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One-Step Synthesis of a Platinum Nanoparticle with Carbon Materials Using a Phenylazomethine Dendrimer as a Template

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A phenylazomethine dendrimer was developed for the one-step preparation of a platinum nanoparticle–carbon nanocomposite. The dendrimer formed a complex with platinum tetrachloride ($PtCl_4$) in a chloroform–acetonitrile mixed solvent. The coordination behavior between the dendrimer and the platinum salts was confirmed by UV–vis and ^1H NMR titration experiments. The obtained dendrimer–$PtCl_4$ complexes were pyrolyzed under a nitrogen atmosphere at 1000 °C, and converted to spherical and dispersed platinum nanoparticles on a pyrolytic graphite identified by transmission electron microscopy (TEM). A high resolution TEM (HR-TEM) image of the products showed some lattice fringes attributed to the presence of Pt(111) in the particles, and X-ray photoelectron spectra (XPS) of the products corresponded to those of Pt(0). These results indicated that $PtCl_4$ was perfectly converted to metallic platinum through this pyrolysis condition. Raman spectra showed that the dendrimer remained as an amorphous carbon after pyrolysis. The electrode modified with the product showed a catalytic activity for dioxygen reduction, which electrochemically confirmed that part of the carbon was porous enough to let the substrate go through and to reach the platinum surface.

Metal nanoparticles are promising candidates for novel catalyst materials.[1] Because nanoparticles have much greater specific surface areas than general bulk materials, they are appropriate catalysts for surface reactions, e.g. hydrogenation or aerobic alcohol oxidation.[2,3] Moreover, nanoparticles can be present homogeneously with a suspension as well as heterogeneously on a support, and can also be recollected and reused. In particular, some metal nanoparticles show "size effect," meaning a special catalytic activity depending on their sizes.[4] In the case of fuel cells,[5] carbon materials with size-controlled and well-dispersed platinum nanoparticles are strongly desired as an electrode catalyst.

The issue of applying nanoparticles is to develop a method to prevent aggregation among them and to control their particle sizes. Bare metal nanoparticles are prone to aggregate readily, which causes an increase of particles size and a decrease of surface area. Many processes are reported to overcome these issues by using organic materials, such as a surfactant,[6] mesoporous material,[7] or dendrimer.

Dendrimers are useful materials as template molecules for the fabrication of metal nanoparticles. The dendrimer is a macromolecule that has definite structure and molecular weight.[8–10] It is also known that the dendrimer can form a kind of capsule owing to its "shell effect."[11,12] The inner space of the dendrimer is nanometer-size and fixed; therefore, the fabrication of a metal nanoparticle inside the dendrimer is a good method to produce a precisely-shaped product. Moreover, the dendrimer shell also prevents aggregation between the nanoparticles without strong adsorption on its surface, so its surface activity is not lost.

Recently, several research groups have reported procedures to make metal nanoparticles using dendrimers as the template.[13–15] In these methods, a metal nanoparticle, which consisted of metals such as Au, Ag, Cu, Pd, and Pt, is fabricated in two steps; at first, a metal precursor was loaded into the dendrimer, and then reduced. The structures of the dendrimer-encapsulated nanoparticles were investigated in detail by AFM, TEM, SAXS, and SANS, and they informed that the nanoparticle had a uniform size and remained in the dendrimer.[16,17]

Polyamideamine (PAMAM) dendrimers are materials that are mainly used for this purpose. PAMAM dendrimers are easy to obtain; however, their frames consist entirely of single bonds so that they are degradable at high temperature. Additionally, since the coordination chemistry has been ambiguous,[18,19] the way to control the amount of the precursor for the nanoparticle is still uncertain.

We have synthesized an original-type dendrimer consisting of a phenylazomethine frame.[20–25] This dendrimer has several unique properties, such as high thermostability,[20] a rigid structure,[20] and unique coordination behavior.[21,22] We also found that when it was heated at high temperature the phenylazomethine dendrimer was carbonized[26] like other conjugated linear polymers[27] and dendrimers,[28] which is a unique property due to the highly aromatic structure. The phenylazomethine dendrimer is the only dendrimer that has these two distinguished properties, precise metal assembly and the ability to carbonize, and it is an interesting method to fabricate carbon–metal nanocomposites at the same time by pyrolysis of the phenylazomethine dendrimer–metal complex. We now describe the novel one-step fabrication of a platinum nanoparticle on a carbon material using a phenylazomethine dendrimer as a template (Fig. 1).

Experimental

Chemicals. The phenylazomethine dendrimers were synthesized by a convergent method following a literature procedure.[23]

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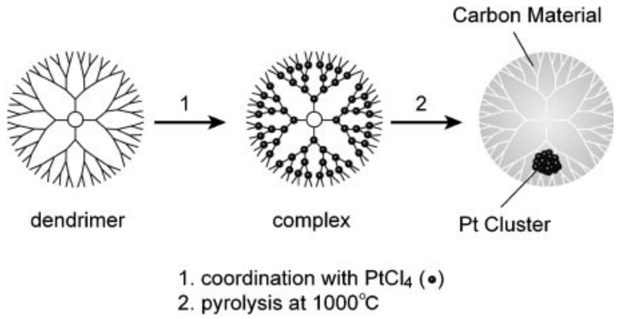


Fig. 1. Schematic illustration of fabrication of a platinum nanoparticle using a phenylazomethine dendrimer by pyrolysis.

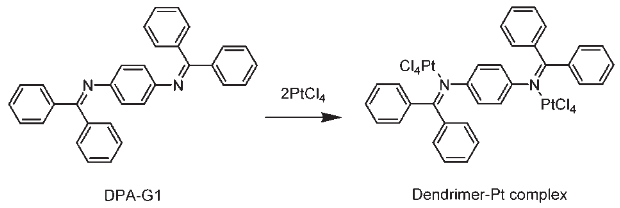
The phenylazomethine dendron was synthesized up to generation 4 (G4) by repeating the dehydration and oxidation reaction.[24] A porphyrin was employed as the core molecule due to its high thermostability.

$PtCl_4$, dehydrated solvents (acetonitrile and chloroform), and other compounds were purchased from Kanto Kagaku Co., Ltd., and used as received. Other platinum compounds, $PtCl_2$(cod),[29] $PtCl_2$(dmso),[30] $PtCl_2(PhCN)_2$,[31] $PtCl_2$(dien),[32] $PtCl_2$(bampy),[32] $PtCl_2$(terpy),[32] and $Pt(NH_3)_5OTf_4$,[33] were synthesized following the referential methods.

Instruments. UV–vis spectra were recorded using a Shimadzu UV-3150 spectrometer with a quartz cell having a 1 cm optical length. Dehydrated solvents were used as solvents. NMR spectra were obtained using a JEOL JNM-GX400 (400 MHz) with TMS as the internal standard. TEM images were taken using a TECNAI F20 (200 keV) that adapted an energy dispersive X-ray spectrometer (EDX). Cu grids with either plastic (collodion) or carbon substrata were purchased from Oken Shoji, Inc. XPS spectra were obtained using a JEOL JPS-9000MC or JPS-9000MX with Mg Kα radiation. Elemental analysis was performed at the Central Service Facilities for Research of Keio University. Raman spectra were recorded using a CHROMEX Raman-One-CCD. The irradiated wavelength was 532 nm. Noises in the form of spikes in the spectra were removed by data processing. Pyrolysis was carried out in an electric furnace (Marusho Denki, Inc. SPM65-16V) under a N_2 atmosphere in a crucible. Electrochemical measurements were performed on a BAS ALS-750 multipurpose electrochemical workstation. A glassy carbon disk electrode ($\phi = 3.0$ mm) or a platinum electrode ($\phi = 1.5$ mm) was used as a working electrode. The electrode surface was polished with alumina paste just before use. An SCE electrode and a platinum coil were used as the reference and the counter electrodes, respectively. Cyclic voltammetry was carried out in a 1.0 M $HClO_4$ aq solution that was thoroughly bubbled beforehand, the atmosphere was kept consistent by flowing air or N_2 gas during experiments.

Results and Discussion

Loading of Platinum Compound into the Dendrimer. The fabrication of metal nanoparticles using a dendrimer template usually takes two steps. In the first step, a precursor of the nanoparticles, usually a metal ion or metal salt, is loaded into the dendrimer. Second, the precursor is converted to a nanoparticle by reduction. Generally, the precursor is loaded by complexation with the donating groups in the dendrimer. Because the amount of the loaded precursor determines the size of the product, it is very important to confirm the coordination chemistry between the dendrimer and the precursor.



Scheme 1. Complexation of $PtCl_4$ to the imine groups.

In this study, our objective was to fabricate a nanoparticle consisted of platinum because of its ability as a catalyst. We had already found that the phenylazomethine dendrimer coordinates $SnCl_2$[22–24] and $FeCl_3$,[25] but platinum salts had never been examined. So at first, we searched for a platinum compound that is coordinated well by the phenylazomethine dendrimer.

DPA-G1 was used as the model compound for a phenylazomethine dendrimer (Scheme 1). We have already confirmed that a DPA-G1 quantitatively coordinates $SnCl_2$ in a chloroform–acetonitrile (1:1) mixed solvent and forms a 1:1 complex on each of the two imine groups.[21] Since the color of the DPA-G1 solution changes obviously by coordination from pale yellow to orange, it is easy to conclude whether or not the metal salt has been coordinated by the imine groups.

As a result of examinations, it was concluded that the Pt(II) compounds, $PtCl_2$(cod), $PtCl_2$(dmso), $PtCl_2(PhCN)_2$, $PtCl_2$(dien), $PtCl_2$(bampy), and $PtCl_2$(terpy), were never coordinated by the imine groups in the mixed solvent; whereas Pt(IV) compounds, $PtCl_4$ and $Pt(NH_3)_5OTf_4$, were certainly coordinated. This is rather curious phenomenon because many Pt(II) compounds have been reported to be coordinated by an amine or pyridine, e.g., cisplatin to DNA.[34] We suppose it is related to the difference of Lewis acidity and "hardness" or the difference of the substitution lability between Pt(II) and Pt(IV), which has before reported;[35] however, it has not been totally clarified. Owing to the easy accessibility, we employed the $PtCl_4$ as platinum precursor.

A UV–vis spectral titration was carried out between DPA-G1 and $PtCl_4$ to confirm the coordination property (Fig. 2). With the addition of $PtCl_4$, the spectra of the DPA-G1 solution changed almost linearly. The spectra subtracted the absorbance due to $PtCl_4$ showed isosbestic points,[25] indicating the progress of a single reaction. The theoretical curve based on a hypothesis of a 1:1 coordination[23] was well fitted to the experimental result, and the coordination constant was estimated to be ca. 3800 M^{-1}.

A similar result was obtained from the ^1H NMR titration (Fig. 3). The singlet signal around 6.5 ppm, which was assigned[20] to the central benzene of DPA-G1, shifted to a lower magnetic field upon the addition of $PtCl_4$. Other signals also more or less shifted depending on the correlation with the N atom that bonded to the platinum. It was also observed that the whole spectra became simple by the addition of $PtCl_4$, which means that the C=N double bonds were polarized by coordination to the metals. Because the polarized bond can rotate freely like a single bond,[36] the difference of *cis–trans* isomers disappears and the NMR spectra become simple. All of these observations proved that $PtCl_4$ was coordinated by

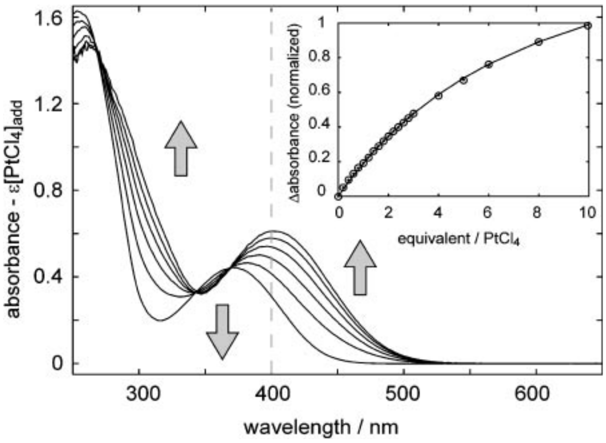


Fig. 2. UV–vis spectral change of 100 µM DPA-G1 upon the addition of $PtCl_4$ in a mixed solvent (chloroform + acetonitrile = 1:1, 25 °C). The absorption of the added $PtCl_4$ was subtracted. Inset: The titration curves obtained from the experiment monitored at 400 nm (dot) and calculated (line) values.

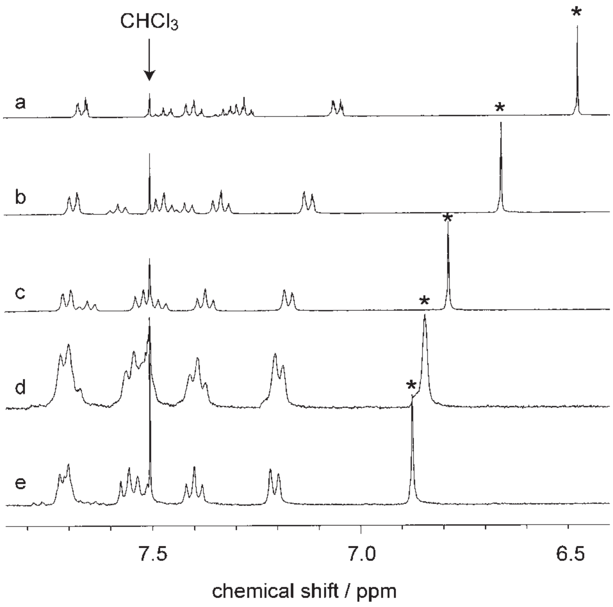
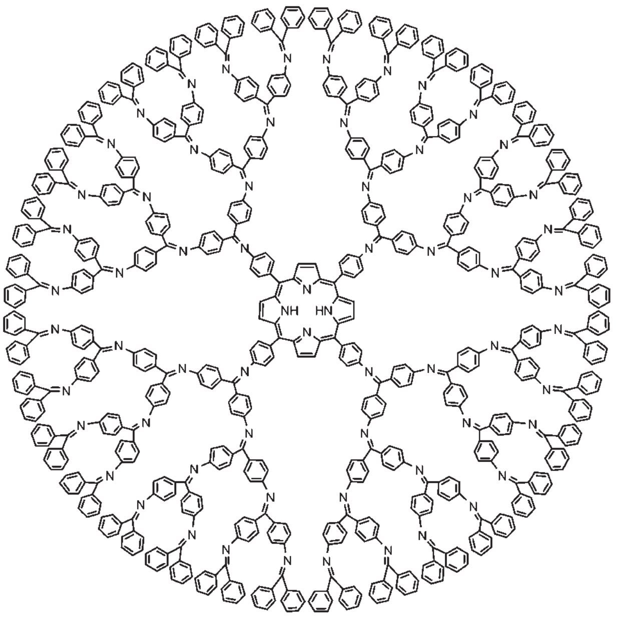


Fig. 3. ^1H NMR spectral change of 6.53 mM DPA-G1 upon the addition of (a–e) 0, 1.0, 2.0, 3.0, and 4.0 equivalent of $PtCl_4$ in the mixed solvent (chloroform-*d* and acetonitrile-d_3 = 1:1, 25 °C). The singlet (*) was assigned to the central phenyl protons. The chemical shift was referred to TMS = 0.00 ppm.

the imine nitrogen. The coordination constant was also estimated to be $650\,M^{-1}$ by the same method on the UV–vis experiment; however, it was suspicious because some precipitation was observed under the NMR condition.

Fabrication of a Platinum Nanoparticle by Pyrolysis. The phenylazomethine dendrimer has a very high thermostability and the $Td_{10\%}$ is above 500 °C.[37] At higher temperatures, the dendrimer decomposes but more than 50% of its mass remains as a graphitic product without entire dissociation as a gaseous product. On the other hand, $PtCl_4$ decomposes to $PtCl_2$ at 334 °C, then to Pt at 505 °C. From this knowledge, we expected that if the dendrimer–$PtCl_4$ complex was pyrolyzed at a high temperature, $PtCl_4$ would be converted into a metallic platinum cluster with a graphite material and would form a novel class of catalyst.



Scheme 2. G4 phenylazomethine dendrimer having a porphyrin core used as a template.

For this purpose, a G4 phenylazomethine dendrimer having a porphyrin core (Scheme 2) was employed because it has good thermostability and many (60) imine groups to coordinate $PtCl_4$. The dendrimer and 60 equivalents of $PtCl_4$ were mixed in the same solvent mentioned above, and evaporated to dryness. The obtained red dendrimer–$PtCl_4$ complex was pyrolyzed in the electric furnace at a heating rate of 50 °C min^{-1} up to 1000 °C. After pyrolysis, the complex was converted into a black char.

The product was dispersed in methanol (sometimes sparkled) by supersonic waves, then 5 µL of that was cast on the TEM grid and dried. The TEM observations showed that the product consisted of spherical particles and an ambiguous residue (Fig. 4a). The EDX measurement confirmed that the particles were platinum. From this image, it was supposed that the $PtCl_4$ was converted into platinum nanoparticles by this method, but the dendrimer complexes were considerably fused to each other and the product was much larger than expected.[38]

To avoid the fusion, we attempted to disperse the dendrimer–$PtCl_4$ complex on silica gel and pyrolyze it together. The obtained light gray product was dissolved in 1 M NaOH to remove the silica gel. The alkaline solution was directly cast on the grid and observed by TEM. The obtained image showed well-dispersed spherical particles. The size distribution was relatively small, but the mean particle size was still large, 3.62 nm in diameter (Figs. 4b and 4c). In contrast, the products obtained by the same method but without the dendrimers were much larger (more than 20 nm in diameter) and irregular. It suggests that the carbon material that originated from the dendrimer controls the particle size and prevents aggregation of the platinum nanoparticles with each other.[39–42]

The high-resolution TEM image showed some lattice fring-

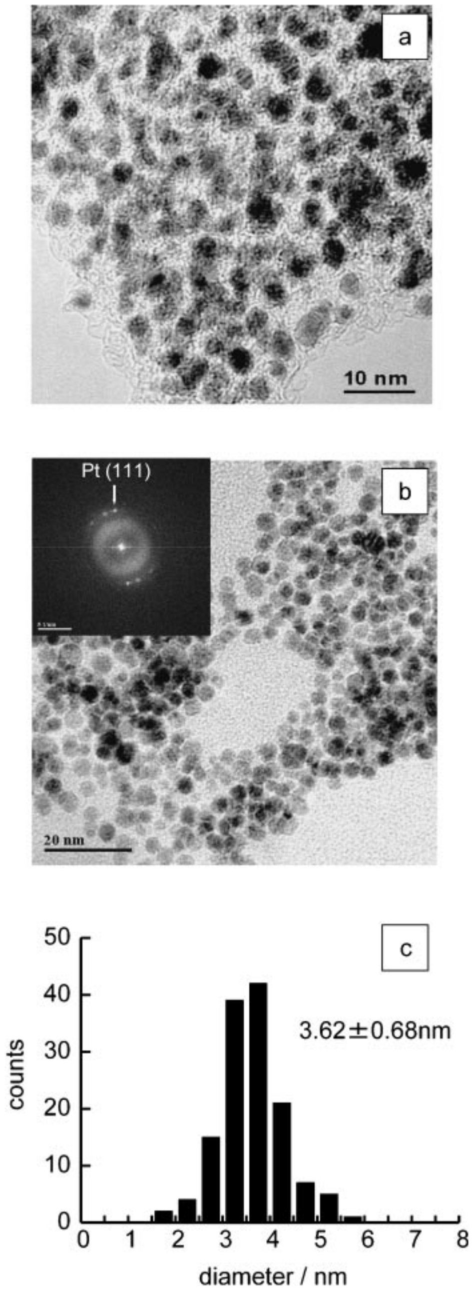


Fig. 4. TEM images of the products (a) directly pyrolyzed and (b) dispersed on silica gel before pyrolysis. Inset: FFT image of the HR image. (c) The histogram prepared from the image (b).

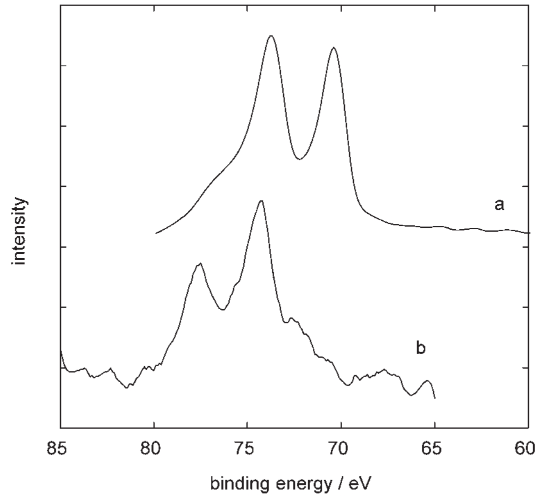


Fig. 5. XPS spectra of Pt_{4f} peaks for the products (a) after and (b) before pyrolysis.

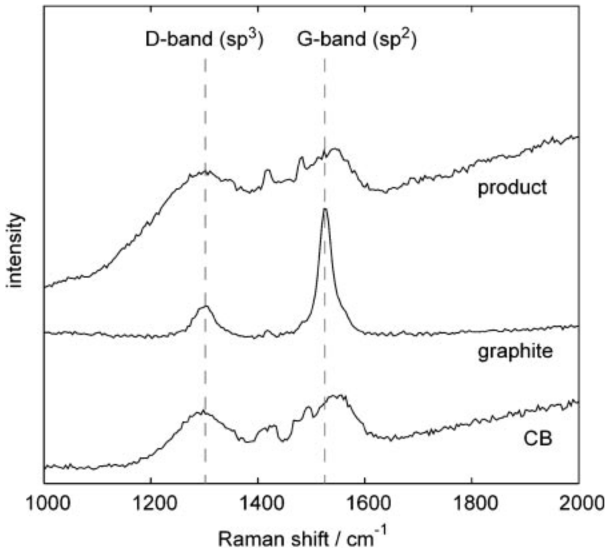


Fig. 6. The Raman spectra of carbon materials. (a) The pyrolysis product, (b) graphite powder, and (c) carbon black.

es on each particle that were attributed to Pt(111) because of the distance, 0.22 nm.[39] It indicated that the nanoparticle consisted of crystalline platinum. The XPS results showed Pt_{4f} signals of the product at 70.4/73.8 eV, which were identical to those of the bulk platinum; whereas the peaks of the dendrimer–$PtCl_4$ complex were at 74.3/77.6 eV, corresponding to those of the Pt(IV) compound (Fig. 5).[42] Consequently, it was confirmed that the dendrimer–$PtCl_4$ complex was perfectly converted to metallic platinum and formed a crystalline structure.

The second interest was the state of the dendrimer after pyrolysis. From the elemental analysis, the CHN ratio for the pyrolyzed compound was 94.5:2.0:3.5, though it was for only the flammable part. Considering that the calculated CHN ratio of the Por-G4 is 87.0:5.1:7.9, the pyrolyzed product contained more carbon. Therefore, it was natural to regard the pyrolyzed product of the dendrimer as a kind of carbon material, and Raman spectrometry is the general method to identify the chemistry of carbon compounds.[43] The Raman spectra of the products showed two peaks in the range of 1000–2000 cm^{-1} attributed to the D-band (sp^3 carbon) at 1300 cm^{-1} and to the G-band (sp^2 carbon) at 1500 cm^{-1} (Fig. 6). The intensity of each peak was nearly equal, which was more similar to a carbon black than to a graphite powder. Therefore, we concluded that the products after pyrolysis consisted of an amorphous carbon.

Catalytic Activity of the Platinum Nanoparticle. The Raman spectra showed that the dendrimer remained as the carbon material after pyrolysis. If it completely covered the platinum nanoparticle, it would not work as a catalyst because the

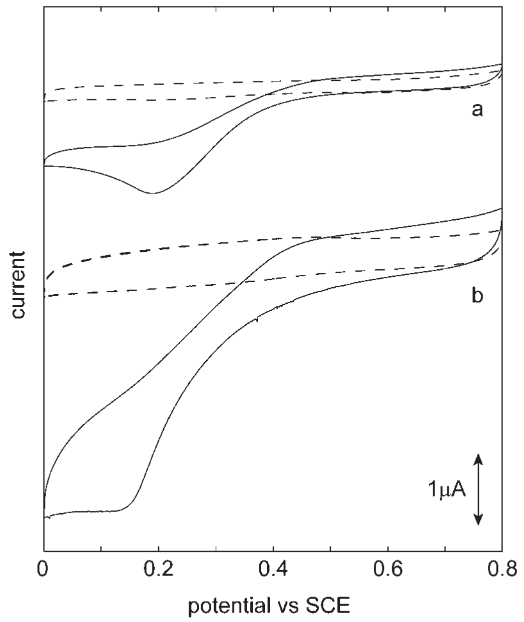


Fig. 7. Cyclic voltammograms of (a) the bulk platinum electrode ($\phi = 1.5\,\text{mm}$) and (b) the platinum nanoparticle modified electrode ($\phi = 3.0\,\text{mm}$). Solid line: in air, dash line: in nitrogen. Solution: 1.0 M $HClO_4$.

carbon would prevent a substrate from approaching the platinum surface. To probe the condition of the Pt–C nanocomposite, we employed the cyclic voltammetry method. Platinum is known as one of the most active electrochemical catalyst for dioxygen reduction, so examining its catalytic activity for dioxygen reduction electrochemically would inform the property of the platinum nanoparticle.

We used a modified electrode technique[40] for this purpose. The obtained nanoparticle was dispersed in methanol with Nafion, and then the dispersed "catalyst ink" was cast on a glassy carbon electrode and dried. Cyclic voltammograms of the modified electrode in an acid solution showed a distinct current increase around 0.7 V vs SCE under air, whereas it disappeared under a N_2 atmosphere (Fig. 7). With a bare GC electrode, no current increase appeared at that potential, even under air. These results indicated that the platinum nanoparticle worked as the catalyst for the dioxygen reduction. Concerning the reduction potential, the catalyst was as active as the bulk platinum electrode. Therefore, it was concluded that the platinum nanoparticle maintained its activity in spite of being in the carbon material. It was also theorized that the carbon was porous enough to let dioxygen approach the platinum surface.

Summary

In this paper, we report a novel procedure to fabricate a platinum nanoparticle on a carbon material in a one-step synthesis. The phenylazomethine dendrimer was able to coordinate a Pt(IV) compound, such as $PtCl_4$, on the imine groups, as confirmed by UV–vis and ^{1}H NMR spectral titration. The dendrimer–$PtCl_4$ complex could convert to a platinum nanoparticle by pyrolysis, but the product was larger in size than expected. The obtained material consisted of the metallic platinum cluster made from $PtCl_4$ and the amorphous carbon made from the phenylazomethine dendrimer. The product worked well as the electrochemical catalyst for dioxygen reduction.

By this method, both the platinum nanoparticles and the carbon support can be synthesized at the same time in one step from a single precursor, the dendrimer–platinum complex. It is also notable that the products have a high platinum content up to 70% by mass, but the platinum particles are still well-dispersed because the dendrimer adequately prevents the aggregation of the platinum. Consequently, we fabricated a novel Pt–C nanocomposite using the phenylazomethine dendrimer, which is expected to work as a good catalyst. Quantitative analysis for the catalytic activity is now under investigation.

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