# TITLE : ELECTROCHEMICAL PROPERTIES OF DENDRIMER ENCAPSULATED METAL NANOPARTICLES

1.INTRODUCTION

We propose to study the electrochemical properties of dendrimer-encapsulated metal nanoparticles (DEMNs). These materials were discovered by our group in 1998. DEMNs are prepared as shown in Scheme 1. These DEMNs are prepared by addition of metal ions into a hydroxyl-terminated dendrimeric solution. The metal ions then form coordination complexes with tertiary amine groups inside of the dendrimer. Following reduction of the metal ions with $NaBH_4$, coalescence of zerovalent metal atoms into a cluster confined in interior of the dendrimer is observed. DEMN type catalysts have several advantages compared to other kinds of catalysts : 1) The solubility of DEMN can be controlled by altering the dendrimeric peripheral groups 2) These nanoparticle type catalysts provide a high surface-area to volume ratio 3) The dendrimeric peripheral groups can act as a selective gate for molecular permeation 4) The dendrimer can be employed as a well defined template for nanoparticles because the structure of the dendrimer is stable and uniform 5) The agglomeration of nanoparticles can be prevented by the dendrimer template.
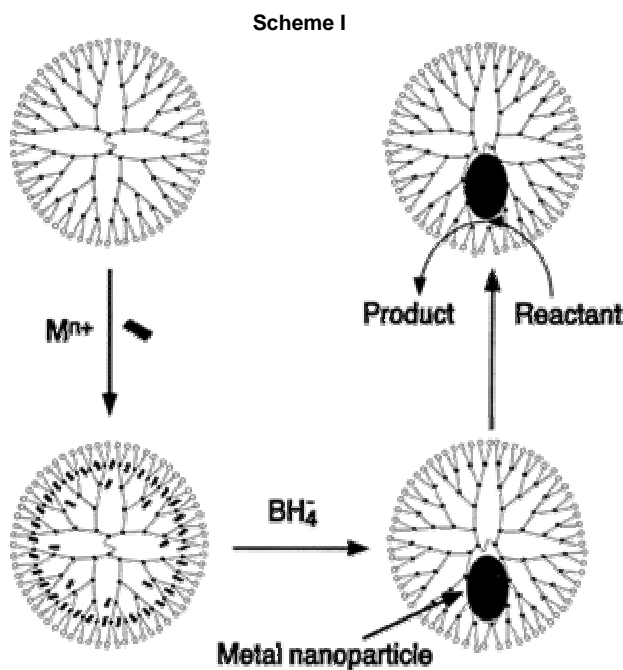
Scheme I

Scheme 1. Synthesis of DEMN
(Crooks R. M. *et al. Acc. Chem. Res.*
2001, 34, 181-190)

Metal nanoparticles are gaining interest for thier potential applications in fields such as catalysts and nanotechnology. Many scientists recently have been devoted to investigate the characteristics of nanoparticles and to try to utilize nanoparticles as a basic material for miniaturized devices because of their important properties exerted from small metal nanoparticles. It has been previously assumed that the properties of metal particles are not affected by their size. But this postulation is not applicable to very small nanoparticles with diameter less than 10 nm and such small nanoparticles demonstrate different properties from macroscopic metal particles. The ratio of atoms on the surface to atoms within the interior increases in the nanoparticle and the surface of nanoparticles greatly affects physical properties of particles. Especially, the optical and physical properties of nanoparticles are changed depending on their size.

The electrochemical properties of small metal particles are especially important for application of nanoparticles in the semiconductor industry. The electronic structure of

nanoparticles are between the discrete energy bands of atoms and continuous energy bands of bulk metals. In nanoparticle systems, the electrochemical properties are strongly dependent on their size difference from bulk metals. If one charge is present in nanoparticles, this charge prevents the addition of another charge. As a result, the staircase shape can be observed in the current-voltage curves. This is called the "Coulomb blockade" effect. Each step in the staircase is due to charging of nanoparticles by one electron and the difference between the current peaks in the voltammogram are inversely proportional to the nanoparticle radius.

   DEMNs are highly stable and can be easily applied to versatile systems because the dendrimer peripheral groups can be easily modified. In addition, DEMNs have certain unique properties that we believe will be important for catalysis. However at the present time we know little about the physical and chemical properties of these materials. A detailed electrochemical study will provide information about intrinsic characteristics of DEMNs.

2. BACKGROUND

2.1 Nanoparticle

   The term "nanoparticle" refers small metal clusters with in the 1 -10 nm size range. This size is comparable with the size of molecules and as a result, nanoparticles exhibit optical, magnetic, electronic and catalytic properties different from bulk metals. Additionally nanoparticles have size-tunable characteristics depending on the dimension of nanoparticles. These special characteristics of nanoparticles have been attracting many scientists for their potential application in industry. Nanoparticles have been prepared from various metal ions and the size and shapes of nanoparticles can be adjusted by controlling concentrations of metal ions, reducing agent and stabilizer. Nanoparticles are usually synthesized in ultra high vacuum (UHV) or nanoporous supports like metal oxide support, silica, zeolite cage, diamond and polymer support to increase stability.

   These nanoparticles can be employed as template materials for fabrication of functional microdevices. In addition, nanoparticles shows catalytic activities different from those of bulk material due to significantly high surface to volume ratio. Several studies revealed surprising catalytic activities of nanoparticles including hydrogenation, hydrosilylation, oxidation of carbon monoxide, electrooxidation, and Suzuki cross coupling reaction. Even though metal nanoparticles have strong catalytic activities, the application of nanoparticles has been limited because metal nanoparticles are unstable and aggregate easily. Therefore several methods have been introduced to improve the stability of nanoparticles by using organic ligands, polymers, oxides and micelles. These additional layers outside of nanoparticles provide a way to alter the surface properties and reactivity of nanoparticles by modification of their surface. The immobilization of nanoparticles on substrate surfaces by introducing reactive ligands was also shown to be possible.

2.2 Dendrimer Encapsulated Metal Nanoparticle (DEMN)

Poly(amidoamine)(PAMAM) starburst dendrimers are fabricated by successive Michael addition and amidation reactions. As a result the interior of dendrimer consists of tertiary amines, amide groups and methylene groups. This PAMAM dendrimer was applied as a template for the nanocatalysts. Metal ions can be strongly held inside of a dendrimer because tertiary amines within the dendrimer are a good ligand for many transition metals. These metal ions are converted to neutral atoms by addition of a reducing agent like $NaBH_4$ and quickly coalesce into zerovalent metal nanoparticles with 1- 2 nm diameters. Several metal ions have been tested for this approach including Pd^{2+}, Cu^{2+}, Pt^{2+}, Ni^{2+}, Fe^{3+}, Mn^{2+} Au^{3+}, and Ru^{3+} and the formation of metal nanoparticles were confirmed by transmission electron microscopy (TEM) and observing changes in UV spectroscopy.

The catalytic activity of DEMN for hydrogenation reactions was tested by using allyl alcohols in aqueous solution. The result indicated that the substrates could access the metal nanoparticle inside of a dendrimer. Reasonable turn over frequency (TOF) values for the hydrogenation of allyl alcohols was observed but this hydrogenation is strongly affected by dendrimer generation and steric properties of substrates. For example, TOF was decreased as the generation of dendrimers increased from G4 to G8 and higher TOF was obtained for linear allyl alcohol than branched allyl alcohol. This strong dependence on the structure is originated from steric crowding on the dendrimer periphery. The number of peripheral groups increases as the generation of dendrimer increases therefore the dendrimer becomes less porous and this interferes with the penetration of substrates.

Even though there have been some attempts to use dendrimers as a permeable spacer that lead multilayer formation of metalates in studying electrochemical properties of metalates, the studies on the electrochemical properties of metal nanpoparticle inside of a dendrimer is relatively rare until now. Therefore the investigation of electrochemical properties of DEMN may assist the application of DEMN in more diverse application.


2.3 Monolayer Protected Cluster (MPC)

Murray et al. successfully fabricated Au nanoparticles stabilized by alkanethiol molecules. These molecular protected metal nanoparticles are formed by addition of alkanethiols to the solution of $AuCl^{4-}$ in organic solvent followed by reduction with $NaBH_4$. The structure of resulting MPCs is similar to the dendrimer but these MPCs have a less dense periphery than dendrimers. They called this structure as "soft objects with hard cores". The chemical properties of MPCs are strongly affected by ligands around metal clusters and the reactivity and solubility can be altered by changing ligands attached to the metal cluster by associative ligand exchange reaction.

Their spectroscopic study reveals distinct steplike tendencies in spectra of very small monodisperse Au clusters with 1 - 2 nm diameters. This molecular-like property was observed in electrochemical studies too. The most interesting property of MPC is their quantized double layer capacitance charging. The charging process of very small capacitance by single electrons can be observed in the voltammetry of MPC solutions. The difference in observed potential due to single electron charging is inversely proportional to double layer capacitance (C_{CLU}) by the equation ($\Delta V = e/C_{CLU}$). ΔV should exceed $k_b T$ to obtain discernible differences in potential intervals. This can be achieved by very small C_{CLU}. For that reason, discrete peaks can be observed in the

voltammogram of MPCs because MPCs have sub attofarad capacitance. The spacing of current peaks in voltammograms reflects characteristics of metal clusters because the charging process of metal clusters is affected by size and electrostatic properties of metal clusters. In addition, the charge state of nanoparticle cores can be recognized by the quantized double layer charging process. This quantized double layer charging phenomena is very similar to previous studies on coulomb staircase behavior of single MPC with STM. But these well discretized double layer charging steps become obscured if the cores of MPC are not monodisperse. This idea can be applied to DEMN systems too. The investigation of current peaks in voltammograms will provide information about properties of metal nanoparticles inside of dendrimers including the monodispersity of the nanoprticles.

   The characteristics of surface attached MPC's multilayers were alsoinvestigated. The mixed monolayer (alkyl and carboxylic acid) protected Au nanoparticles are immobilized on the Au substrates modified by carboxylic acid groups. This multilayer can be fabricated on the Au substrates by formation carboxylate /M^+/carboxylate ion linkages. In the voltammogram, the peak current linearly increased with an increase of scan rate and this is the electrochemical characteristic of surface confined monolayers.
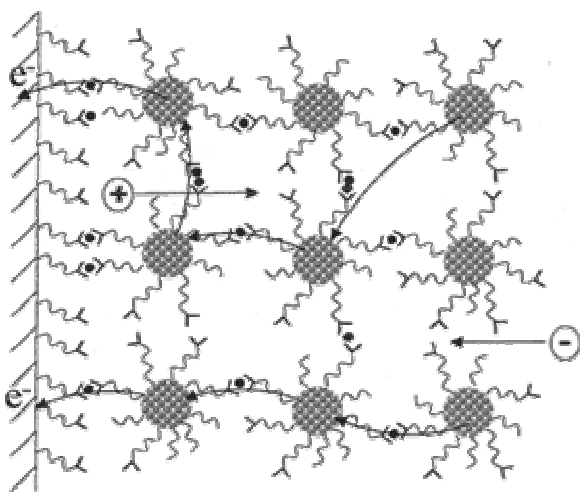
Scheme 2. Multilayers of Au MPCs assembled on a Au electrode (Hicks J. F. *et al. JACS* **2001**, 123, 7048)

More recently they studied electron-dynamics between nanoparticles from diffusion-like electron transport in multilayer films (scheme 2). In this case, potential changes at the electrode drive redox reactions at the interface and this reaction propagates throughout the films by electron hoping until equilibrium is achieved in entire films. The electron hoping process is a tunneling reaction from core to core of MPCs and interrupted by linkages between the MPCs. This electron hoping rate can be measured by using a potential step chronoamperometry method but the electron hoping rate is usually too fast to measure in accessible ranges. Thus the introduction of long tunneling bridges between MPCs with sufficient thickness allowed them to achieve measurable electron transfer rates in addition to assist movement of counter ions for charge compensating the film. In this study, relatively large peak separations in the voltammogram were observed when the distance between the MPCs increased by long bridges. This means that the peak separation is related to dynamics of electron transfer.
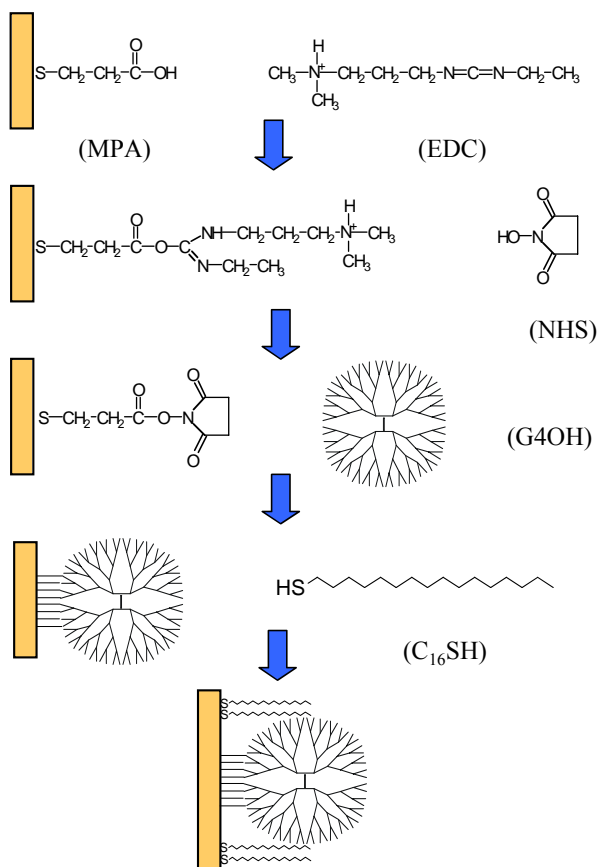

3. PRELIMINARY RESULT

3.1 Multilayer Formation via Self-Assembly (SA) Method

The SA method has been widely applied to fabricate organic thin film on the substrate for DNA chips, catalysts and biosensing devices. However it was hard to employ water sensitive or unstable molecules in the formation of self-assembled monolayers because SA is typically performed in aqueous solution. The formation of multilayer-films using water sensitive molecules was achieved by vapor phase deposition application. The thin film fabricated in absence of the solution showed a stability comparable to the film prepared in solution phase and similar properties.

Amino thiophenol (ATP) monolayers were fabricated on the Au substrate as a base layer for construction of multilayer-films by vapor phase deposition and active amine groups were than present on the surface. The second layer can be formed on the surface by introducing succinyl chloride (SUC-Cl) via amide bond formation between the amine group on the surface and acid chloride group of SUC-Cl. In this reaction, just one of the acid chloride groups of the bifunctional SUC-Cl reacted with the surface confined amine group while the other acid chloride group remains unreacted on the surface. Therefore this active surface could be employed for subsequent reaction with amine terminated molecules and multilayers with more than five layers could be fabricated on the surface by successive dosing of SUC-Cl and hexamethylene diamine. Tetrafluoromethyl benzoyl chloride (TFMBC) was reacted with amine functional group terminated surface to form the final layer. Each step of the multilayer formation was confirmed by observing changes in IR spectra and ellipsometric film thickness.

The reactivity of films was estimated by comparing intensities of C-F stretching mode in the IR spectra with that of the ATP-TFMBC bilayer-film fabricated in solution and assuming that the coverage of the film prepared in solution is 100 %. The estimated surface coverage of the films was between 30-50 %.

3.2 Dendrimer Immobilization

The immobilization of dendrimers has been studied by many scientists to facilitate the application of dendrimers as sensors and catalysts. Previously our group successfully confined a dendrimer on the surface via amide bond formation reaction. Beside our group, there have been many attempts to immobilize dendrimers on various substrates but usually amine terminated dendrimers have been used for this purpose due to

Scheme 3. Immobilization of a Dendrimer on the Surface

higher activity of amine groups than hydroxyl groups. However hydroxyl terminated dendrimers are more favorable for fabrication of DEMN because the primary amine groups on the periphery can form coordination complexes with metal ions. Therefore amine-terminated dendrimers could be precipitated upon formation of nanoparticles.

The confinement of hydroxyl terminated dendrimers on the gold substrate is achieved via a coupling reaction. 3-mercaptopropionic acid (MPA) was employed as a base monolayer on the Au substrate and as a result, a carboxylic acid terminal group was fabricated on the surface. Carboxylic acid groups on the surface were converted to more active leaving group by the reaction with ethylene dimethyl propyl amonium carbodimide (EDC). This coupling reaction resulted in a shift of carbonyl group peak from 1724 cm^{-1} to 1717 cm^{-1} and a new peak was observed at 1643 cm^{-1} in the IR spectra. The shift of the carbonyl band to lower frequency can be explained by the electron-withdrawing-effect. The substitution of carboxylic acid OH groups with less electronegative (less electron withdrawing) groups lowered the carbonyl band frequency. In addition, the new peak at 1643 cm^{-1} can be assigned as the C=N stretching mode of surface confined EDC. These observation showed that EDC was successfully coupled to the surface. The subsequent reaction of N-hydroxy succinimide (NHS) with themodified surface result in fabrication of a very reactive surface with good leaving groups. The carbonyl band shifts to a higher frequency (1722 cm^{-1}) from 1717 cm^{-1} and the disappearance of the peak at 1643 cm^{-1} upon substitution confirmed the completion of the surface modification reaction.

The hydroxyl-terminated dendrimer could be confined on the surface via substitution reactions and the immobilization of the dendrimer on the surface results in strong amide peaks in the IR spectra. But this film was easily removed from the surface after application of a potential. Therefore $C_{16}SH$ was introduced to increase stability by filling the void area in the film and this mixed organic film showed higher stability than the film without $C_{16}SH$. The film stability was estimated by comparing the intensity of the amide I band before and after scanning. This film was more stable in organic electrolyte than aqueous electrolyte. The intensity of the amide I band was not changed even after 30 scans in the organic electrolyte. This maybe due to the lower solubility of the dendrimer in organic solvent.
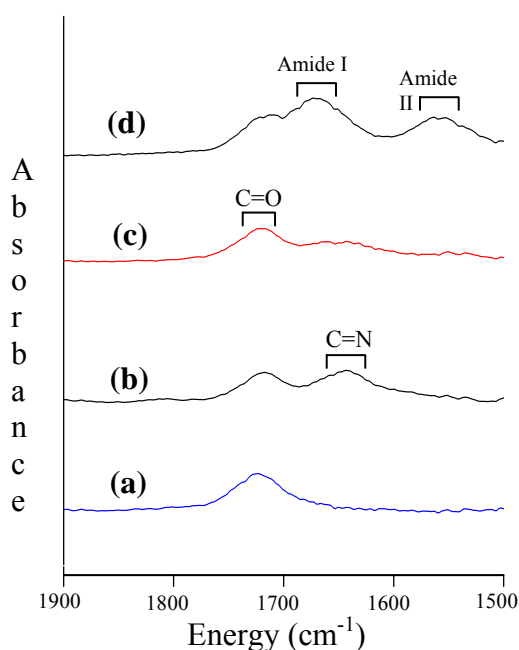
Figure 1. FTIR-ERS spectra (a) a MPA monolayer on Au (b) the MPA monolayer after reaction with EDC (c) the resulting active surface after reaction with NHS (d) Au/MPA/NHS bilayer after substitution reaction with dendrimer.

4. PROPOSED REASEARCH

4.1 Effect of Metal Nanoparticle Composite (Pd, Pt, Au)

Nanoparticles that consist of noble metals have been extensively studied because these metals are important as catalysts for many organic reactions and charge carriers in nanocomposite systems. Our group previously fabricated metal nanoparticles of Cu, Pd and Pt inside of dendrimers. However these metal nanoparticles showed different photochemical properties and stabilities due to the composite of nanoparticles.

Palladium is an important industrial material for its strong catalytic activity. Therefore many methods have been applied to stabilize Pd nanoparticles to facilitate the application of Pd nanoparticles in catalytic systems. In addition to our group, there have been attempts to stabilize Pd nanoparticles by alkanethiol monolayers. In the previous study, differential pulse voltammetry (DPV) experiments were performed to compare the electrochemical properties of Pd and Au MPCs. The Au MPC showed well defined peaks in DPV but smeared and less regularly spaced peaks are observed in the Pd nanoparticle systems. Therefore I expect to observe similar phenomena in the dendrimer system in the voltammograms but there may be some differences because nanoparticles are less densely passivated by dendrimers compared to alkanethiols.

The gold nanoparticle system has been most extensively studied compared to other noble metals because gold nanoparticle can be easily stabilized by using alkanethiols and are not easily oxidized. There have been several attempts to stabilize gold nanoparticles by using dendrimers. The fabrication of gold nanoparticles inside of the dendrimer was shown possible by making charged dendrimer and modifying peripherals of the dendrimer with sugar, cyclodextrin and methyl ester groups.

There have been relatively few studies about nanoparticles consisting of Pt and studies on electrochemical behavior of Pt nanoparticles are rare. Yoo et al. previously prepared Pt nanoparticles stabilized by polyacrylic acid on nanoporous Al_2O_3 catalyst and our group has previously reported Pt nanoparticles stabilized by dendrimers even though the ligand exchange reaction was relatively slow. It was observed that Pt nanoparticles inside of dendrimer are able to communicate with the electrode without need for mediators and this observation is somewhat promising to study electron transfer between nanoparticles.

These metal nanoparticles showed different surface plasmon bands in the UV-Vis spectra depending on the oxidation state and nanoparticle compositions. Therefore it is expected that each metal nanoparticle inside of a dendrimer will affect electron transfer behavior in different ways and as a result, electrochemical properties of each DEMN will be expressed in voltammetry experiments differently.

4.2 Effect of Metal Nanoparticle Size (40, 60)

The size of metal nanoparticles and the length and property of passivated monolayers affect the electrochemical behavior of the nanoparticle. Whetten's group previously demonstrated that small gold nanoparticles showed size dependent step like behavior in the optical spectra. They fabricated gold nanoparticles passivated by alkylthiols and compared optical spectra of gold nanoparticles ranging in size from 1.4 to 9 nm. The steplike structures in optical spectra were observed only in the spectra of small
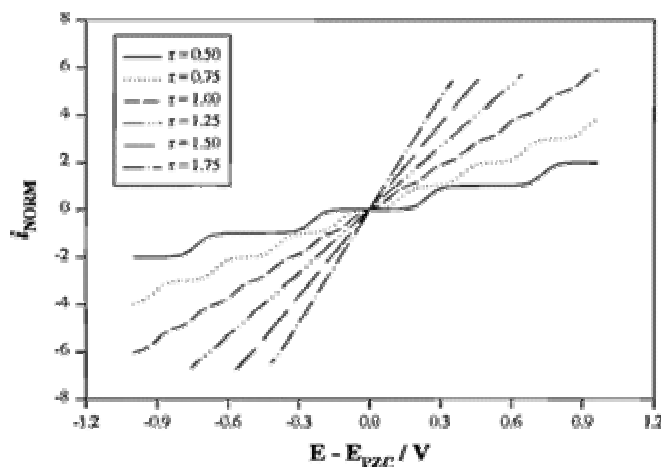
Figure 2. Steady state microelectrode Voltammetry simulations for MPCs with various core sizes

nanoparticles less than 2 nm. Furthermore, the size-dependent electronic relaxation in gold nanoparticles was studied. In general, the electronic relaxation time of large particles is slow and the electronic relaxation time decreases if the particle sizes decrease because the enhanced surface collision rate in small particles facilitate electron relaxation. They compared electro-dynamics of Au_{55} (2 nm diameter) and Au_{13} clusters. The relaxation times were 1 and 300 ps for Au_{55} and Au_{13} clusters respectively. The slower relaxation time was observed in the smaller particle. These results are not correlated with normal behaviors of metal particles. Therefore they concluded that the molecular behavior was observed in very small metal particles and the properties of metal particles were changed from bulk to molecular-like behavior even between 55 and 13 atoms clusters.

The electrochemical study revealed similar results with optical spectroscopic studies. Chen et al. fabricated monolayer protected Au nanoclusters with various core metal cluster sizes from 1 nm to 3.5 nm and demonstrated the size-dependent and step-like responses in the voltammograms. The charging step was more prominent for the smaller Au clusters with diameter less than 2 nm. However these charging steps become less defined as the Au cluster sizes increased. The peak spacing in the voltammograms was dependent on the core size of MPCs. In the classical coulomb staircase, the peak spacing followed the equation $\Delta V = e/C_{CLU}$ and double layer capacitance (C_{CLU}) is proportional to the radius of the metal cluster. Therefore the peak spacing decreases as the size of metal cluster increases. The larger peak spacing in the voltammograms was observed in the small metal clusters but due to the charging steps were hardly discerned in the metal clusters with the diameter more than 2 nm.

The optical and electrochemical studies showed very consistent results and these stimulate us to investigate size dependent properties of DEMNs. Our group successfully prepared Pd_{40}, Pd_{60}, Pt_{40} and Pt_{60} nanoparticles inside of dendrimers. The diameters of particles were proportional to the number of atoms as expected. For example, the diameters of Pt_{40} and Pt_{60} nanoparticles measured by TEM showd 1.4 ± 0.2 nm and 1.6 ± 0.2 nm each and these nanoparticles are comparable to MPCs. Therefore I think particle size-dependent electrochemical responses can be observed in DEMNs although it is not possible to vary size of the nanoparticle in great degree because the space inside of the dendrimer is limited.

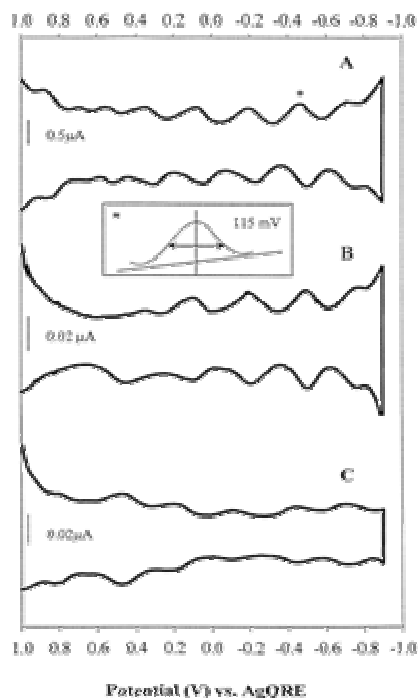4.3 Effect of Dendrimer Generation (G4, G6, G8)

Figure3. DPVs showing charging events for (A) C6MPC (B) C8 MPC (C) C10 MPC.

The size of the dendrimer increases and the peripheral of the dendrimers becomes more dense as generation increases. But the interiors around the core where we assumed nanoparticles are placed is not altered. Therefore the distance between nanoparticle and peripheral of dendrimer will change as dendrimer generation increases.

As I mentioned earlier, C_{CLU} is a function of the radius of the metal cluster. In addition, C_{CLU} is dependent on the thickness of the protected monolayer by the following equation.

$$C_{CLU} = 4\pi\varepsilon\varepsilon_0 r(r+d)/d$$

where d is thickness of monolayer, r is radius of nanoparticle, ε is dielectric constant of the monolayer. For example, the diameter of G4, G6 and G8 dendrimers are 4.5 nm, 5.4 nm and 6.7nm respectively. If we assumed the diameter of nanoparticle is 2 nm, d become 1.25 nm, 1.7 nm, and 2.35 nm for each. Consequently C_{CLU} decreases as the dendrimer generation increases. Therefore ΔV will be larger for the higher generation dendrimer than the G4 dendrimer. I expect approximately 13 % and 27 % increased value for G6 and G8 dendrimers compared to G4 dendrimer. In the previous study, the electrochemical properties of C6 and C12 alkanethiol monolayer protected MPCs were investigated. The peak spacing in the DPV curves were affected by alkylchain length of MPCs. Larger peak spacing was observed for the MPC with C12 alkanethiol compared to MPC with C6 alkanethiol and this result is similar to my expectations.

4.4 Formation and characterization of Dendrimer-Nanoparticle Nanocomposites

Our group was previously fabricated very stable Au colloids stabilized by amine-terminated dendrimers. These nanocomposites were prepared by in-situ reduction of HAuCl$_4$ in the presence of dendrimers. The size of nanoparticles could be controlled by generation of dendrimers and larger colloids were formed with the lower generation dendrimers. Cox et al. successfully constructed nanocomposite consisting of metalate and PAMAM dendrimers via layer by layer deposition. Polyoxometalates and phosphomolybdate were used for the metalate and these metalates are negatively charged. Therefore multilayers could be formed on the ATP modified Au electrode by electrostatic interaction between metalate and the protonated amine group of dendrimer. Three redox peaks were found in the CV and the peak currents are directly proportional with scan rates. They observed electrochemical responses depending on scan rates and number of layers. The dendrimers in the multilayer films affected the mass transfer but did not prevent the electron transfer.

The nanoparticles stabilized by the dendrimer shell have been vigorously studied but the electrochemical studies on the nanoparticles between the dendrimers are relatively rare compared to the optical spectroscopic studies. Moreover, in the case that the nanoparticles were stabilized by dendrimer peripheries, the nanoparticle will be located in the center of dielectric medium. On the contrary, I suspect that the position of the nanoparticle inside of the dendrimer is not in the center of the dendrimer. This is different from MPCs. Therefore the electrochemical response of nanoparticles stabilized by the peripheries of the dendrimers may be different from DEMNs. I expect these difference may be observed in the voltammetry experiments.

V. SUMMMARY and CONCLUSION

The objective of my research is to fabricate a stable thin-film consisting of DEMNs on the electrode surface and study electrochemical properties of this film. In this system, dendrimers serve as building blocks for the film and the stabilizer of nanoparticles. I propose a series of studies that will discover the factors that affect electron transfer in the film including particle size, generation of dendrimer and the composition of nanoparticles. In addition, I propose to study on the film fabricated by alternative deposition of nanoparticles and dendrimers.