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Electrocatalytic Detection of Hydrogen Peroxide Using Palladium-Nanoparticle Dispersed Carbon Film Electrodes

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We prepared palladium (Pd)-nanoparticle-dispersed graphitelike carbon (Pd NDC) film by cosputtering Pd and carbon by radio frequency (RF) sputtering. The preparation method is very simple and reproducible, and the Pd content can be well controlled. We studied the film with respect to its structural characterization and electrochemical properties. Transmission electron microscopy (TEM) images show that the structure of the carbon film is graphitelike and that the Pd particles are highly dispersed in the carbon matrix. The Pd nanoparticle size is very uniform with a diameter of about 4 nm, which is larger than that of previously reported platinum nanoparticles formed in graphite-like carbon film. Electrochemical properties, such as the electrocatalytic oxidation of hydrogen peroxide, are studied by cyclic voltammetry and hydrodynamic measurement. The current density of hydrogen peroxide concentration at a Pd NDC film electrode was higher than that at a Pd bulk electrode. As a result, we found that the relationship between hydrogen peroxide and current density at Pd NDC film is much more linear than that at a Pd bulk electrode with high stability.

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1. Introduction

Highly dispersed metal nanoparticles have been attracting growing interest because of their excellent electrocatalytic properties. Platinum or palladium nanoparticles have been studied with a view to applying them to fuel cells^(1–4) and electrochemical detection.⁽⁵⁾ There are several methods for preparing metal particles including chemical reduction,^(6,7) photolysis,⁽⁸⁾ a microwave technique,^(9,10) an electrochemical process,^(11–15) metal evaporation,^(16–19) gas phase reduction⁽²⁰⁾ and decomposition.^(21–23) Most of the above methods can produce nanoparticles on a supported surface or colloidal dispersions. However, very few papers have reported the preparation of uniform metal nanoparticles in carbon films. McCreery and coworkers^(24,25) have reported the synthesis of nanoscale Pt (0) particles in glassy carbon (not only on the surface) by the incorporation of Pt in the glassy carbon precursor followed by thermolysis at 600°C. The fabricated Pt nanoparticles in the carbon exhibit high electrocatalytic activity for the reduction of H⁺ and dioxygen. Joo *et al.*⁽²⁶⁾ synthesized highly dispersed Pt nanoparticles supported on ordered nanoporous arrays of carbon.

More recently, our group reported graphitelike carbon films containing dispersed metal nanoparticles prepared by the RF cosputtering of carbon and metal.⁽⁵⁾ Carbon-film electrodes with dispersed Pt nanoparticles exhibit higher electrocatalytic activity for hydrogen evolution, the electroreduction of dioxygen and the electrocatalytic oxidation of hydrogen peroxide when we compared the current densities after normalizing the electrode surface area with the Pt content.⁽²⁷⁾ To detect biomolecules, we obtained a more stable background current than that at a bulk Pt electrode when we modified the electrode using glucose oxidase.⁽²⁸⁾ The carbon-film electrode with dispersed Pt nanoparticles proved to be suitable for detecting trace levels of biomolecules. We achieved a lower detection limit for acetylcholine and choline at the carbon-film electrode with dispersed Pt nanoparticles by microbore high-performance liquid chromatography using a postcolumn enzyme reactor.⁽²⁹⁾ High electrocatalytic activity for the reduction of hydrogen peroxide was also achieved using nanoparticle-iridium (Ir)-dispersed carbon-film electrodes, which have been employed to detect L-glutamate after modification.⁽²⁹⁾ In contrast, carbon film containing copper (Cu) or nickel (Ni) nanoparticles shows high electrocatalytic activity for sugar oxidation.^(30,31) We achieved improved detection limits for sugars by developing graphitelike carbon film containing highly dispersed Ni nanoparticles for use as a detection electrode in high-performance liquid chromatography.⁽³¹⁾

Here, we report the preparation and characterization of highly dispersed palladium (Pd) nanoparticles in a graphitelike carbon film. The preparation is very simple since we can obtain the film by cosputtering Pd and carbon at a relatively low temperature. We studied the electrocatalytic oxidation of hydrogen peroxide for use in electroanalytical applications such as biosensors.

2. Experimental Procedure

2.1 Reagent

Hydrogen peroxide (30%) and H_2SO_4 were purchased from Kanto Chemical Co. Ltd. (Tokyo, Japan). Phosphate-buffered saline solution (PBS) containing potassium, sodium, and chloride ions, 0.15 M (pH 7) was obtained from Gibco (Grand Island, NY, USA) and was used as received. Water used in the experiments was purified by Mili-Q (Millipore, Bedford, MS, USA).

2.2 Sputter deposition of electrode

The Pd-nanoparticle-dispersed carbon (Pd NDC) film electrode was formed by an RF method by cosputtering Pd and carbon simultaneously (ANELVA, FP-21, Japan). The target was composed of Pd pellets placed on a carbon plate, as shown in Fig. 1. The Pd content of the carbon film can be controlled by changing the number of Pd pellets. We prepared the Pd NDC film on a Si wafer. Before sputtering, the pressure of the vacuum chamber was kept at 1.0×10^{-7} Torr. The pressure of the Ar gas used was 1.0×10^{-2} Torr. The temperature of the Si substrate was maintained at 200°C , and the RF power was 200 W. The thickness of the deposited film was 40 nm. The wafer was then cut into a rectangle shape, and a plastic tape (with a 3-mm-diameter hole) was fixed to it to form a disk electrode. An electrical contact was established near the edge of the chip. A Pd bulk electrode (3 mm diameter) for flow measurement was purchased from BAS Co. Ltd. (Tokyo, Japan).

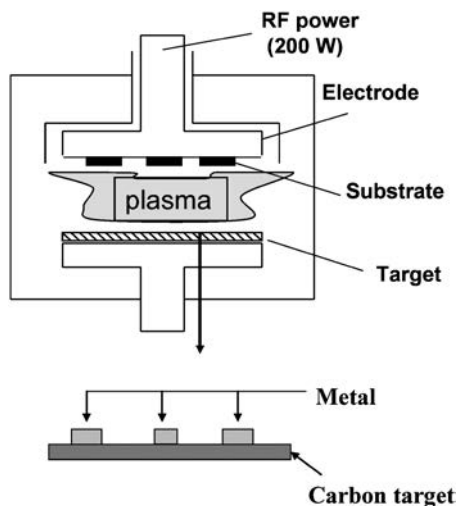


Fig. 1. Schematic representation of RF sputtering equipment for Pd nanoparticle-dispersed carbon film preparation.

2.3 Apparatus

X-ray photoelectron spectra (XPS) were obtained using an X-ray photoelectron spectroscope (XPS5700, Physical Electronics, Inc., USA) using monochromatic Al $K\alpha$ radiation (1486.6 eV). Metallic Pd pellets obtained from Furuuchi Chemical Corporation (Tokyo, Japan) were used for comparative XPS measurements. We observed the film using a transmission electron microscope (TEM) (H-9000UHR, Hitachi Ltd., Japan) by peeling the film from the silicon substrate. We used an acceleration voltage of 200 kV for the TEM observation.

We carried out the electrochemical measurements using an ALS/CHI 802 electrochemical analyzer (CH Instruments, Inc., USA). Cyclic voltammetry (CV) was performed using a three-electrode cell consisting of a Pd NDC film working electrode, an Ag/AgCl (3 M KCl) reference electrode and a platinum auxiliary electrode. Flow injection analysis (FIA) experiments were undertaken using an HPLC Class-VP system, or a CMA 102 dual syringe pump (CMA Microdialysis, Sweden), an LC-4C amperometric detector, and a thin-layer radial-flow cell (BAS, West Lafayette, IN, USA).

3. Results and Discussion

3.1 Film structure

Figure 2 shows a typical TEM image of the top view of the Pd NDC film. The atomic content of the Pd in the film was 7.8%. The Pd particles (black and round clusters) were highly dispersed and isolated from each other in the carbon matrix. The average size of the Pd particles was 4 nm and did not change when we varied the Pd content (7.8–14.1%). The size distribution was in a narrow range, as observed in the TEM image. The Pd particle size is much larger than those of the Pt and Ir nanoparticles in our previously reported carbon films.^(28,29) High resolution XPS spectra indicate that

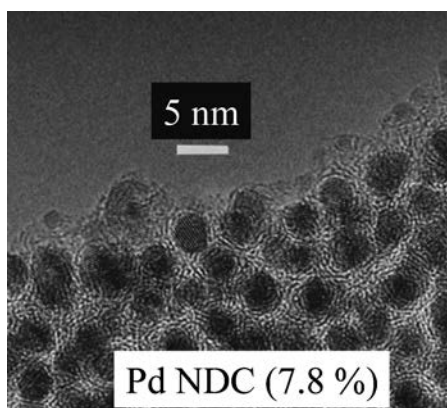


Fig. 2. TEM image of 7.8% Pd NDC film. The film was observed after physically peeling it from the silicon wafer.

the Pd 3d peak of the Pd NDC film (Pd:12%) has a small shoulder at around 337 eV. In contrast, no such shoulder was observed in the spectra of the Pd bulk electrode. This result suggests that the Pd nanoparticles in the PD NDC film contained a small amount of oxide (probably PdO₂).

3.2 Cyclic voltammetry

The electrocatalytic properties of the Pd NDC film electrode were compared with those of a bulk Pd electrode. Figures 3(a) and 3(b) show cyclic voltammograms of 7.8% Pd NDC film and Pd bulk electrodes, respectively, in a 0.1 M phosphate buffer solution at different potential scan rates. We deoxygenated the sample solution using argon gas before undertaking the measurement. The potential scan rate was 20–500 mV/s. The oxidation current, which is attributed to the oxidation of the Pd surface (Pd to PdO₂) started at 0.4 V vs Ag/AgCl at both electrodes, and reduction peaks can be observed at 0 and 0.1 V for Pd NDC and Pd bulk electrodes, respectively. The currents are almost proportional to the scan rates, indicating the surface redox reaction of Pd. The reduction current at the bulk Pd electrode is about 3 times larger than that at the Pd NDC electrode. In spite of the 7.8% Pd content, the Pd NDC reduction peak is relatively large. There are two possible reasons. One is that the Pd particles are distributed more densely near the surface of the film. The other is that the contribution of the Pd atoms on the Pd nanoparticle surface to the redox reaction is greater than that of Pd atoms at the Pd bulk

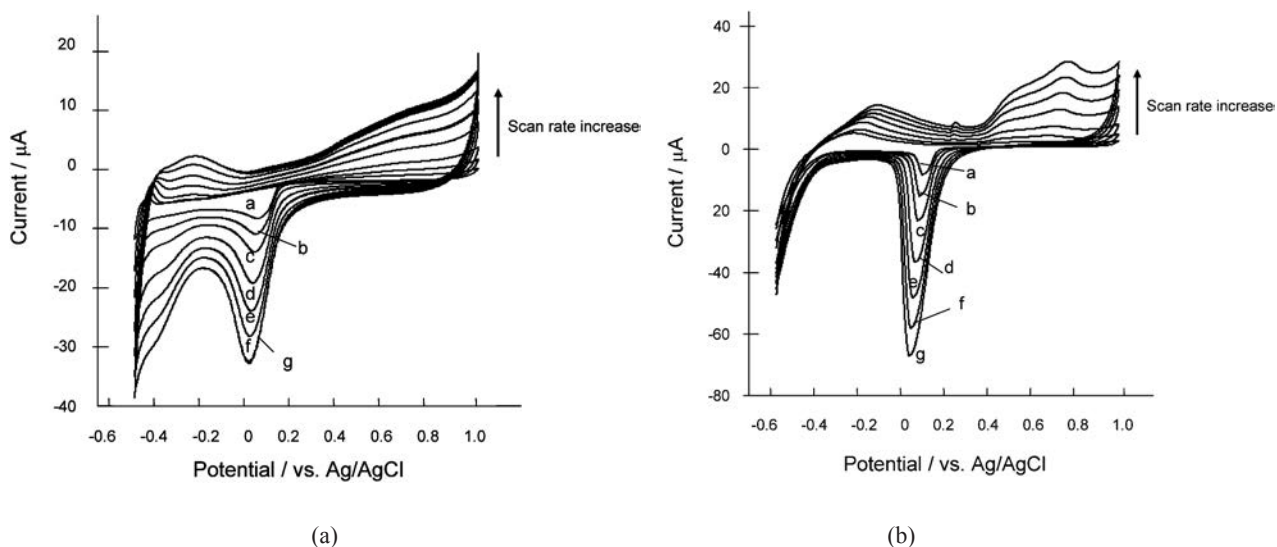


Fig. 3. Voltammograms for (a) 7.8% Pd NDC film and (b) Pd bulk electrode in 0.1 M phosphate buffer solution at different scan rates. a: 20 mV/s, b: 50 mV/s, c: 100 mV/s, d: 200 mV/s, e: 300 mV/s, f: 400 mV/s and g: 500 mV/s.

surface. However, further analytical studies should be performed if we are to understand the mechanism fully. Figure 4 compares the electrocatalytic currents for 1 mM H_2O_2 at Pd NDC and Pd bulk electrodes at different scan rates. With pure carbon film without Pd, no electrocatalytic current increase was observed by adding 1 mM hydrogen peroxide. The oxidative electrocatalytic current increases from 4.7 to 45 μA in the presence of 1 mM H_2O_2 using the Pd NDC film electrode, whereas it increases from 13.8 to 57.1 μA using the Pd bulk electrode (both measured at 0.6 V with 500 mV/s scan rate). This suggests that an almost similar electrocatalytic current can be observed at the Pd NDC despite the smaller redox reaction of Pd, indicating that the electrocatalytic property at the Pd NDC electrode is greater than that at the Pd bulk electrode. Compared with the redox current at Pd without H_2O_2 , the electrocatalytic oxidation current increases as the potential scan rate increases in the slow flow rate region. However, the current at both electrodes saturated in a higher scan rate region indicating that the electrocatalytic oxidation of hydrogen peroxide becomes a rate-determined step at higher scan rates. In our previous experiment, we used the Pt NDC film electrodes with Pt contents from 6.5% and obtained similar sensitivity to that of bulk Pt electrode when measuring 1 mM hydrogen peroxide. This result is similar to that at Pd NDC with 7.8% Pd content, suggesting better catalytic activity of Pt NDC film. However, the average diameter of Pt and Pd nanoparticles is 2.5 nm and 4.0 nm, respectively (about 4 times volume difference). This size difference might affect electrocatalytic activity of the film.

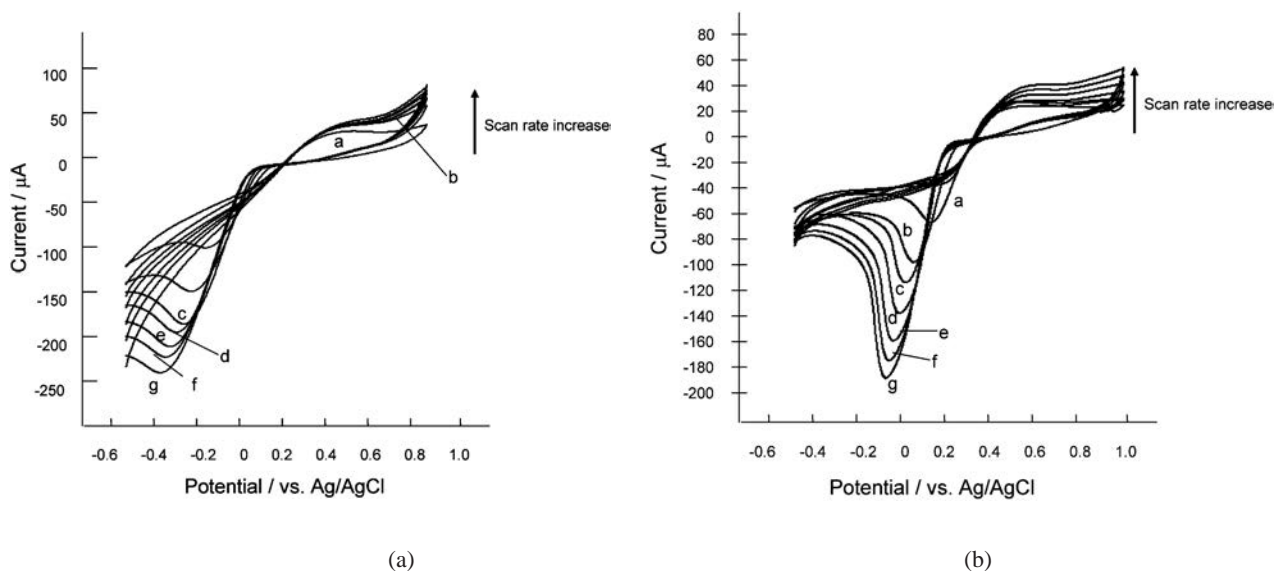


Fig. 4. Voltammograms for 1 mM hydrogen peroxide at (a) 7.8% Pd NDC film and (b) Pd bulk electrodes in 0.1 M phosphate buffer solution at different scan rates. a: 20 mV/s, b: 50 mV/s, c: 100 mV/s, d: 200 mV/s, e: 300 mV/s, f: 400 mV/s and g: 500 mV/s.

3.3 Hydrodynamic voltammograms and FIA analysis for hydrogen peroxide

The highly sensitive and stable determination of hydrogen peroxide is very important in terms of applying the electrode as a biosensor. Since a high electrocatalytic current was observed for hydrogen peroxide at the Pd NDC film electrode, we studied the performance of the electrodes by employing them for flow measurement. Figure 5 shows hydrodynamic voltammograms for hydrogen peroxide on Pd NDC and bulk Pd electrodes. For this experiment, the Pd content of the Pd NDC film was 14.1%. The magnitude of the current was normalized on the basis of the Pd content. The oxidation currents start to increase at both electrodes from 0.2 V and reach a steady state above 0.4 V. The normalized current density at the Pd NDC film electrode is about 3 times that at the Pd bulk electrode.

Figure 6 shows calibration curves for hydrogen peroxide at Pd NDC film and Pd bulk electrodes in an FIA measurement. The current density at the Pd NDC film is higher than that at the Pd bulk electrode on the basis of the results provided by hydrodynamic voltammograms. The difference between the currents of the two electrodes is not very large at concentrations lower than 300 μM . However, the current at the Pd bulk electrode is saturated at higher concentrations, indicating that the linear concentration region at the Pd NDC film electrode is wider than that at the Pd bulk electrode. This also suggests the high electrocatalytic activity of the Pd nanoparticles in the carbon film. The inset in Fig. 6 shows the reproducibility of the current for each concentration. We measured each concentration three times. We obtained excellent reproducibility, as shown in the figure. In our previous report, we observed a more stable baseline for the carbon-film

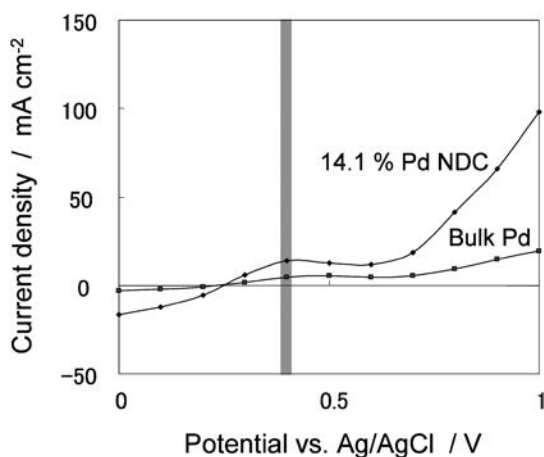


Fig. 5. Hydrodynamic voltammograms for 1 mM hydrogen peroxide at Pd NDC film and Pd bulk electrodes. The Pd content of the Pd NDC film is 14.1%.

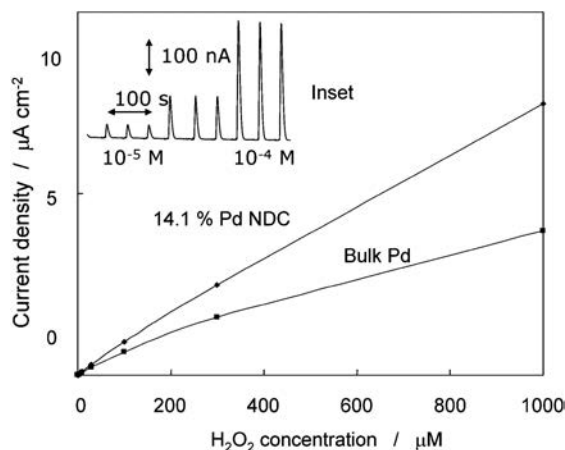


Fig. 6. Calibration curve for hydrogen peroxide at Pd NDC film and Pd bulk electrodes in FIA analysis. The Pd content of the Pd NDC film is 14.1%. The applied potential is 0.5 V vs Ag/AgCl. The inset shows the reproducibility of the signals at different concentrations. The injected volume was 20 μl .

electrodes with dispersed Pt nanoparticles than that for the Pt bulk electrode.⁽²⁸⁾ The baseline current at the bulk electrode decreased continuously because the Pt surface was gradually oxidized and deactivated. Using the Pd NDC film electrode, the baseline is also very flat, similar to that of a Pt-nanoparticle-dispersed carbon-film electrode. In addition, the background noise level at the Pd NDC film electrode is lower than that at the Pd bulk electrode. These results clearly indicate that our Pd NDC film electrode is a very suitable material for biosensor fabrication.

4. Conclusion

We developed a carbon-film-based electrode suitable for biosensor application by cosputtering Pd and carbon. The film consists of Pd nanoparticles in a graphitelike carbon film. The Pd nanoparticles in the film were an average of 4 μm in diameter and their chemical structure was a mixture of Pd metal and Pd oxide (probably PdO₂). The film electrode exhibited excellent electrocatalytic activity for oxidizing hydrogen peroxide. As a detector for FIA analysis, the film electrode had a wider linear concentration range than that of a Pd bulk electrode when we injected different concentrations of H₂O₂. The signal is very reproducible with a low background noise level, indicating that our film electrode is suitable as a detector for various electrochemical sensors.

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