A Polymer Interface for Varying Electron Transfer Rate with Electrochemically Formed Gold Nanoparticles from Spontaneously Incorporated Tetrachloroaurate(III) Ions

Jiseon Song and Chan Kang[*]

Department of Chemistry, Research Institute of Physics and Chemistry, Chonbuk National University, Chonju 561-756, Korea
[*]*E-mail: chankang@chonbuk.ac.kr*

This paper presents a novel simple method for introducing gold nanoparticles in a poly(4-vinylpyridine) (PVP) polymer layer over a glassy carbon (GC) electrode with the aim of forming a tunable electrochemical interface against a cationic ruthenium complex. Initially, $AuCl_4^-$ ions were spontaneously incorporated into a polymer layer containing positively charged pyridine rings in an acidic media by ion exchange. A negative potential was then applied to electrochemically reduce the incorporated $AuCl_4^-$ ions to gold nanoparticles, which was confirmed by the FE-SEM images. The PVP layer with an appropriate thickness over the electrode blocked electron transfer between the electrode and the solution phase for the redox reactions of the cationic $Ru(NH_3)_6^{2+}$ ions. However, the introduction of gold nanoparticles into the polymer layer recovered the electron transfer. In addition, the electron transfer rate between the two phases could be tuned by controlling the number density of gold nanoparticles.

Key Words : Poly(4-vinylpyridine), Gold nanoparticles, Tunable interface, Ion exchange, Electron transfer

Introduction

Electrode reactions or electrocatalytic reactions have been carried out as part of a continuing search for catalysts with gold nanoparticles in electrochemistry.[1-3] Nanometer-sized monolayer-protected gold clusters behave as soluble nano-electrodes with multi-electron transfer and electrical double layer charging properties.[1] Fifteen oxidation states were electrochemically resolved in monolayer protected gold clusters.[4] The electrode reactions of 1,1-dinitrocyclohexane, dioxygen, and carbon monoxide were catalyzed, and some different catalytic activities were found compared with bulk electrodes.[1-3,5] Confining the gold nanoparticles to an electrode surfaces is an important issue for their utilization in electrode reactions. The attachment of gold nanoparticles to a mercaptobenzene film on a GC electrode has been reported.[6] Another gold nanoparticle thin film was prepared by dissolving decanethiolate-encapsulated gold nanoparticles and 1,9-nonanedithiol in an organic solvent.[7,8] The gold nanoparticles prepared in the solution phase were spontaneously adsorbed onto the electrochemically oxidized electrode surface.[9] Since gold nanoparticles can be considered to be nano-scale electrodes, a film of a self-assembled organically modified silica gel and gold nanoparticles was suggested as an interface with a tunable barrier.[10,11] Some metal nanocrystals have been electrochemically formed, and their shapes and sizes were controlled with the applied potential and time,[12] or by using some polymers and surfactants.[13] Gold nanocrystals were also electrochemically synthesized in the presence of poly(*N*-vinylpyrrolidone) and their size and shape could be controlled. In this experiment the poly(*N*-vinylpyrrolidone) dissolved in solutions was

considered to be both the coordinating and the stabilizing agent.[14,15] Polymer micelles, where the nucleation and growth of gold nanoparticles proceeded, were introduced. The micelles are nanoreactors and templates for the nanoparticle synthesis.[16-20] Seeding growth from a small sized gold seed produced size controllable gold nanoparticles.[21-24]

There are many advantages of gold nanoparticles in polymer matrices including stability with less aggregation, synthetic versatility, and many potential applications in various fields.[25,26] Physical adsorption on the surface was reported[9] but they may be relatively unstable to be detached from the surface or sometimes moved to aggregate. The nanoparticles inside the polymer matrix will stay very stable and the advantageous polymer properties such as ion transfer, immobilizing redox active species, control of mass transfer, and physical durability will be combined. A preparation of nanoparticles in poly(styrene)-*b*-poly(2-vinylpyridine) star-block copolymer showed an improved stability against long term aggregation.[27,28] Gold nanoparticles derivatized with a thiol monolayer were easily incorporated into electrochemically generated poly(3-octylthiophene) films.[29] On the other hand, constructions of polyelectrolyte/gold nanoparticle multilayers using a layer-by-layer self-assembly technique have been reported.[30-33] In one of those multiplayer films, the sensitivity in the electrochemical detection of nitric oxide molecule was dependent on the concentration of gold nanoparticles, and the loading of nanoparticles into the polyelectrolyte multiplayer film could be easily controlled.[17]

This paper proposes a new simple method for introducing gold nanoparticles in a poly(4-vinylpyridine) polymer matrix over a glassy carbon electrode. Initially, $AuCl_4^-$ ions

were spontaneously incorporated into the anion exchange polymer layer by ion exchange and electrochemical reduction followed to produce gold nanoparticles. This preparation, in comparison to the previous reports, is considered to be based on new concept of the ion exchange incorporation and electrochemical formation in preparing the nanoparticles in the polymer matrix. With the prepared electrode, varying the electron transfer kinetics in the redox reactions of $Ru(NH_3)_6^{2+}$ ions was investigated and a tunable electrochemical interface was suggested as the amount of gold nanoparticles acting as nano-sized electrodes in the layer could be controlled.

Experimental

Materials. Commercial reagent grade chemicals were used as received. Hydrogen tetrachloroaurate (III) trihydrate ($HAuCl_4 \cdot 3H_2O$), Poly (4-vinylpyridine) (PVP, average molar mass 160,000), 1,12-dibromododecane ($Br(CH_2)_{12}Br$), and Hexaammineruthenium(II) chloride ($[Ru(NH_3)_6]Cl_2$) were purchased from Aldrich. The deionized water was purified by passage through a purification train (Human power II$^+$, Human Co.) and used for the solution preparations. Solutions of $Ru(NH_3)_6^{2+}$ were freshly prepared before each experiment and the bottle was stored in a refrigerator after removing the dissolved air by argon purging. A commercially available glassy carbon (GC) electrode (Kosentech Co.) was used as the working electrode.

Apparatus and procedures. The electrochemical measurements were carried out in a two-compartment cell closed with a Teflon cap through which the electrodes and a gas bubbling system had been fitted. A GC (area, 0.071 cm^2) working electrode and a platinum auxiliary electrode were in one compartment, which was separated by fritted glass from the other compartment where the Ag/AgCl reference electrode was held. An electrochemical analyzer (CH-Instruments, Model 600A), which was controlled using a personal computer, was used for electrochemical measurements. Ultra high resolution field emission scanning electron microscopy (UHR FE-SEM) images were obtained using a Hitachi model S-5500 instrument provided by the Korea Basic Science Institute.

A polymer-modified GC working electrode was prepared by dropping an aliquot of a mixture containing 1.5 mg/mL of PVP and 0.36 mg/mL of a 1,12-dibromododecane solution in methanol over a previously alumina (0.3 μm) polished GC surface and allowing the solvent to evaporate in air.[34] The amount of the dropping aliquot was controlled where necessary. The dried film thickness was roughly estimated as about 0.5 μm with an aliquot of 5 μL of the given mixture over the glassy carbon electrode.[34] The electrode was then kept overnight in an oven at 70 °C in order to introduce cross-linking *via* the double quaternization of the pyridine groups *via* a reaction with 1,12-dibromododecane. The film showed a good stability in solutions for several hours.

The potentials were read and quoted with respect to the

Ag/AgCl (3 M KCl) reference electrode with a potential of 0.22 V *vs*. NHE. The current densities were based on the geometric surface area. The supporting electrolyte was 0.1 M KCl and 5.0 mM HCl. All the experiments were carried out at room temperature (22 ± 1 °C).

Results and Discussion

Incorporation of $AuCl_4^-$ ions into a poly(4-vinylpyridine) layer and an electrochemical nanoparticle formation. Scheme 1 shows the mechanism for how the $AuCl_4^-$ ions were incorporated into the PVP layer and how the incorporated ions were electrochemically reduced to form the gold nanoparticles. When a GC electrode with a PVP polymer layer was immersed in an acidic solution containing $HAuCl_4$, the amines of the pyridine rings of the polymer chains were protonated and became positive. The $AuCl_4^-$ ions migrated to the polymer layer through ion exchange (Scheme 1A). It was expected that nanoparticles would be formed in the polymer layer if the appropriate potentials were applied to reduce the $AuCl_4^-$ ions inside the layer (Scheme 1B).

Figure 1A shows the voltammograms for the electroreduction of $AuCl_4^-$ ions incorporated in the PVP layer. The GC electrode with the PVP polymer layer was initially immersed in an aqueous solution of 0.5 mM $HAuCl_4$ containing 0.1 M KCl and 5.0 mM HCl for 50 min. The electrode was removed from the solution, thoroughly rinsed, and transferred to a pure supporting electrolyte. An initial pretreatment scanning showed an undeveloped feature and the first voltammogram with a distinctive wave was obtained in 5 min after the electrode introduction into the cell. Figure 1A-a, which was the first voltammogram in 5 min,
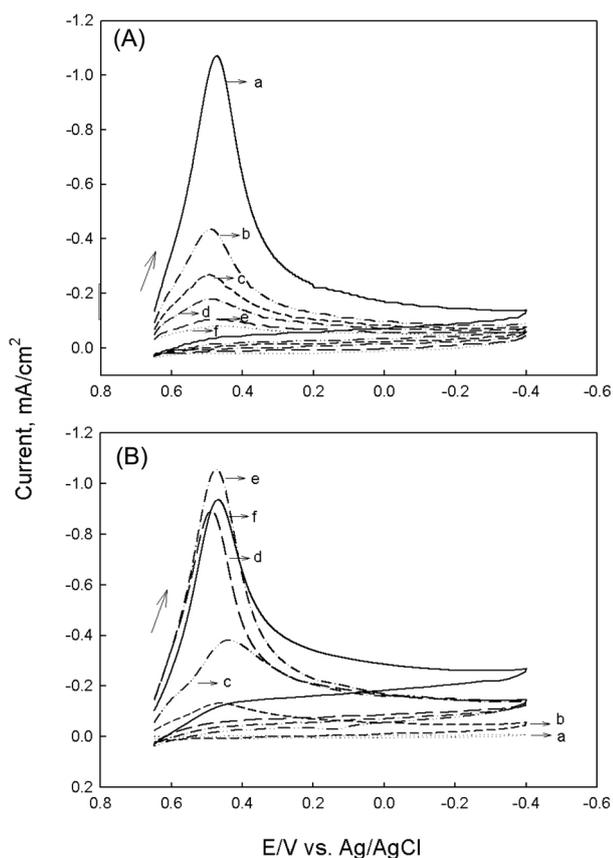
A. Incorporation of $AuCl_4^-$ ions
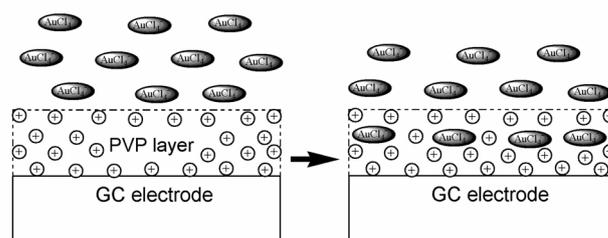
B. Formation of gold nanoparticles by the electro-reduction of $AuCl_4^-$ ions

$\left(\ \text{\large⬭} = AuCl_4^-;\ \text{\large⬤} = Au\ \text{nanoparticle}\ \right)$
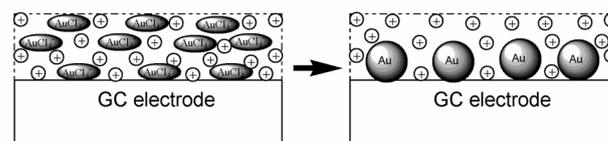
Scheme 1. The incorporation of $AuCl_4^-$ ions into a poly(4-vinylpyridine) polymer layer and electrochemical formation of gold nanoparticles.

A Polymer Interface for Varying Electron Transfer Rate

Bull. Korean Chem. Soc. **2007**, Vol. 28, No. 10   1685

Figure 1. (A) Cyclic voltammograms in a pure supporting electrolyte. A GC electrode coated with 8 μL of a 1.5 mg/mL PVP and 0.36 mg/mL 1,12-dibromododecane mixture was used. The electrode, which had been previously immersed in a 0.5 mM $HAuCl_4$ solution for 50 min, was used. The first (a), 2nd (b), 3rd (c), 5th (d), 11th (e), and 20th (f) voltammograms after 5 min from the immersion of the introduction of the electrode into the cell solution were shown. (B) Cyclic voltammograms in a pure supporting electrolyte with the same GC electrode as Figure 1A. The electrode, which had been previously immersed in a 0.5 mM $HAuCl_4$ solution for 0 min (a), 10 min (b), 20 min (c), 30 min (d), 50 min (e), and 70 min (f), was used. Supporting electrolyte: 0.1 M KCl + 5.0 mM HCl. Scan rate: 50 mV/s.

showed a cathodic wave at 0.45 V. No reduction wave was observed on the electrode without the $AuCl_4^-$ ion incorporation (Figure 1B-a). Therefore, the cathodic wave at 0.45 V was assigned to the reduction of $AuCl_4^-$ ions in the PVP layer. In the second voltammogram in another 5 min, the cathodic wave at 0.45 V was still observed (Figure 1A-b), which indicates that the $AuCl_4^-$ ions in the polymer layer was not completely reduced during the initial first negative scanning. For the complete reduction of the $AuCl_4^-$ ions, about ten repetitive scans were required. The immersion time of the electrode in the $AuCl_4^-$ solution to check the level of $AuCl_4^-$ ion incorporation was controlled and the currents of the cathodic wave increased gradually with increasing the immersion time from 10 min to 50 min (Figure 1B-b through 1B-e). The incorporation of the anions appeared to be saturated approximately 50 min after immersing the electrode. Even at an immersion time of 70 min,
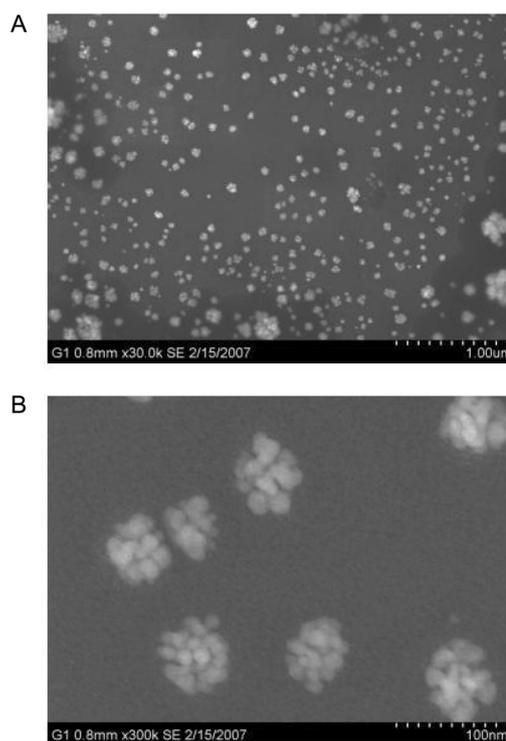
Figure 2. FE-SEM images of the GC electrode surface. The same polymer-modified electrode for Figure 1 was used. The electrode was initially immersed in a 0.5 mM $HAuCl_4$ solution for 20 min and the incorporated $AuCl_4^-$ ions were reduced by the cyclic voltammetric scanning, as shown in Figure 1.

slight decrease of the peak current was observed, but this decrease is within an error limit showing no more increase of the wave (Figure 1B-f).
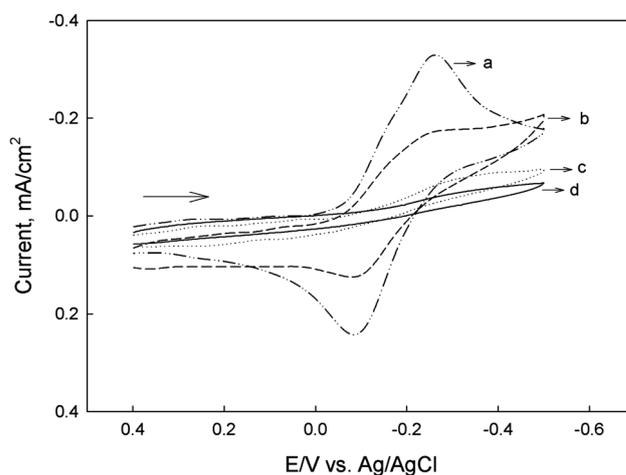
FE-SEM images of the formed nanoparticles in the polymer layer. Ultra high resolution FE-SEM images of the electrode surface showed the formation of the gold nanoparticles in the PVP layer. Figure 2 shows the images of an electrode, which had been previously immersed in a 0.5 mM $HAuCl_4$ solution for 20 min, and exposed to a similar potential to that shown in the voltammogram of Figure 1B-c. Repeatitive scanning was carried out until all the $AuCl_4^-$ ions in the layer were reduced. In Figure 2A, groups of nanoparticles were observed. The nanoparticles were not uniformly distributed and they seemed to be formed in a little aggregated state. The nanoparticles might be formed in different pores in ion-conducting polymer to give such a non-uniform pattern.[35] Figure 2B of more enlarged image shows clearer shapes of the nanoparticles with the sizes of 10 nm to 30 nm as round-shaped bright spots. Figure 3 shows the images obtained after the PVP coated electrode had been immersed in the $HAuCl_4$ solution for 50 min. Figure 3A shows the nanoparticles of higher density formed on the electrode surface as more $AuCl_4^-$ ions were incorporated into the layer as a result of the longer immersion time. Round shaped nanoparticles were also shown in Figure 3B. No such spots were observed in another image from an identically prepared electrode without the immersion process. Different patterns of the nanoparticle formation would
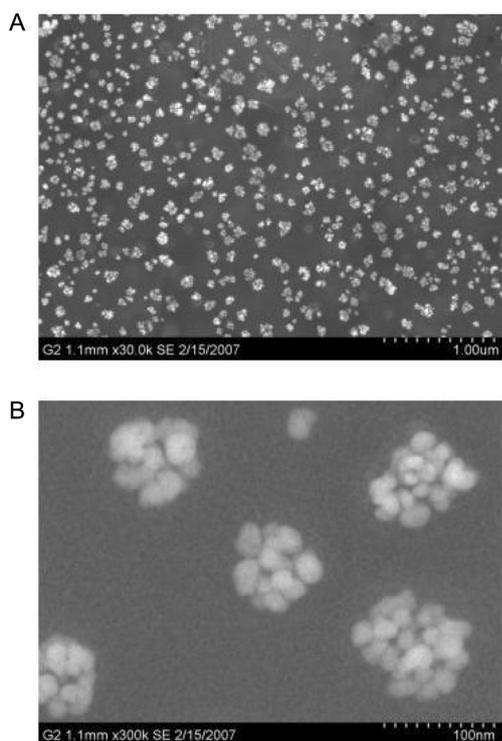
Figure 3. FE-SEM images of the GC electrode surface. The same polymer-modified electrode for Figure 1 was used. The electrode was initially immersed in a 0.5 mM HAuCl$_4$ solution for 50 min and the incorporated AuCl$_4^-$ ions were reduced by the cyclic voltammetric scanning, as shown in Figure 1.

Figure 4. Cyclic voltammograms in a 3.0 mM Ru(NH$_3$)$_6^{2+}$ with a GC electrode. The electrode was coated with 0 μL (a), 5 μL (b), 7 μL (c), and 8 μL aliquot (d) of 1.5 mg/mL PVP and 0.36 mg/mL 1,12-dibromododecane mixture. The other conditions were the same as shown in Figure 1.

be obtained by controlling the particle size or the particle density, which would be affected by various parameters such as the HAuCl$_4$ concentration or applied potential. At this stage, the density of the particles could be controlled as shown in Figures 2 and 3 but no precise method to control the shape and the size of the particles has been established yet even though various experimental trials have been carried out.

Redox reactions of the Ru(NH$_3$)$_6^{2+/3+}$ couple at glassy carbon surfaces coated with poly(4-vinylpyridine) layers. Because the PVP polymer has anion exchanging properties, the cations will not be able to migrate into the polymer layer. No electron transfer will be allowed when cations are to be reduced or oxidized on the layer over the electrode surface due to the presence of an anion exchanging polymer layer. Indeed, on a GC electrode, the cyclic voltammograms for the redox reactions of Ru(NH$_3$)$_6^{2+}$ show decreasing electron transfer rates with increasing thickness of the PVP polymer layer. When a bare glassy carbon electrode was used (Figure 4-a), in a 3.0 mM Ru(NH$_3$)$_6^{2+}$ solution, two well-developed redox waves were observed with a peak separation of 170 mV at 50 mV/s. Broadened waves with lower peak currents were observed on the electrodes with the PVP layer, which were prepared by dropping a 5 μL aliquot of a mixture containing 1.5 mg/mL PVP and 0.36 mg/mL 1,12-di-bromododecane (Figure 4-b). The current decreased with increasing polymer layer thickness (Figure 4-a through 4-d). When an 8 μL aliquot of the same polymer mixture was

used to prepare the electrode, no voltammetric wave was obtained indicating the complete blocking of electron transfer between the ruthenium complex and the electrode surface (Figure 4-d).

It was believed that the blocked electron transfer rate could be recovered by introducing an electron transfer mediator into the PVP layer, and it was expected that the gold nanoparticles formed in the layer might be used as such mediators. The same electrode used in Figure 4-d, which has a sufficiently thick polymer layer to stop the redox reactions of the ruthenium complex, was prepared, immersed in a solution containing 0.5 mM HAuCl$_4$ to incorporate AuCl$_4^-$ ions into the polymer layer, and transferred to a pure supporting electrolyte. Gold nanoparticles were formed inside of the PVP layer by reducing the incorporated AuCl$_4^-$ ions with a potential step to 0.1 V for 600 s from 0.8 V. The applying time was enough to reduce the AuCl$_4^-$ ions in the film completely, which was confirmed with no reductive wave in a cyclic voltammetric measurement as in Figure 1. The electrode was then used to obtain a cyclic voltammogram in a 3.0 mM Ru(NH$_3$)$_6^{2+}$ solution. Figure 5-b shows a slight enhancement of the currents with the electrode, which had previously been immersed in a 0.5 mM HAuCl$_4$ solution for 5 min, compared with that of the electrode with no gold nanoparticles present in the layer (Figure 5-a). There was a gradual increase in the redox waves with increasing immersion time in the HAuCl$_4$ solution for 10 min, 20 min, and 50 min as shown in Figure 5-c to 5-e. As already observed in the FE-SEM images, the longer immersion of the electrode in the HAuCl$_4$ solution produced nanoparticles with high number density in the layer. The apparent heterogeneous rate constants, k°_{app}, were estimated for the redox reactions of the ruthenium complex using the changing peak separations.[36] For the electrodes of voltammograms of Figure 5-c, 5-d, and 5-e, increasing constants were estimated as 7.4 $\times$ 10^{-4} cm/s, 1.9 $\times$ 10^{-3} cm/s, and 5.0 $\times$ 10^{-3} cm/s, respectively. When a
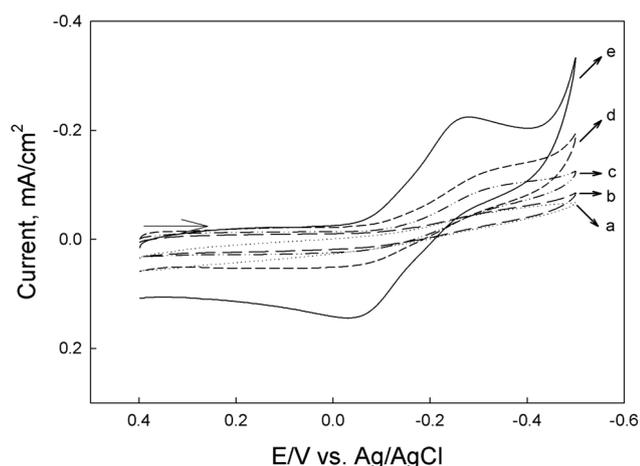
Figure 5. Cyclic voltammograms in a 3.0 mM $Ru(NH_3)_6^{2+}$ with a GC electrode coated with an aliquot of 8 μL of 1.5 mg/mL PVP and 0.36 mg/mL 1,12-dibromododecane mixture coated. The conditions used for the nanoparticle formation: the electrode was initially immersed in a 0.5 mM $HAuCl_4$ solution for 0 min (a), 5 min (b), 10 min (c), 20 min (d), and 50 min (e) to allow the incorporated $AuCl_4^-$ ions to be reduced by the potential step to 0.1 V from 0.8 V for 600 s in a pure 0.1 M KCl + 5 mM HCl supporting electrolyte. The other conditions were the same as shown in Figure 1.

bare GC electrode was used, a value of 3.5×10^{-2} cm/s was obtained. This indicates that the electron transfer rate could be tuned by controlling the number of the gold nanoparticles formed inside of the PVP layer. Considering the polymer film layer thickness of the hundred-nanometer scale as mentioned in the experimental section, it was difficult to believe that the electron transfer was through just a single nanoparticle of about 30 nm size. As shown in Figure 2 and 3, the electron transfer was probably through the cluster of the nanoparticles, which has a hundred-nanometer scale. Compared with Figure 4-a, which was obtained on the bare GC electrode, the smaller rate constant at the electrode surface for Figure 5-e was obtained. Therefore, the electron transfer would still be deficient through the polymer layer through the fractional area in the PVP layer not occupied by gold nanoparticles.

Conclusions

$AuCl_4^-$ ions were spontaneously incorporated into the PVP layer, which has an anion exchanging property. The application of a reductive potential produced stable gold nanoparticles in the polymer layer. The density of the nanoparticles formed could be controlled by the amount of $AuCl_4^-$ ions incorporated and some aggregated forms were observed. At this stage, a suitable condition needed to control the size and distribution of the nanoparticles has not been clearly established, which will require further study. The gold nanoparticles formed in the PVP layer toward the cationic $Ru(NH_3)_6^{2+}$ ions may be considered to be nano-electrodes. The electron transfer kinetics could be finely tuned by controlling the nanoparticle density, which deter-

mined the fractional active areas over the surface.

In comparison to the already reported methods for preparing nanoparticle-polymer composite materials, the present method is now considered to be another new synthetic approach to prepare stable nanoparticles in an anionic polymer layer. The procedure is simple and a collection of nanoelectrodes can be easily prepared. A controllable electrode interface can be tailored for various electrode applications.

The gold nanoparticles show different catalytic activity in several electrode reactions from the bulk gold electrode or other conventional electrodes.[1-3,5] It was also reported that some catalytic activities are dependent on the nanoparticle sizes.[37-40] In such points of views, confining the gold nanoparticles on the conventional electrode surfaces and controlling the nanoparticle size and density are considered to be important issues for developing sensors or catalytic systems, and for the fundamental understanding of the interface structures. The present report gives another way tailoring the electrochemical interface and further studies are going on to prepare the system more precisely.

References

1. Templeton, A. C.; Wuelfing, W. P.; Murray, R. W. *Acc. Chem. Res.* **2000**, *33*, 27.
2. El-Deab, M. S.; Ohsaka, T. *Electrochem. Commun.* **2002**, *4*, 288.
3. Ryoo, H.; Kim, Y.; Lee, J.; Shin, W.; Myung, N.; Hong, H.-G. *Bull. Korean Chem. Soc.* **2006**, *27*, 672.
4. Quinn, B. M.; Lijeroth, P.; Ruiz, V.; Laaksonen, T.; Kontturi, K. *J. Am. Chem. Soc.* **2003**, *125*, 6644.
5. Kumar, S.; Zou, S. *J. Phys. Chem. B* **2005**, *109*, 15707.
6. Harnish, J. A.; Pris, A. D.; Porter, M. D. *J. Am. Chem. Soc.* **2001**, *123*, 5829.
7. Zhong, C. J.; Zheng, W. X.; Leibowitz, F. L. *Electrochem. Commun.* **1999**, *1*, 72.
8. Leibowitz, F. L.; Zheng, W.; Maye, M. M.; Zhong, C.-J. *Anal. Chem.* **1999**, *71*, 5076.
9. Shin, H.; Kang, C. *Anal. Sci.* **2003**, *19*, 1667.
10. Bharathi, S.; Nogami, M.; Ikeda, S. *Langmuir* **2001**, *17*, 1.
11. Cheng, W.; Dong, S.; Wang, E. *Langmuir* **2002**, *18*, 9947.
12. Finot, M. O.; Braybrook, G. D.; McDermott, M. T. *J. Electroanal. Chem.* **1999**, *466*, 234.
13. Reetz, M. T.; Helbig, W. H. *J. Am. Chem. Soc.* **1994**, *116*, 7401.
14. Huang, S.; Ma, H.; Zhang, X.; Yong, F.; Feng, X.; Pan, W.; Wang, X.; Wang, Y.; Chen, S. *J. Phys. Chem. B* **2005**, *109*, 19823.
15. Ma, H.; Huang, S.; Feng, X.; Zhang, X.; Tian, F.; Yong, F.; Pan, W.; Wang, Y.; Chen, S. *ChemPhysChem.* **2006**, *7*, 333.
16. Liu, S.; Weaver, J. V. M.; Save, M.; Armes, S. P. *Langmuir* **2002**, *18*, 8350.
17. Jaramillo, T. F.; Baeck, S.-H.; Cuenya, B. R.; McFarland, E. W. *J. Am. Chem. Soc.* **2003**, *125*, 7148.
18. Kuo, P.-L.; Chen, C.-C.; Jao, M.-W. *J. Phys. Chem. B* **2005**, *109*, 9445.
19. Lu, J. Q.; Yi, S. S. *Langmuir* **2006**, *22*, 3951.
20. Chen, S.; Guo, C.; Hu, G.-H.; Wang, J.; Ma, J.-H.; Liang, X.-F.; Zhang, L.; Liu, H.-Z. *Langmuir* **2006**, *22*, 9704.

21. He, Y.; Yuan, J.; Shi, G.; Wu, P. *Mater. Chem. Phys.* **2006**, *99*, 253.
22. Cao, L.; Zhu, T.; Liu, Z. *J. Colloid Interface Sci.* **2006**, *293*, 69.
23. Kwon, K.; Lee, K. Y.; Kim, M.; Lee, Y. W.; Heo, J.; Ahn, S. J.; Han, S. W. *Chem. Phys. Lett.* **2006**, *432*, 209.
24. Jana, N. R.; Gearheart, L.; Murphy, C. J. *Langmuir* **2001**, *17*, 6782.
25. Corbierre, M. K.; Cameron, N. S.; Sutton, M.; Mochrie, S. G. J.; Lurio, L. B.; Ruhm, A.; Lennox, R. B. *J. Am. Chem. Soc.* **2001**, *123*, 10411.
26. Chen, W.; Li, C. M.; Chen, P.; Sun, C. Q. *Electrochim. Acta* **2006**, *56*, 2845.
27. Youk, J. H.; Park, M.-K.; Locklin, J.; Advincula, R.; Yang, J.; Mays, J. *Langmuir* **2002**, *18*, 2455.
28. Sohn, B.-H.; Choi, J.-M.; Yoo, S. I.; Yun, S.-H.; Zin, W.-C.; Jung, J. C.; Kanehara, M.; Hirata, T.; Teranishi, T. *J. Am. Chem. Soc.* **2003**, *125*, 6368.
29. Peng, Z.; Wang, E.; Dong, S. *Electrochem. Commun.* **2002**, *4*, 210.
30. Sohn, B. H.; Seo, B. H. *Chem. Mater.* **2001**, *13*, 1752.
31. Hicks, J. F.; Young, S.-S.; Murray, R. W. *Langmuir* **2002**, *18*, 2288.
32. Yu, A.; Liang, Z.; Cho, J.; Caruso, F. *Nano Lett.* **2003**, *3*, 1203.
33. Suk, J.; Lee, J.; Kwak, J. *Bull. Korean Chem. Soc.* **2004**, *25*, 1681.
34. Kwak, J.; Anson, F. C. *Anal. Chem.* **1992**, *64*, 250.
35. Podlovchenko, B. I.; Andreev, V. N. *Russ. Chem. Rev.* **2002**, *71*, 837.
36. Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*, 2nd ed.; Wiley: New York, 2001; p 242.
37. Takasu, Y.; Iwazaki, T.; Sugimoto, W.; Murakami, Y. *Electrochem. Commun.* **2000**, *2*, 671.
38. Arenz, M.; Mayrhofer, K. J. J.; Stamenkovic, V.; Blizanac, B. B.; Tomoyuki, T.; Ross, P. N.; Markovic, N. M. *J. Am. Chem. Soc.* **2005**, *127*, 6819.
39. Bergamaski, K.; Pinheiro, A. L. N.; Teixeira-Neto, E.; Nart, F. C. *J. Phys. Chem. B* **2006**, *110*, 19271.
40. Overbury, S. H.; Schwartz, V.; Mullins, D. R.; Yan, W.; Dai, S. *J. Catal.* **2006**, *241*, 56.