h was roughly 40 nm. In both cases, some short nanorods were observed to form as a minor product.

Figure 2 shows typical FE-SEM images recorded after treatment in the growth solution for 24 h. As shown in the expanded image (Figure 2A), Pd nanocrystals grew up to 60– 80 nm. The most characteristic feature of the formed nanostructure of Pd is that Pd nanocrystals tend to stick to each other. In addition, the stuck gathering was not only on the surface but three-dimensional, i.e., some nanocrystals were observed to grow above the basal nanocrystals. As recognized when we compare with the images in Figure 1B,C, the degree of the gathering increased with the growth time. The nanostructure of Pd grown on ITO was quite different from the cases of Au and Ag, because AuNPs and AgNPs tend to form the dispersed states.^{8,9} Hence, it is inferred that the identity of metal changed such gathering characteristics in the growth process, even though the same capping reagent, CTAB, was uses in all the growth procedures.



Figure 3. UV-visible absorbance spectrum of the PtNP/ITO fabricated with the growth time of 24 h.

To verify this hypothesis, we tried the growth of Pd after the seeding of Au and consequently confirmed that the same nanocrystal growth of Pd occurred. Thus, not depending on the seeding process, PdNPs are expected to grow with increased time in the growth solution.

The appearances of PdNPs were quite crystal-like after being well grown, as shown in Figures 1C and 2A. So, we observed the XRD spectra for the surface of PdNP/ITO. As a result, the peaks of (111), (200), and (220) surfaces were observed in the XRD pattern, showing the formation of typical face-centered cubic (fcc) crystals. Therefore, the present treatment is considered as a practical method to gather Pd nanocrystals on the supporting material with high density. As pointed out for the growth of AuNPs with and without linker molecules, such a formation of less capped nanocrystals is peculiar to our seed-mediated growth.⁸

In addition, utilizing the transparent characteristics of the ITO substrate, the UV-visible absorption spectrum was observed for the PdNP/ITO prepared via 24 h of growth. As the result, a broad absorption peak was observed with the maximum wavelength of 420 nm, as shown in Figure 3. This value would be reasonable for the PdNPs of 60–80 nm, judging from the absorption maxium reported for the 50-nm Pd nanocubes. Thus, the optical characteristics of NPs are inferred to be reserved despite the gathering of PdNPs.

Because the zoomed-out images (Figure 2B,C) shows that a kind of porous surface composed of Pd nanocrystals was formed on the ITO surface, the modified nanomaterials might be effective for the electrochemical measurements due to the large surface area or porous characteristics. Thus, in the following sections, we observe some electrochemical responses using the PdNP/ITO as the working electrode. While the Pd bulk working electrode is used to compare the electrochemical responses, the surface of the bulk metal is flat enough in comparison with the PdNPs attached surfaces.

Electrochemical Impedance of PdNP/ITO Electrodes Measured for the [Fe(CN)₆]^{4–}/[Fe(CN)₆]^{3–} Couple. To evaluate the effect of Pd nanocrystals on the charge-transfer resistivity, we measured the electrochemical impedance of the PdNP/ ITO electrodes that were prepared with different growth periods. Electrochemical impedance spectra were recorded 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–} As shown in Figure 4, the R_{ct} values were observed to decrease with the increase in the growth period, reflecting the correlation of the R_{ct} values with the degree of the crystal growth of PdNPs in the FE-SEM images (Figures 1 and 2). The R_{ct} values were determined to be 0.41 k Ω cm² for the bare ITO electrode and 0.31, 0.23, and



Figure 4. 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 bare ITO electrode (a) and PdNP/ITO electrode prepared via (b) 4 h, (c) 12h, and (d) 24 h of growth.

0.14 k Ω cm² for the PdNP/ITO electrodes prepared with a growth time of 4, 12, and 24 h, respectively. For a reference, that of the Pd bulk electrode was ca. 17 k Ω cm².

It is interesting that, while the $R_{\rm ct}$ value of the Pd bulk electrode was quite large, the increase of PdNPs on ITO was found to reduce the $R_{\rm ct}$ values. The decrease in $R_{\rm ct}$ with the attachment of NPs is similar to the cases of AuNPs and AgNPs.^{9–11} The resistivity of Pd metal ($10.8 \times 10^{-6} \Omega$ cm) is greater than that of Au and Ag metals (2.4×10^{-6} and $1.62 \times 10^{-6} \Omega$ cm). However, the results of the impedance measurement showed that the charge transfer resistivity was significantly lowered by the crystal growth of PdNPs, and that the lowered degree was comparable to the cases of AuNPs and AgNPs after 24 h of growth.^{9–11} This lowered $R_{\rm ct}$ value would be a reflection of the dense and more than monolayer attachment of Pd nanocrystals, as shown in Figure 2, in which the state of Pd is quite different from that in the Pd bulk electrode.

In addition, we carried out the electrochemical impedance measurement also in 1.0 M KCl solution containing 0.5 mM $[Fe(CN)_6]^{3-}$ and 0.5 mM $[Fe(CN)_6]^{4-}$ The resulted plots showed straight lines for all the PdNP/ITO electrodes, implying the low charge-transfer resistivity in 1.0 M KCl. For a comparison, the R_{ct} values were ca. 0.03 and 0.28 k Ω cm² for the bare ITO and Pd bulk electrodes, respectively.

Cyclic Voltammograms of the $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ Couple on PdNP/ITO Electrodes. To investigate the applicability of the PdNP/ITO electrode for typical redox systems, cyclic voltammograms of $[Fe(CN)_6]^{4-}$ were observed in 1.0 M KCl and 0.1 M phosphate buffer solution. Hereafter, the PdNP/ ITO electrode used was that prepared after 24 h of growth. The recorded voltammograms are shown in Figure 5 together with those obtained with the bare ITO and Pd bulk electrodes.

In 1.0 M KCl solution, the redox behaviors were essentially same for all the electrodes, except the currents observed at the sides of the redox peaks of the $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ couple, as shown in Figure 5A. This result indicates that the difference was not significant in 1.0 M KCl.

In contrast, an interesting difference was observed in 0.1 M phosphate buffer, as shown in Figure 5B. That is, reversible redox peaks were best observed with the PdNP/ITO electrode (curves c), while the peaks were quasireversible with the bare ITO electrodes (curves a) or less appeared with the Pd bulk electrodes (curves b). Judging from the differences in the R_{ct} values between 1.0 M KCl and 0.1 M phosphate buffer solution mentioned in the previous section and the probability of the absorption of phosphate ion, etc., the quasireversible responses in Figure 5B, curves a and b, may be reasonable in 0.1 M



Figure 5. Cyclic voltammograms of 1.0 mM $[Fe(CN)_6]^{4-}$ in (A) 1.0 M KCl solution and (B) 0.1 M phosphate buffer solution (pH 7.0) with (a) a bare ITO electrode, (b) a bulk Pd electrode, and (c) PdNP/ITO electrode prepared via 24 h of growth. Scan rate, 50 mV s⁻¹. Geometric electrode areas: (a, c) 0.031 and (b) 0.020 cm². The current axis was normalized by dividing the surface areas.

phosphate buffer solution. Hence, it is considered that the PdNP/ ITO has some additional effects to exhibit the reversible response of Figure 5B, curve c.

In the redox reaction of $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$, the responses should be governed by the diffusion processes, and the diffusion layer is expected to be far more than the thickness of the layer of PdNPs. Thus, the improvement characteristics of the PdNP/ITO electrode cannot be explained with changes in the increased surface of Pd in PdNPs. As shown by the impedance results, the R_{ct} values were 0.14, 0.41, and ca. 17 k Ω cm² for the PdNP/ITO, base ITO, and Pd bulk electrodes, respectively. Hence, by attaching on the surface of ITO, PdNPs are inferred to change the nature of the interfaces to reduce the charge-transfer resistivity. In addition, the porous surface of PdNPs may reduce the adsorption of phosphate ions.

At any rate, as the most noticeable feature here, it was found that the PdNP/ITO was superior to the Pd bulk electrode in terms of the reversibility. If we assume only the surface of Pd is working as electrode on the PdNP/ITO, such a difference is difficult to consider. Thus, it is inferred that a unique interface could be fabricated by attaching PdNPs on the ITO surface. This result is similar to the case of AgNP/ITO electrode for the redox of $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-.9}$

Electrocatalytic Property of PdNP/ITO Electrode for the Reduction of Oxygen. Because the electrocatalytic property of PdNPs for oxygen is well-known and examined in previous works,^{3,26} we observed the voltammetric responses with the present PdNP/ITO electrode. Figure 6 shows the cyclic voltammograms recorded with the PdNP/ITO, Pd bulk, and bare ITO electrodes in the air-saturated 0.1 M KCl solution, together with that recorded with the PdNP/ITO electrode in the N₂-saturated 0.1 M KCl solution.

As shown in this figure, an apparent catalytic reduction response was observed for the PdNP/ITO and Pd bulk electrodes having almost the same peak potential, though the current magnitude was different. Compared with the Pd bulk electrode, the peak current was ca. 1.8 times larger with the PdNP/ITO



Figure 6. Cyclic voltammograms recorded with the PdNP/ITO electrode prepared via 24 h of growth for (a) air-saturated and (b) N_2 saturated 0.1 M KCl solutions and with (c) a Pd bulk electrode and (d) a bare ITO electrode for air-saturated 0.1 M KCl solution. Scan rate: 50 mV s⁻¹. Geometric electrode area: (a, b, d) 0.031 cm² and (c) 0.020 cm². The current axis was normalized by dividing the surface areas.



Figure 7. Cyclic voltammograms obtained with (A) the PdNP/ITO electrode and (B) the Pd bulk electrode in the solution containing 0.5 M H_2SO_4 . In part A, the potential was reversed at various potentials. Scan rate: 50 mV s⁻¹. Geometric electrode area: (A) 0.031 cm² and (B) 0.020 cm². The current axis was normalized by dividing the surface areas.

electrode. For this reason, it is expected that the total surface area of Pd in the present Pd/ITO electrode is larger than that of the Pd bulk electrode, as inferred from the FE-SEM image of Figure 2C. Thus, depending on the target electrochemical reactions, it was found that PdNPs could take part in the electrode reactions effectively as electrocatalysts utilizing the larger surface area.

Hydrogen Adsorption and Absorption on PdNP/ITO Electrode. As recently carried out for Pd thin films of 10 monolayers and 100 μ m,³¹ cyclic voltammetric measurements should give useful information about the hydrogen adsorption and absorption. Thus, the cyclic voltammograms in 0.5 M H₂SO₄ were recorded using the PdNP/ITO electrode.

Figure 7 shows the cyclic voltammograms recorded in the anodic scans by changing the reversed potentials. In this potential region, the oxidative formation of PdO and PdO₂ and their reduction responses are observed.³³ As shown in this figure, the voltammeric responses observed with the Pd bulk and PdNP/



Figure 8. Cyclic voltammograms obtained with (A) the PdNP/ITO electrode and (B) the Pd bulk electrode in the solution containing 0.5 M H_2SO_4 . In part A, the potential was reversed at various potentials and in part B at -0.28 V. Scan rate: 50 mV s⁻¹. Geometric electrode area: (A) 0.031 cm² and (B) 0.020 cm². The current axis was normalized by dividing the surface areas.

ITO electrodes were roughly similar, though a slight change of the wave-shape and the magnitude of the reduction current was observed (which are discussed later).

In contrast, in the negative-going scan for the potential region of hydrogen adsorption and absorption, remarkable differences were observed concerning the onset and the magnitude of the reduction current (Figure 8). While the increase of the reduction current started from ca. -0.2 V and the current magnitude was limited even at -0.28 V as in Figure 8A, the onset of the reduction with the Pd bulk electrode was observed from ca. 0 V, and the reduction current increased monotonically as in Figure 8B.

A similar observation for the reductive current with the polycrystalline Pd electrode has been reported in comparison with that of 200-nm Pd film, and the reason for the difference was attributed to the different volume of Pd to absorb hydrogen.³¹ Compared with the results on the 200-nm Pd film,³¹ the start of hydrogen adsorption/absorption was rather smaller and the level-off current region lasted to the negative potential region. Thus, it is expected that the present response with the PdNP/ITO would be further evidence of the limited volume of PdNPs, which should be inferred from the SEM images in Figure 2. The present result in Figure 8 clearly indicated that the PdNPs had characteristics similar to those of the Pd thin film concerning very limited absorption of hydrogen into the Pd metal.³¹ Thus, it is expected that the PdNP/ITO electrode would be an interesting alternative to the thin Pd film, though the limited volume is similar but the composition is different, i.e., smooth film and porous characteristics.

As a minor feature in the voltammeric responses with the PdNP/ITO electrode in Figure 8A, neither a couple of the absorption peak nor separated peaks for α - and β -phases, which were observed on the Pd thin films,³¹ were recorded. This is presumably because of the *iR* drop in the PdNP/ITO electrode, because the shape of the present voltammograms is similar to the result for the Pd thin film on reticulated vitreous carbon.³⁴

In addition, we can extract some more features of the PdNP/ ITO as an electrode from the voltammetric results in Figure 7. The results in Figure 7A show that the reduction waves of PdO increased, accompanying a slight negative potential shift as the reversed potential became positive. This tendency is similar to the results with the Pd bulk electrode³³ and the Pd films.³¹ However, as a marked difference from the previous results, the magnitude of the negative shift is smaller than those reported with the Pd bulk electrode³³ and the Pd films.³¹ The reason for the negative shift of the reduction wave of PdO was explained with the ever-increasing stability of the PdO layer as the positive increase of the reversed potential.³³ Therefore, in the present PdNP/ITO electrode, it is expected that the proceeding formation of the Pd oxides is different from those of the bulk surface and film states. Because the surface oxidation of Pd should proceed easily and evenly for the PdNPs judging from the limited very small volumes of PdNPs contacting with the conducting ITO support, the changes in the formed states of Pd oxides on PdNPs should be less sensitive to the reversed potential in comparison with the bulk surface or film. Thus, the reductive responses in Figure 7A would be a reflection of the characteristics of PdNPs.

In addition, compared with the response recorded with the Pd bulk electrode (Figure 7B), two features can be noted. The first is the difference in the magnitude of the reduction peaks of PdO. If the thin surfaces of all PdNPs are responsible for the reduction peak, the magnitude of the reduction current should have become larger in Figure 7A on the basis of the large surface area per volume of PdNPs in the FE-SEM images (Figure 2). However, actually, the peaks in Figure 7A recorded with the PdNP/ITO electrode were smaller than that in Figure 7B recorded with the Pd bulk electrode. Thus, it is inferred that all the surfaces of PdNPs not necessarily took part in the oxidation and the reduction, or the surface layer of the Pd bulk electrode responsible for the oxide formation is thicker than the scale of PdNPs. The second feature is a few humps observed in the positive-going scan only with the PdNP/ITO electrode (Figure 7A). Because some characteristic oxidation peaks have been reported for the well-defined surfaces of Pd,³⁵ the appearance might be due to the crystallographic surfaces of PdNPs.

In the above results, some characteristics of PdNPs such as nanosized particles and thin layers were explicitly presented. While the thin layer modification with Pd materials has been mainly performed by forming the films, the present PdNPs' attachment would be an alternative method to modify the conducting surface with very small amount of Pd.

Conclusions

In the present work, Pd nanocrystals were successfully attached and grown on the ITO surfaces using the seed-mediated growth method. While some short nanorods were formed as a minor product, the PdNPs having crystal-like appearance, whose size was 60–80 nm, were densely modified on the ITO surface after 24 h of growth. Because the PdNPs tend to stick to each other in the growth treatment, which is particular to Pd and not observed for Au or Ag, the ITO surfaces could be modified with a kind of porous structure composed of Pd nanocrystals.

The electrochemical impedance measurement of the PdNP/ ITO electrode showed a significant decrease of the chargetransfer resistivity, which is comparable to the cases of AuNPs and AgNPs.^{9–11} Despite the high resistivity of Pd in comparison with Au or Ag, the dense modification by Pd nanocrystals is inferred to improve the charge transferring situations at the interface. The same effect was observed for the electrochemical reaction of the $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ couple in 0.1 M phosphate buffer. Thus, the PdNP/ITO electrode can be regarded as a unique modified electrode in which the NPs at the interface promote the electron-transfer reactions. Furthermore, PdNPs themselves have the electrocatalytic functions for peculiar reactions, as shown for the reduction of oxygen.

The cyclic voltammetric measurements in $0.5 \text{ M H}_2\text{SO}_4$ showed some characteristics due to the limited volume and the dispersed state of PdNPs. While Pd thin films have been utilized in some applications, the present modification of PdNPs may be the alternatives, judging from some advantages of the proposed method, e.g., (1) the large surface area per volume, (2) the not strongly capped or covered surfaces, and (3) the ease of the preparation, i.e., just a simple two step immersion, of the present PdNP/ITO.

Because the proposed seed-mediated growth was applicable to the modification of the GC surface, the approach is expected to be utilized in the surface modification for catalytic uses as well as for electrochemical measurements.

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