

Research Proposal

Dendrimer-Encapsulated Metal Nanoparticle Thin Films on solid
Surfaces: Preparation, Characterization and Applications to
Electrocatalysis

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1. Introduction

Metal nanoparticles are of great interest in many areas because of their unique physical and chemical properties. For example, if the size of particles is reduced to the nanometer scale, their electronic and optical properties change depending on their size. Additionally, because of their high surface-to-volume ratios, metal nanoparticles can be used as efficient catalysts.

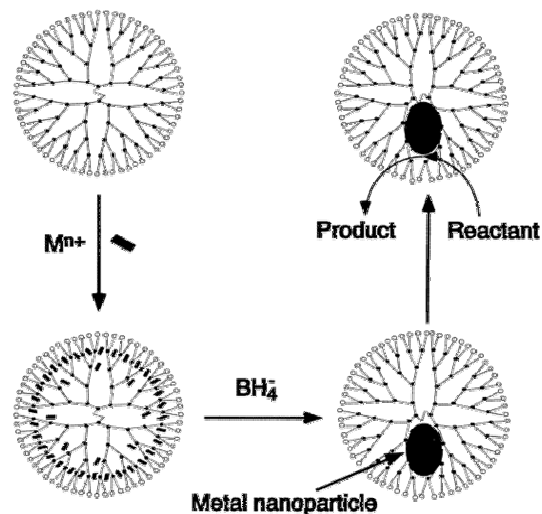


Figure 1. Schematic illustration of preparation of dendrimer-encapsulated metal nanoparticles (Crooks et al. *Acc. Chem. Res.* **2001**, *34*, 181-190)

Our group has previously demonstrated the preparation of nanometer size (<3 nm) metal and semiconductor nanoparticles using dendrimers as templates.¹⁻⁸ These dendrimer-encapsulated nanoparticles (DENs) are prepared by loading metal ions into the interior of dendrimers, and then chemically reducing the metal ions to yield encapsulated nanoparticles. (Figure 1) DENs are interesting for the following reasons: (1) the encapsulated nanoparticles are small (<3 nm) and in some cases nearly monodisperse; (2) the particle size can be controlled by selecting different dendrimer generations and metal-ion-to-dendrimer ratios; (3) encapsulated nanoparticles are confined partially by steric effects, and therefore at least part of the surface is available for catalytic reactions; (4) dendrimer branches and surface groups can be used as selective gates to control access of small molecules to the encapsulated nanoparticle;^{9,10} (5) the solubility of DENs can be tuned by modifying the peripheral groups of the dendrimer.^{7,8} Taken

together, these five points suggest that DENs may be useful for applications in homogeneous and heterogeneous catalysis.

In my research, I will study electrocatalytic applications and characterization of monometallic and bimetallic DENs. In order to achieve this objective, I will prepare the desired metal nanoparticles within dendrimers having surface functional groups that can be used to immobilize DENs on electrode surfaces. I will also use electrochemical methods, such as cyclic voltammetry, and rotating disk electrode and rotating ring-disk electrode voltammetry, to evaluate their electrocatalytic activity, and to understand their electrocatalytic mechanism and efficiency.

2. Background

2.1 Dendrimer-encapsulated nanoparticles (DENs) as catalysts

Dendrimer-encapsulated metal nanoparticles have been studied as homogeneous and heterogeneous catalysts in many reactions, such as hydrogenation,^{3,5,9,11,12} Heck reaction,¹³ Suzuki reaction,¹⁴ and electroreduction of oxygen² because they have a high surface-to-volume ratio and part of surfaces is available for the approach of substrates. Our group previously reported that size-selective hydrogenation of olefins was possible using Pd DENs.⁹ In this work,

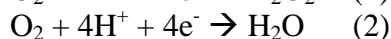
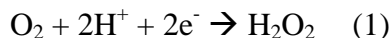
by utilizing different generations of dendrimers, the packing density on the dendrimer periphery could be controlled. Therefore, the substrates selectively reach metal nanoparticles through dendrimers depending on the size of substrates and the steric crowding of dendrimer periphery. Our group also has shown the application of Pt DENs to electrocatalytic reduction of oxygen.² Pt DENs physisorbed directly on Au electrode show electrocatalytic activity, which means metal DENs can be utilized as electrocatalysts.

2.2 Immobilization of Dendrimers on solid surfaces

Immobilization of dendrimers on surfaces has been previously studied. The first example of covalent attachment of dendrimers to a solid surface was reported by our group.^{15,16} Amine-terminated PAMAM dendrimers were immobilized via amide bond formation on a self-assembled monolayer presenting carboxylic acid surface groups. It was also reported that amine-terminated PAMAM dendrimers themselves form self-assembled monolayers (SAMs) on Au surfaces and that the dendrimer structure is compressed by coadsorption of hexadecylthiol. Surface-confined dendrimers can act as molecular gates, in that redox-active molecules selectively approach the electrode surface through dendrimers. PAMAM dendrimers also have been used to prepare multilayer films. Regen *et al.*¹⁷ reported the construction of multilayer dendrimer (PAMAM) films using a method involving coordination chemistry. They prepared an amine-functionalized silicon surface and used K₂PtCl₄ as a linker between amine groups at the surface and amine groups on dendrimer surfaces. This process could be repeated many times to build up multilayers of dendrimers having thicknesses of *ca.* 100 nm. Instead of K₂PtCl₄, poly[maleic anhydride-co-(methyl vinyl ether)] (Gantrez) has also been used as a linker via reaction of amine groups of dendrimers and anhydride groups of Gantrez.¹⁸

2.3 Electrocatalytic reduction of oxygen

The electrochemical reduction of oxygen (O₂) to water (H₂O) is an important subject for cathodes of fuel cells, because slow reduction of oxygen is the most limiting factor in the energy conversion efficiency of fuel cells. Therefore, the development of efficient catalysts and electrodes has been a focus in this field. It is well known that Pt is the most effective catalyst for oxygen reduction. However, the optimization of Pt catalysts, such as reducing particle size and increasing catalytic activity, is essential because of the high cost and limited supply of Pt. Pt-catalyzed reduction of oxygen yields two possible products as shown in equations (1) and (2).



in which (1) is a 2-electron reduction and (2) is a 4-electron reduction. It is known that Pt catalyzed oxygen reduction mainly has a 4-electron process.

2.4 Electrochemistry

Electrochemistry is a powerful technique that can be used to characterize small metal nanoparticles. Simple cyclic voltammetry measurements can determine redox potentials and onset potentials for a catalytically active material. For example, with good electrocatalysts, redox overpotentials will be lower and the amount of current will be higher. For a more detailed understanding of reaction kinetics, rotating disk electrode (RDE) and rotating ring-disk

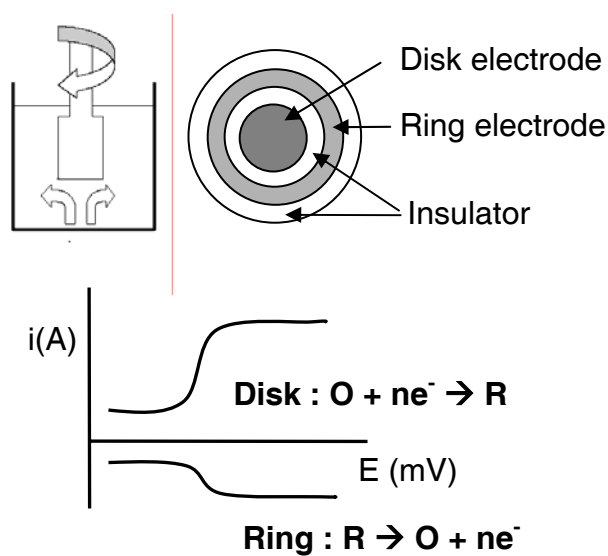


Figure 2. Schematic of rotating ring disk electrode and voltammograms

amounts of H_2O versus H_2O_2 formed by the reduction of oxygen in the presence of different catalysts.

electrode (RRDE) measurements can be utilized.¹⁹ Figure 2 shows a schematic of a RRDE and a typical voltammogram. The RRDE is composed of a disk electrode and a ring electrode which are imbedded into an insulator such as Teflon, epoxy resin, or another plastic. RDE experiments are often carried out to obtain a series of current-potential curves at different rotation rates. The data are then evaluated in terms of the Koutecky-Levish equation to evaluate kinetic parameters for the relevant reactions. The annular outer electrode of an RRDE provides a means for evaluating the product of the redox reaction at the disk electrode. This provides a convenient means for determining product distributions, such as the relative

3. Preliminary Results

The first part of my proposed research is to prepare stable and electrochemically active metal DEN films on electrode surfaces. Accordingly, metal DENs have been immobilized on Au surfaces via covalent amide bonds. To prepare covalently attached metal DEN films, I used fourth-generation amine-terminated, poly(amidoamine) (PAMAM) dendrimers (G4-NH_2). Our group has previously shown that DENs can be prepared within hydroxyl-terminated PAMAM dendrimers (G4-OH), but the peripheral hydroxyl groups are very difficult to link to SAMs in aqueous solvents. In contrast the primary amines groups of G4-NH_2 dendrimers are easy to attached activated acid-terminated monolayers. However, the peripheral amine groups also complex metal ions, which leads to dendrimer precipitation. My first objective, therefore, was to demonstrate that Pt and Pd DENs could be prepared within amine-terminated PAMAM dendrimers, and that the resulting composites could be linked to a surface.

3.1 Preparation of Pt and Pd dendrimer-encapsulated nanoparticles (DENs) within amine-terminated PAMAM dendrimer²⁰

The preparation of Pt and Pd DENs is carried out in two steps: First, Pt and Pd salts are mixed with G4-NH_2 in an acidic aqueous solution for sufficient time (76 h for Pt and 30 min for Pd) to allow for complete complexation of metal salt and the interior amine groups. Because the exterior amines ($\text{pK}_a = 9.2$) are more basic than the interior amines ($\text{pK}_a = 6.3$),²¹ metal ions selectively coordinate to the interior amines at low pH. Second, the dendrimer-encapsulated metal ions are reduced with excess NaBH_4 to yield zerovalent Pt and Pd DENs. Figure 3 shows UV-vis spectra of Pt and Pd DENs before and after reduction. After addition of the Pt salt to the

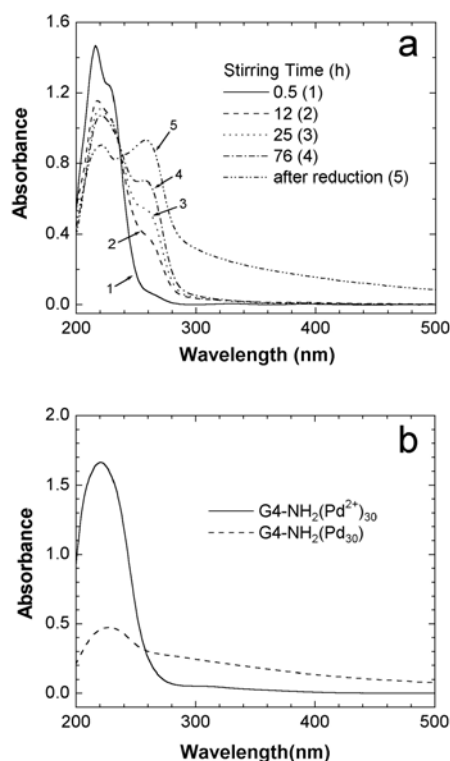


Figure 3. (a) Time-resolved UV-vis absorbance spectra of $G4-NH_2(Pt^{2+})_{30}$ solutions over a 76 h period and 15 min after reduction with $NaBH_4$ to yield $G4-NH_2(Pt_{30})$ (b) UV-vis spectra of $G4-NH_2(Pd^{2+})_{30}$ and $G4-NH_2(Pd_{30})$ solutions. The concentration of dendrimers was $50 \mu M$ for (a) and $2.5 \mu M$ for (b). The optical path length was 0.1 cm for (a) and 1.0 cm for (b)

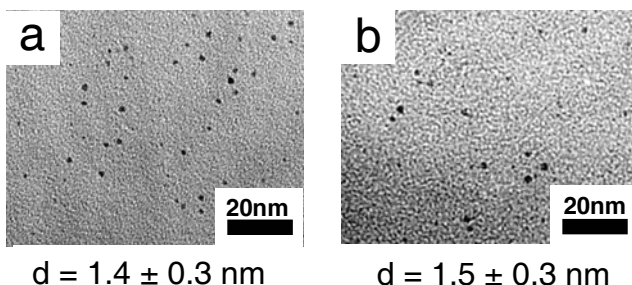


Figure 4. TEM images of (a) $G4-NH_2(Pt_{40})$ and (b) $G4-NH_2(Pd_{40})$

$G4-NH_2$ solution, the peak at 260 nm, resulting from coordination of the Pt complex with interior amines, grows in intensity throughout the 76-hour period, and simultaneously the peak at 216 nm decreases and shifts slightly to 220 nm. These changes are a consequence of ligand-exchange reactions between chlorine ligands and the interior amine groups. After reduction, the spectrum shows a broad, featureless absorption at wavelengths >300 nm which is consistent with the formation of colloidal Pt. (Figure 3a) Similarly, after addition of the Pd salt solution, the ligand-to-metal charge-transfer (LMCT) peak for the Pd^{2+} -amine interaction is centered at 221 nm. After reduction the broad, featureless absorption at low energies, as well as the peak at 230 nm, arises from interband transitions of the intradendrimer Pd nanoparticle. (Figure 3b)

Figure 4 shows high-resolution transmission electron microscopy (HRTEM) images for $G4-NH_2(Pt_{40})$ and $G4-NH_2(Pd_{40})$ DENs. Analysis of 100 randomly selected particles shows that the average diameters for the Pt and Pd DENs are 1.4 ± 0.3 nm and 1.5 ± 0.3 nm, respectively. These particle sizes and distributions are comparable to those obtained for Pd and Pt DENs prepared with hydroxyl-terminated PAMAM dendrimers although the particle sizes are larger than the value of 1.1 nm calculated for a Pd or Pt particle containing 40 atoms with face-centered cubic packing.^{2,3}

3.2 Synthesis and characterization of DEN thin films.²⁰

Previous studies showed that amine-terminated dendrimers (without encapsulated nanoparticles) could be covalently attached to electrode surfaces to yield stable monolayers.^{15,16} Using a similar procedure, we synthesized monolayer Pd DEN films by attaching $G4-NH_2(Pd_{30})$ to an 11-mercaptoundecanoic acid (MUA) self-assembled monolayer (SAM) on Au surface as follows. First, a MUA

monolayer was prepared by immersing a Au wafer into a 1mM ethanolic solution of MUA. The MUA substrates were then reacted with ethyl chloroformate and 4-methylmorpholine dissolved in DMF or CH_2Cl_2 for 1 h. This resulted in the formation of an activated anhydride surfaces. These activated surfaces were then reacted with Pd DENs in aqueous solution to yield covalently linked DEN films on Au surfaces.

To characterize the DEN films, Fourier transform infrared external reflection spectroscopy (FTIR-ERS) was carried out. Spectrum 1 in Figure 5a was obtained following coupling of G4- $\text{NH}_2(\text{Pd}_{30})$ to an activated MUA SAM and subsequent sonication in water for 30 s. The amide I and II bands present at 1665 cm^{-1} and 1550 cm^{-1} , respectively, indicate that the dendrimer is present on the surface. Spectrum 2 in Figure 5b was obtained using the same film, but after sonication in water for 5 min at pH 2. Analysis of the height of the amide I bands before and after sonication in acid indicates that 94% of the DEN film remains on the surface. Figure 3b shows an analogous experiment carried out the film prepared by omitting ethyl chloroformate. In this case, the DENs are likely attached to the surface via electrostatic interactions between the acid terminal groups of MUA and the peripheral primary amines of the dendrimer. After sonicating this film in water for 5 min at pH 2, only 78% of the amide I peak remains. These results indicate that the activated Pd DEN film is more robust than the unactivated Pd DEN film due to covalent bond formation. There is one more feature which suggests covalent bond formation in the activated film. After sonication in acid only the unactivated film (spectrum 2, Figure 5b) reveals a distinct shoulder at 1726 cm^{-1} . This band corresponds to the terminal carboxylic acid groups of the MUA SAM, and it indicates that many of the acid groups are protonated after acid treatment. The absence of this band in Figure 5a indicates the absence of free acid groups, and this in turn suggests nearly complete conversion of the acid to amide linkages between the dendrimer and the SAM.

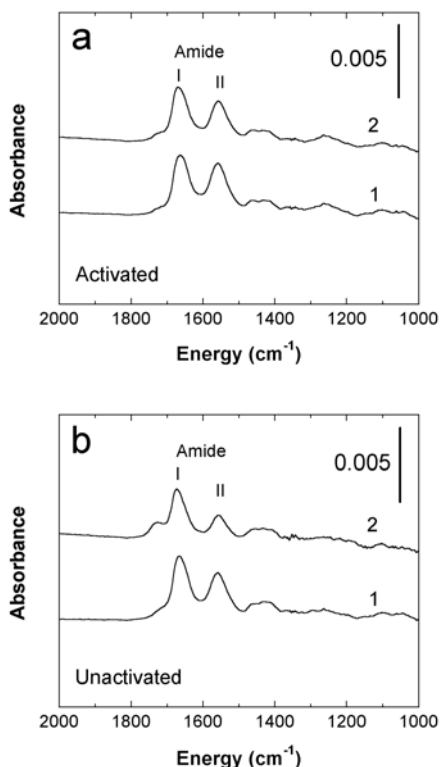


Figure 5. FTIR-ERS spectra of a Pd DEN film attached to a MUA SAM (a) with and (b) without activation of the SAM. In both (a) and (b), spectrum 1 was obtained after sonication in water at pH 7 for 30 s and spectrum 2 was obtained after sonication in water at pH 2 for 5 min.

4. Proposed Research

My preliminary results show that metal nanoparticles can be prepared within PAMAM dendrimers having amine groups, and that these DENs can be immobilized on Au substrates via covalent bonds providing high stability. Here, I propose my future research based on the above preliminary results.

4.1 Application of DENs to electrocatalytic reduction of oxygen.

Platinum is known as the most effective catalyst for oxygen reduction in fuel cells. We have previously shown that Pt DENs exhibit catalytic activity for oxygen reduction.² However, the film used for this study was prepared by direct adsorption of Pt DENs to a gold surface, and therefore these films were not very stable. I plan to compare the results of electrocatalytic oxygen reduction using covalently linked DEN films with those reported in this previous study. Briefly, Pt DEN films are used as electrodes in O₂-saturated H₂SO₄ solution, and the oxygen reduction peak is observed. Comparison of these data with dendrimer films prepared in the absence of encapsulated Pt will show if the Pt DENs have electrocatalytic activity in our films. A successful result will mean that Pt nanoparticles can communicate electrically with the electrode.

Ohsaka *et al.*²² recently reported that nanometer size (20 nm – 200 nm) Au particles electrodeposited on Au electrode show catalytic activity for oxygen reduction while large gold particles (0.5 – 1.5 μm) do not. They also showed that the mechanism of oxygen reduction with Au nanoparticles is different than for Pt. As mentioned previously, the oxygen reduction reaction catalyzed by Pt normally proceeds via a direct 4-electron process to yield water directly. In contrast, oxygen reduction catalyzed by Au nanoparticles proceeds by a 2-step, 4-electron (overall) pathway via an intermediate, H₂O₂. Because our group has previously shown that Au nanoparticles can be prepared within amine-terminated dendrimers, I plan to immobilize Au DENs on Au electrode by the same method described for Pd and Pt DENs. Then, I will perform cyclic voltammetry experiments to determine the electrocatalytic properties of Au DENs. Because DENs are more monodisperse in size than the nanoparticles used for previous studies, it may be possible to better understand the mechanism for oxygen reduction using nanoscopic Au nanoparticles.

4.2 Rotating disk electrode (RDE) and rotating ring disk electrode (RRDE) measurements.

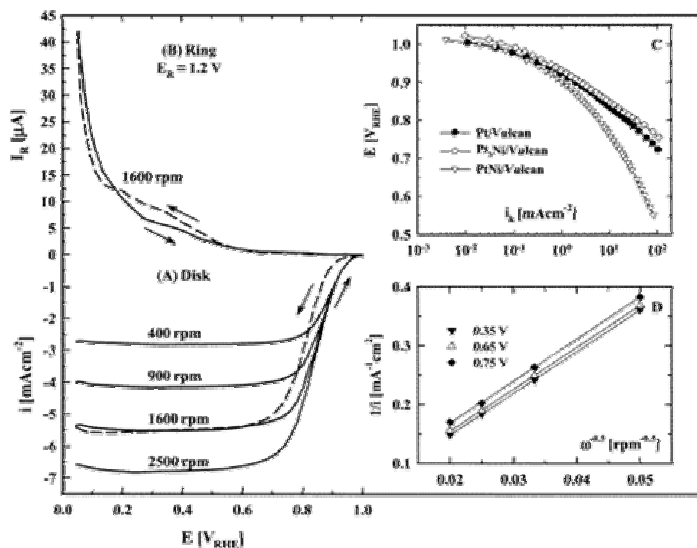


Figure 6. Examples of the RRDE voltammogram (a), b), Tafel plots (c) and Koutecky-Levich plots (d). (Paulus *et al.* *J. Phys. Chem. B* **2002**, 106, 4181)

To evaluate the kinetic efficiency of Pt and Au DEN films, I will use the RDE and RRDE techniques. First, the RDE experiments with various rotating rates allow us to use Koutecky-Levich equation as follows:¹⁹

$$\frac{1}{i} = \frac{1}{i_K} + \frac{1}{0.62nFAD_O^{2/3}\omega^{1/2}\nu^{-1/6}C_O^*}$$

i : Measured current

i_K : Kinetic current given by as

$$FAk_f(E)C_O^*$$

F : Faraday constant

A : Electrode area

D_O : Diffusion coefficient of O

ω : Electrode rotation rate

ν : Kinetic viscosity

C_O^* : Concentration of O

Plotting $1/\omega^{1/2}$ versus $1/i$ (Figure 6(d)) gives a straight line having an intercept corresponding to the kinetic current, i_K . In addition, the slope of the straight line provides information about the number of electrons in the oxygen reduction reaction. Second, Tafel plots (η versus $\log i$, Figure 6(c)) can be used to access the exchange current, i_0 , which is an important kinetic parameter. The Tafel equation¹⁹ is

$$\log i = \log i_0 - \frac{\alpha F \eta}{2.3 RT}$$

Third, The RRDE method allows us to measure the product distribution in the oxygen reduction reaction (H_2O_2 versus H_2O) and gain insight into the reaction pathway. The details of RRDE experiments are as follows. The RRED method is a generation/collection experiment because the ring electrode collects the product formed at the disk electrode. The first set of experiments will involve calibration of the RRDE. I will measure the collection efficiency of the RRDE system using the well-known redox couple: $[Fe(CN)_6]^{3-/4-}$. Then, RRDE experiments will be carried out to monitor the oxygen reduction reaction with Pt DEN films. Because H_2O_2 selectively re-oxidizes to oxygen on the ring electrode, I can calculate the product ratio between H_2O_2 and H_2O by using the following equation²³:

$$X_{H_2O_2} = \frac{2i_R/N}{i_D + i_R/N}$$

$X_{H_2O_2}$: Fraction of H_2O_2 formation

i_R : Ring current

i_D : Disk current

N : Collection efficiency

This result will show the pathway of the oxygen reduction reaction with Pt DEN catalysts.

Generally, the 4-electron pathway (H_2O) is considered to be the most important on polycrystalline Pt in impurity-free, aqueous acidic electrolytes. The 4-electron pathway is also the major route on Pt single crystals, except for Pt(111) and Pt(100) surfaces. When oxygen is reduced on these surfaces within the hydrogen adsorption/desorption region, nearly quantitative conversion to H_2O_2 is observed.²³⁻²⁵ Therefore, the evaluation of the pathway from the RDE and RRDE experiment will show the crystalline property of Pt DENs. This method can be one of methods to characterize such small metal DENs.

4.3 Improvement of catalysts using bimetallic DENs.

As mentioned earlier, the optimization of Pt catalysts for oxygen reduction reactions, such as reducing particle size and improving films and electrolyte conditions, is critical because of their high cost and limited supply. Another way to improve Pt catalysts is to discover a catalyst that is more active than Pt for oxygen reduction or to reduce the amount of Pt without reducing catalytic activity. Accordingly, various bimetallic and trimetallic Pt alloy particles have been studied to improve catalytic activity. For example, Paulus *et al.*²⁶ reported carbon supported Pt-based alloy catalysts (Pt-Ni and Pt-Co, particle size is *ca.* 4 ± 2 nm) for oxygen reduction reaction. They compared the catalytic properties of these materials to pure Pt, and

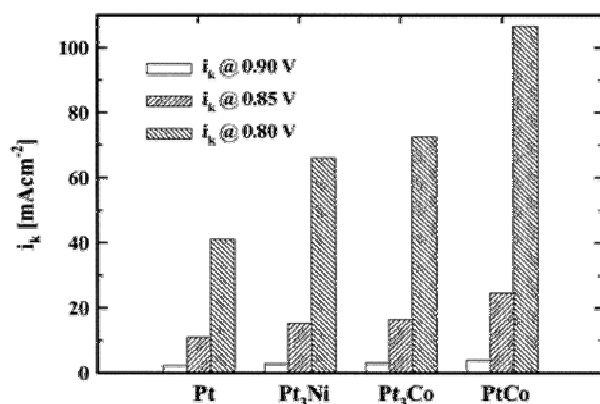


Figure 7. Histograms showing the kinetic current densities at different potential with Pt, Pt-Ni and Pt-Co. (Paulus *et al. J. Phys. Chem. B* **2002**, 106, 4181)

reactions compared to pure Pd or Pt catalysts.¹¹ Therefore, Pt-Pd DENs may also show the enhancement of catalytic activity in oxygen reduction reaction. If there is any enhancement of catalytic activity, I will find optimal metal ratio of Pt and Pd. Pt-Au is another good candidate because both of the metals have electrocatalytic activities as it is mentioned earlier and have been prepared within dendrimers. Pt-Ni and Pt-Co can be tested, however, we need to study first the preparation and characterization of Ni and Co DENs which have not yet been examined.

4.4 Preparation of metal DEN thin films by other methods

In this part, I propose other methods to prepare DEN thin films. I have shown the preparation of DEN thin films by covalent attachment to MUA SAM on Au substrates. However, I may need some other methods to use different substrates, to prepare multilayer films or to simplify the immobilization process.

First, since most of RRD and RRDE experiments for oxygen reduction reaction have been studied with carbon electrodes, DENs may need to be attached to carbon surfaces. It has been reported that amine groups can be covalently grafted on glassy carbon electrodes by electrochemical oxidation of amines.²⁸⁻³⁰ I can use this method to make a first layer having carboxylic acid on carbon electrodes, followed by attachment of DENs to the first layer. Moreover, I may be able to attach DENs to the carbon surfaces directly using surface amine groups in the dendrimers.

Second, it may be necessary to prepare multilayer DEN films to increase the amount of metal in the films. In this case, linkers between each dendrimer layer are needed. As I showed earlier, (See 2.2 in the background section) K_2PtCl_4 can be used as a linker molecule¹⁷ and K_2PdCl_4 also could be used as Pd has similar coordination chemistry to Pt. Organic molecules having bifunctional groups and polymers can also be used as linkers.

Third, I propose another method to prepare DEN film as follows: dithiol SAMs can be immobilized on solid substrates by themselves or with alkylthiols. After the SAM formation, surface thiol groups can be used to immobilize DENs via metal-thiol interactions. This can be done by simply immersing a dithiol film into a DEN solution. I expect that DENs can be attached to the surface while remaining in the dendrimer or the nanoparticles can be extracted

demonstrated a small activity enhancement (a factor of 1.5) for the 25% Ni and Co and a large enhancement (a factor of 2-3) for the 50% Co. (Figure 7) The proposed reduction mechanism was the same as for pure Pt catalysts: the 4-electron reduction. These experiments were carried out using RDE and RDDE techniques. Since there are several bimetallic DENs which have been reported,^{8,11,27} I will test their catalytic activities using the RDE and RRDE methods. Pt-Pd bimetallic DENs will be the first combination, because we have a lot of experience with those metals. Our group has demonstrated that bimetallic Pd-Pt DENs have higher catalytic activity in hydrogenation

from the dendrimer to the surface as our group has shown in solution.³¹ Dithiol molecules also can be used as linkers in preparation of multilayer films. However, thiol groups may contaminate some part of the catalytic metal nanoparticle surface.

5. Summary and Conclusions

I propose the study of metal DENs immobilized on solid surfaces using electrochemical methods, such as cyclic voltammetry, and rotating disk electrode and rotating ring-disk electrode voltammetry. First, Pd and Pt DENs are prepared within amine-terminated PAMAM dendrimers and these DENs are immobilized via covalent bond formation on a self-assembled monolayer having carboxylic acid surface groups. Then, these films are used as electrodes to perform electrochemical experiments. Since Pt is an excellent catalyst for oxygen reduction reactions, Pt DENs can be applied to electrocatalytic reduction of oxygen. RDE and RRDE measurements will show the kinetics and mechanism of the oxygen reduction reaction in our system. Electrochemical measurements will be a good method to characterize metal DENs that are normally difficult to characterize due to their small sizes. In addition, bimetallic DENs such as Pt-Pd and Pt-Au can be utilized to improve the catalytic activity in electrochemical reactions. I also propose other methods to prepare DEN films.

This study will allow us not only to apply metal DENs to electrocatalysis, but also to understand the chemical and physical properties of metal DENs.

6. References

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