Electrochemistry on Alternate Structures of Gold Nanoparticles and Ferrocene-Tethered Polyamidoamine Dendrimers[†]

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Self-assembled systems with polyamidoamine (PAMAM) dendrimers combined with gold nanoparticles have been widely studied because of their potential applications in molecular electronics, catalyst carriers, chemical sensors, and biomedical devices. In our work, gold nanoparticle monolayers and multilayers with pure and ferrocene-tethered PAMAM dendrimers as cross-linking molecules were deposited on a mixed self-assembled monolayer of gold substrates. The various generations of PAMAM dendrimers can be covalently attached to mercaptoundecanoic acid mixed with a mercaptoundecanol self-assembled monolayer. Cyclic voltammograms show that redox peak currents on the alternate multilayers of gold nanoparticles and ferrocene-tethered PAMAM dendrimers increase as the number of layers increases. Fourier transform IR external reflection spectroscopy and scanning electron microscopy support the results from electrochemical measurements.

Key Words : Au nanoparticle, PAMAM dendrimer, Ferrocene, Multilayer

Introduction

Materials composed of two- and three-dimensional ensembles of nanoparticle (NP) are becoming increasingly important in analytical and materials chemistry. Indeed, practical applications in nanoelectronic devices, optoelectronic devices, chemical sensors, and catalysts seem imminent.[1-4] Alternate immersion into bifunctional cross-linker and NP solutions produces randomly arrayed structures with controllable thickness. The molecular size of the cross-linker determines NP spacing in the film structures. The Schiffrin[5,6] and Murray[7,8] studies described multilayers of thiol-capped AuNPs, and the Natan study described the optical, electrical, and electrochemical properties of dithiol-linked AuNP films.[9,10] Moreover, there have been a number of studies on polymer composites with nanoscopic and microscopic materials in which exposure to the cationic and anionic polymer solutions is alternated, a method popularized by Decher.[11-13] To isolate AuNPs from each other, researchers applied various factors such as solution concentrations, introduced electrolytes, and measured adsorption time to control polymer thickness. These film structures showed conducting, semiconducting, or insulating properties.

We prepared a series of films by a layer-by-layer deposition of PAMAM dendrimer and AuNPs on Au surfaces by covalent bond. Because PAMAM dendrimers have a well-defined shape and size as well as numerous functional sites, covalently cross-linked PAMAM dendrimers served as structure elements, like bricks, in building up the thin films.[14-16]

We describe here the characteristics of AuNP layers incorporated with ferrocene (Fc)-modified PAMAM dendrimers, which have been proved to be useful building blocks with reversible redox reaction. Thus, ferrocene-containing polymers are currently receiving much attention due to their increasing role in the rapidly growing field of materials science.[17-19] Partially ferrocene-modified PAMAM dendrimer was used as the crosslinker among AuNPs. Electrochemical measurements indicate that multilayered structures of AuNPs with Fc-modified PAMAM dendrimers are capable of electron transfer in the layered film.

Experimental Sections

Materials. The following materials were obtained from Aldrich and were used as received without further purification: $HAuCl_4 \cdot 3H_2O$, sodium citrate dihydrate, ferrocene carboxylic acid, 11-mercaptoundecanoic acid (MUA), ferrocenecarboxaldehyde, ferrocenecarboxylic acid, pyridine, CH_2Cl_2, sodium borohydride, 11-mercapto-1-undecanol (MUO), 1-ethyl-3-(-dimethylaminopropyl) carbodiimide (EDC), N-hydroxysuccinimide (NHS), polyamidoamine (PAMAM) dendrimer (generation 0, 2, and 4), $K_3Fe(CN)_6$, KCl, HCl, and $HClO_4$. C_2H_5OH and CH_3OH were purchased from Merck and 30% H_2O_2 was purchased from Fluka. Ultrapure H_2O (Modulab Modupure System, U. S. filter Corp., >18 MΩ cm) was used for all experiments.

Preparation of AuNPs. In accordance with previous studies, AuNPs were synthesized by the citrate reduction of $HAuCl_4$.[20] All glassware were cleaned in Nochromix (Fisher) and were dried prior to use. An aqueous solution of $HAuCl_4$ (1 mM, 100 mL) was brought to a reflux while vigorously stirring, and then 10 mL of a 38.8 mM trisodium citrate solution was quickly added, which resulted in a color change from pale yellow to deep red. After the color change, the solution was refluxed for an additional 15 min, and was then allowed to cool to room temperature. After the solution reached room temperature, it was filtered through a 0.45 μm

nylon membrane filter (Gelman Sciences, USA). The resulting solution of colloidal particles was characterized by absorption maximum at 520 nm. Transmission electron microscopy indicates particle size of 13 ± 2 nm.

Synthesis of ferrocene-tethered PAMAM dendrimer (G4). Primary amines of NH_2-terminated G4 PAMAM dendrimers were partially modified with ferrocenyl groups through the imine formation by amine-aldehyde reaction. 7.5 mg of ferrocenemonocarboxaldehyde was dissolved in 3.75 mL of methanol, and the mixture was added dropwise to 0.25 mL of 10% (w/w) G4 PAMAM dendrimer solution containing hydrochloric acid as a catalyst. The reaction mixture was stirred slowly for 2 h; then 5 mg of sodium borohydride was added slowly and stirred for 1 h to reduce carbon-to-nitrogen double bonds. The reaction product was purified by lipophilic gel permeation chromatography (Sephadex LH-20, Pharmacia) using methanol as the eluant. The purity and modification levels were determined with ^{1}H NMR spectroscopies. The ^{1}H NMR spectrum verified the completeness of conjugation and reduction reactions as follows.[21] Ferrocenemonocarboxaldehyde: ^{1}H NMR (300 MHz, CD_3OD, TMS) δ 4.30 (s, 5H), 4.70 (s, 2H), 4.86 (s, 2H), 9.88 (s, 1H); Ferrocene-Tethered PAMAM Dendrimer (G4): ^{1}H NMR (300 MHz, CD_3OD, TMS) δ 4.74 (s, 1H), 4.44 (s, 1H), 4.20 (s, 1H), 4.14 (s, 1H), 3.05-2.37 (dendrimer protons).

Synthesis of fluorocarbonylferrocene. A suspension of ferrocenecarboxylic acid (1.15 g, 5 mmol) and pyridine (0.81 mL, 10 mmol) in dry CH_2Cl_2 (25 mL) was cooled to 0 °C under an argon atmosphere and then cyanuric fluoride (1.80 mL, 10 mmol) was added. The contents were stirred for 90 min until a deep red or orange color was observed. Crushed ice in water (25 g) was then added, the suspension was filtered, and the organic layer was separated and washed with cold water (25 mL).[22] Fluorocarbonylferrocene: ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 4.85 (m, 2H), 4.57 (m, 2H), 4.31 (s, 5H).

Preparation of partially ferrocenyl-tethered PAMAM G0, G2 dendrimers using fluorocarbonylferrocene. A

solution of fluorocarbonylferroene (0.2 mmol) in 2 mL dry THF was added to the PAMAM G0, G2 dendrimers. The mixture was stirred at room temperature until completion of the reaction (20 min) and was then purified by chromatography.[23] Ferrocene-tethered PAMAM Dendrimer (G0, 2): ^{1}H NMR (300 MHz, CD_3OD, TMS) δ 4.74 (s, 1H), 4.44 (s, 1H), 4.20 (s, 1H), 4.14 (s, 1H), 3.05-2.37 (dendrimer protons).

Construction of AuNPs monolayer and multilayer with ferrocene-modified dendrimer on gold electrodes. A clean gold electrode was first soaked in ethanolic 4 : 1 mixture of MUO and MUA for 8 to 10 h at room temperature to form the mixed monolayer of MUO and MUA. After an ethanol rinse to remove physically adsorbed MUO and MUA, the electrode was dipped in 10 mM EDC and 5 mM NHS solutions for 2 h to change carboxylate-ended SAM to reactive ester groups. PAMAM dendrimer solution was spotted onto the activated electrode and left to be incubated. This modified substrate was immersed in AuNP solution for 3 h to construct AuNP monolayer. AuNP

Scheme 1. Construction of layered AuNPs with pure and ferrocene-tethered PAMAM dendrimers on Au electrodes.
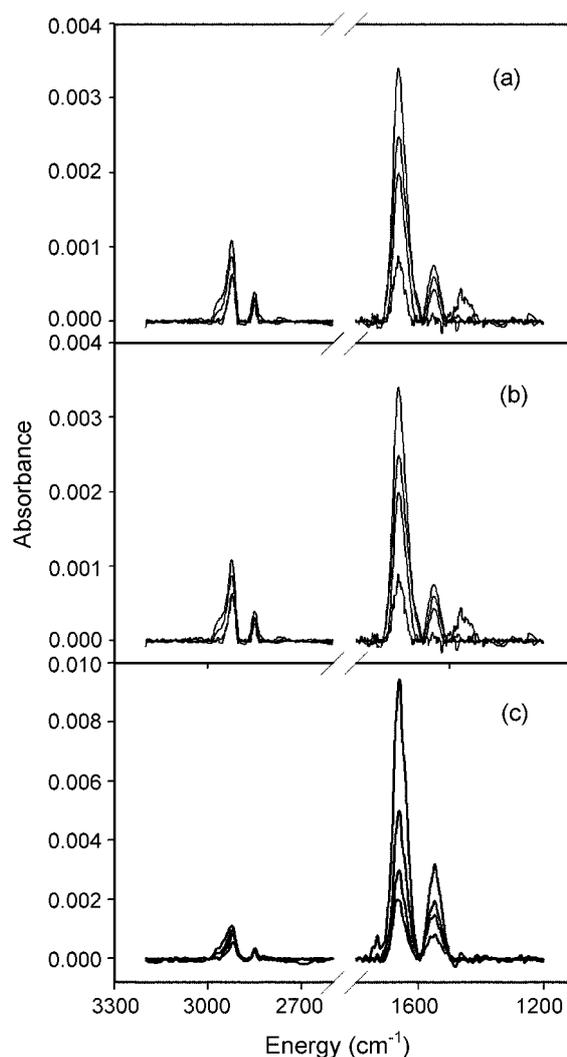
Figure 1. FT-IR of layered PAMAM dendrimers of (a) G0 (b) G2 (c) G4. Absorbance increases as the increase of the number of layers (1st, 2nd, 3rd, 4th layer).

multilayers were constructed by alternate immersion in AuNP and PAMAM dendrimer solutions (see Scheme 1).

Results and Discussion

Characterization of AuNPs on PAMAM dendrimers. We prepared a series of films by the layer-by-layer deposition of PAMAM dendrimer and AuNPs on the surface of a gold electrode by covalent bond.

To confirm covalent attachment and to evaluate the loading of PAMAM dendrimer in AuNP films, we measured FTIR-external reflection spectroscopy (FTIR-ERS) of surfaces modified with three different generations of PAMAM dendrimer (G0, G2, and G4). Figure 1 shows the amide I and amide II bands at 1665 and 1555 cm^{-1}, respectively, and bands resulting from the two kinds of methylene groups present in PAMAM dendrimers at 2926 and 2854 cm^{-1}.[24] The magnitude of all peaks increases as the the number of layers increases. The magnitude of absorbance of all bands increases with the increase of PAMAM generations. The magnitudes of amide I peaks G0, G2, and G4 on seven layered films are around 0.0034, 0.0053, and 0.0095, respectively. This indicates that PAMAM dendrimers make multilayered structures by covalently linking to AuNPs.

Scanning electron microscopy (SEM) verifies the deposition of AuNP multilayers on PAMAM dendrimer-modified Au electrodes. Figure 2 shows the SEM images of AuNPs on multilayered PAMAM dendrimers. Because their topologies are highlighted by the brightness of SEM images, each layer of AuNPs can be distinguished from the monolayered AuNPs. The number of the light particles increases with the number of layers.
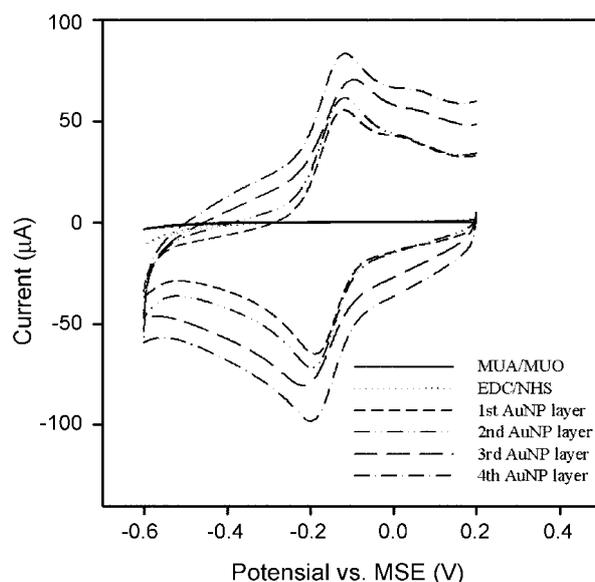
Figure 3. CVs on layered AuNPs with PAMAM dendrimers in 1 mM K$_3$Fe(CN)$_6$ containing 1 M KCl solution. Scan rate = 100 mV/s.

AuNP films on the PAMAM dendrimer-modified Au electrode are characterized by cyclic voltammetry (CV) using two electrochemical probe reactions: (a) the redox reaction of an aqueous solution containing 1 mM Fe(CN)$_6^{3-/4-}$ with 1 M KCl and (b) the gold oxide formation[25] and its reduction in 0.1 M HClO$_4$. The first electrochemical reaction is employed to describe the electron transfer between solution and electrode *via* AuNPs. The latter reaction informs the electrochemical surface area of AuNP films.

An effective electron transfer through the PAMAM dendrimer
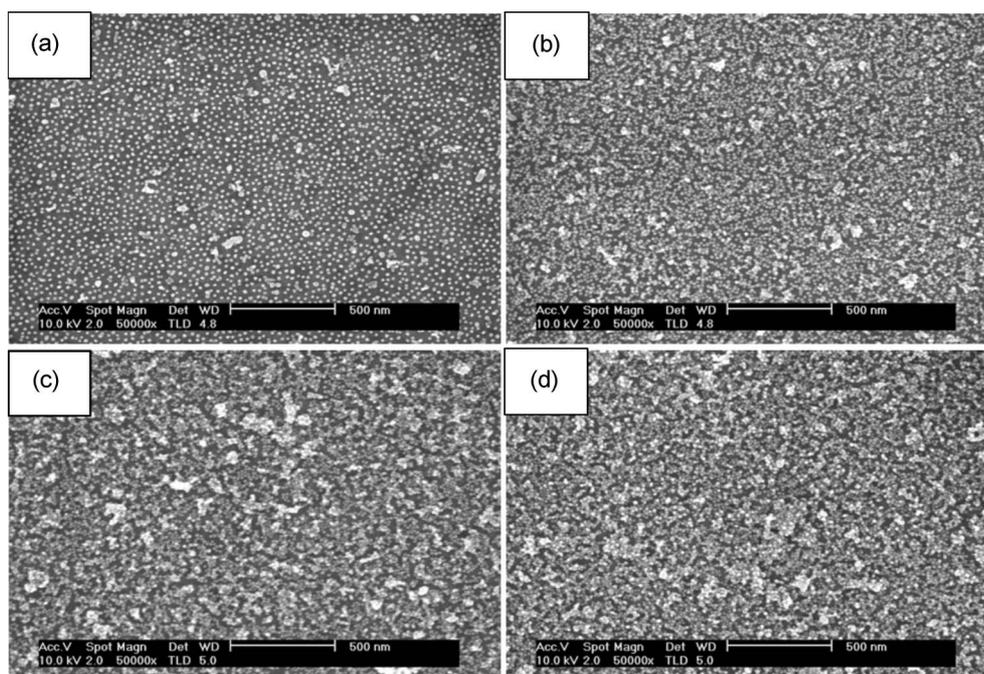
Figure 2. SEM images of Layered AuNPs with PAMAM dendrimers with different layers (substrate: Au electrode) (a) second layer (b) fourth layer (c) sixth layer (d) eighth layer.
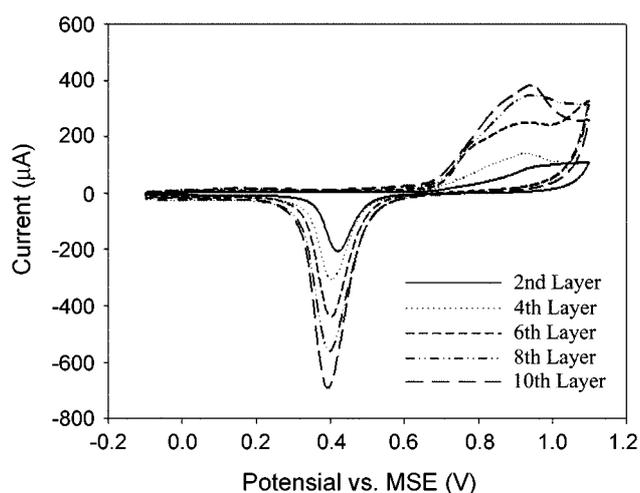
Figure 4. Layered AuNPs oxidation and reduction on PAMAM dendrimers in 0.1 M $HClO_4$ solution. Scan rate = 50 mV/s

films and AuNPs is evident from CV experiments. Repeated deposition of AuNP layers results in steady faradaic currents (Figure 3) because the diffusion limiting process cannot distinguish the microscopic roughness. Instead, charging currents increase with the increase of AuNP layers, coming from the increase in AuNP density.

Figure 4 shows typical CV responses on multilayered AuNP films in 0.1 M $HClO_4$ solution at a scan rate of 50 mV/s. Anodic peaks correspond to the Au oxide formation of AuNPs. Also, cathodic peaks correspond to the subsequent reduction of the Au oxides. The oxidation and reduction peaks in the CVs on the surface of AuNPs increase almost linearly with the increase of AuNP layers, indicating the layer-by-layer construction of AuNP multilayers with PAMAM dendrimers. This alternate immersion method demonstrates the capacity to increase the electroactive areas of the films.

Characterization of AuNP multilayers on Au electrodes with ferrocene-modified PAMAM dendrimers. AuNP multilayers containing electroactive ferrocene units were constructed using layer-by-layer deposition in ferrocene-modified PAMAM dendrimer and AuNP solutions. It has been also demonstrated that electronic charge transport within layer-by-layer self-assembled multilayers of redox polymer can occur by electron hopping between adjacent molecular redox centers that are covalently grafted on the polyelectrolyte backbone.[18]

Figure 5a shows the CV of layered AuNPs on Fc-modified dendrimers (G 4) in 0.1 M $HClO_4$ solution. The peak currents increase with the increase of AuNP layers, revealing that Fc residues located at the outer layers are still electrochemically active. Figure 5b indicates that the peak currents are smaller than those of Figure 5a because electrochemical activities of Fc-dendrimers are shielded when AuNPs occupy the outmost layer.

Figure 6 shows the plots of surface coverage as a function of the number of layers based on the anodic peaks of layered AuNPs on Fc-dendrimers. On the basis of the CVs, the surface coverage of Fc-dendrimers was calculated by
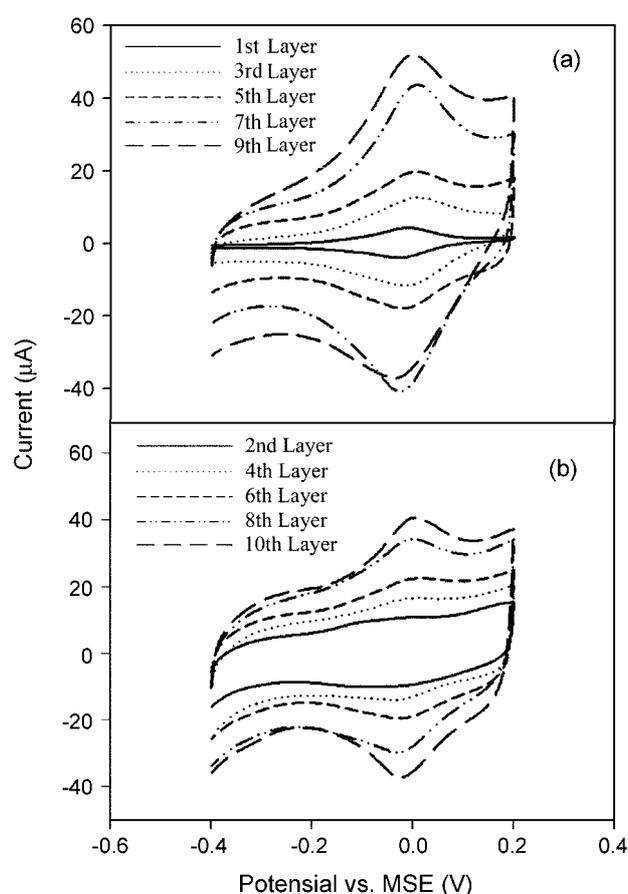
Figure 5. CVs on layered AuNPs with Fc-dendrimers in 0.1 M $HClO_4$ solutions. Fc-dendrimers (a) and AuNPs (b) are finally exposed to the solutions. Scan rate = 100 mV/s.

dividing the total coverage of Fc sites (obtained from the coulometric charge, which was calculated by integrating the anodic peak area in the CV of Figure 5) by the number of Fc sites within a single dendrimer molecule, assuming that all of the Fc sites are electrochemically active.[26] The redox properties of the films depend significantly on the content of Fc moiety in the polymer chains and on the polymer types.

Building up the successive layers, we observed two interesting trends when the outmost layer is made up of AuNP. First, we note that there is a significant decrease in ferrocene coverage, which could arise either from the loss of Fc-dendrimer in AuNP solutions or from the loss of redox activities of some Fc groups on dendrimers. However, there is a steady increase in the amount of surface coverage of AuNPs on Fc-dendrimer layers.Second, we observe shifts of peak potentials for the immobilized Fc when AuNPs are the outmost layer. This behavior is similar to that of the multilayers of glucose oxidase with polyallylamine ferrocene.[27] Figure 6 shows the surface coverage for low generated dendrimers. Compared with highly generated dendrimers, the electron transfer between Fc moieties in low generated dendrimers is less effective because of the low packing densities in the polymer chains.

To investigate the charge transport within the AuNPs on

Electrochemistry on Alternate Structures of Gold Nanoparticles

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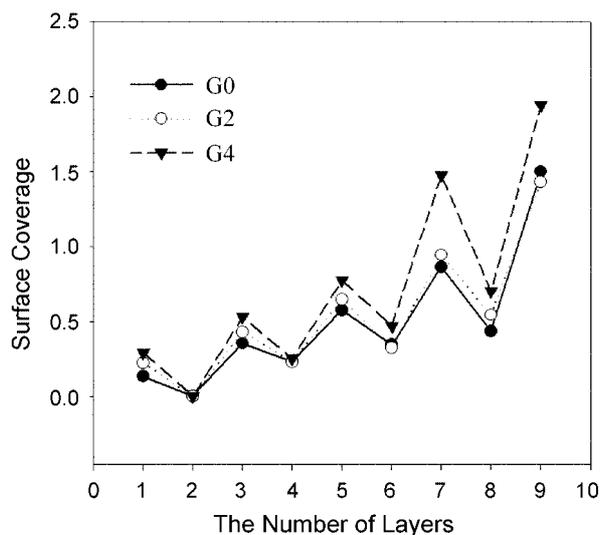
Figure 6. Plots of surface coverage of electroactive ferrocene moieties as layered AuNPs with Fc-PAMAM dendrimers of different generations.

Figure 7. Dependence of anodic peak currents as the scan rates for layered AuNP films on Fc-dendrimers.

Fc-dendrimer films, we measured the plots of the anodic peak current (i_{pa}) as the scan rate increased, as shown in Figure 7. These results suggest that charge diffusion within the film contributes at least partially to the electron transfer for the thicker films. Anzai et al. also observed the same tendency, with charge transfer depending on the thickness of the film for 15% Fc-PAA/PVS films in which the diffusion-free mechanism was observed for one to eight layers.[28] The i_{pa} values increase linearly as the scan rates increase from one to five layers, indicating typical electron transfer features on covalently adsorbed systems of electroactive groups. For further deposited layers, the i_{pa} values do not show linear dependence. Instead, they are proportional to the square root of the scan rate and the redox waves become broader because charge diffusion process prevails.

Conclusions

Materials composed of two-dimensional (2-D) and three-dimensional (3-D) ensembles of NPs are arousing increasing interest in analytical and materials chemistry; metal NP architecture allows the fabrication of devices such as nanoelectronic devices, optoelectronic devices, chemical sensors, and catalysts with great control over selectivity, sensitivity, and functionality. We constructed layered AuNPs on PAMAM dendrimers that were assembled *via* alternate and repetitive exposure of AuNP and dendrimer solutions on Au substrates. PAMAM dendrimers served as covalent cross-linkers to facilitate making the thin film structures. In addition, we synthesized various generations (G0, G2, and G4) of Fc-tethered PAMAM dendrimers. Partially ferrocene-tethered PAMAM dendrimer can be used as a cross-linker among AuNPs and electron transferring mediaters. Layered AuNPs on Fc-modified PAMAM dendrimers demonstrate that the peak currents and surface coverage increase with an increase in the number of layers. Interestingly, surface
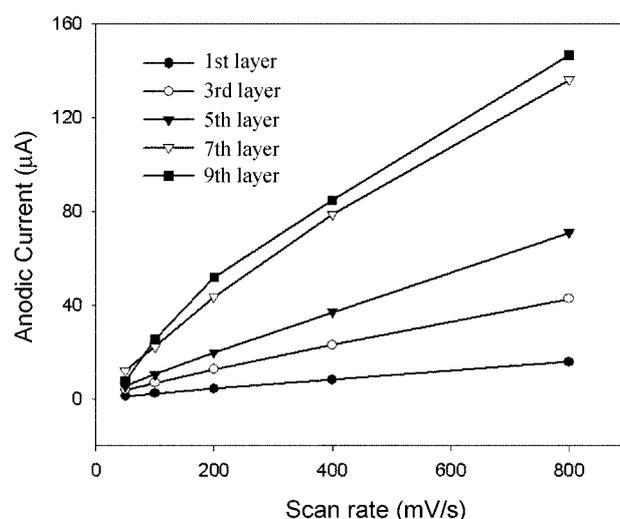
coverage significantly decreases after adsorption of AuNPs, which is caused by either the loss of Fc-dendrimer in the AuNP solutions or the loss of redox activities of some Fc groups on dendrimers. Furthermore, FTIR-ERS and SEM reveal the characteristics of AuNP multilayers with PAMAM dendrimers. These results show linear increases as the layers increase.

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