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Catalytic characterization of hollow silver/palladium nanoparticles synthesized by a displacement reaction

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ABSTRACT

Hollow Ag/Pd nanoparticles have been successfully prepared by a galvanic displacement reaction, in which a small amount of $Pd(NO_3)_2$ is allowed to react with previously synthesized Ag nanoparticles that act as templates. The resulting hollow Ag/Pd (Ag/Pd_{hollow}) nanoparticles are found to be icosahedral and decahedral in structure. The kinetics of electroless copper deposition (ECD) catalyzed by these bimetallic (Ag/Pd_{hollow}) nanoparticles are analyzed using an electrochemical quartz crystal microbalance (EQCM). The results reveal that these Ag/Pd_{hollow} nanoparticles have better catalytic activities than monometallic Ag and Pd nanoparticles. Furthermore, the catalytic activities of these hollow nanoparticles in the ECD bath can be controlled by tuning their alloy ratios in a suitable manner.

1. Introduction

Nanoparticles fabricated from Ag-based alloys find extensive applications in catalysis [1], electrocatalysis [2], and optics because their surface plasmon resonance (SPR) bands appear in the visible region [1–4]. One reason to determine these properties is the structure of the nanoparticles. Hollow nanoparticles fabricated from Ag-based alloys have attracted attention due to their catalytic [5,6] and electrocatalytic activities [2,7], and the SPR characteristics of hollow nanoparticles [2,6,8,9] differ significantly from those of solid nanoparticles. Hollow Ag/Pd nanoshells have been found to show unique catalytic activities when used as catalysts for electroless copper deposition (ECD) [5,10]. ECD has gained considerable significance in the field of nanocircuits [11]. The mechanism underlying ECD involves activation, which is a catalytic reaction triggered by active colloids on the surface of substrates dipped into the electroless bath [12]. The active catalyst acts as an electron carrier for the transfer of electrons from the reducing agent to the copper ions. Hence, the structure and composition of the catalyst can alter the deposition rate and reaction kinetics [13]. In a previous study, the authors prepared spherical Pd nanoparticles and used them as activators for ECD [12–14]. Additionally, for use in the electroless reaction, they synthesized solid nanocatalysts with Pd-rich shells from a Ag/Pd alloy by adding Ag particles to the microstructures of Pd nanoparticles. The nanocatalysts thus prepared showed enhanced catalytic activity [1]. In the present study, we synthesized hollow Ag/Pd (Ag/Pd_{hollow}) nanoparticles via a displacement reaction. In this reaction, a small amount of $Pd(NO_3)_2$ was allowed to galvanically react with the Ag nanoparticles. The slight deposition of Pd ions on the surface of the Ag nanoparticles resulted in a closure of pores and the formation of hollow nanoparticles. Then, we used the synthesized Ag/Pd_{hollow} nanoparticles as ECD activators. We carried out electrochemical quartz crystal microbalance (EQCM) measurements to compare the kinetics of ECD catalyzed by Ag/Pd_{hollow} nanoparticles with different alloy ratios (the Pd content remained constant) and those catalyzed by solid Pd nanoparticles.

2. Experimental

Ag/Pd_{hollow} nanoparticles of different compositions were prepared in the following manner. Initially, silver nitrate ($AgNO_3$, $\sim 5 \times 10^{-5}$ mol) was slowly dissolved in 3 mL of a neutral aqueous solution of 0.1 M sodium *n*-dodecyl sulfate (SDS). Approximately 25 μL of 0.1 M $NaBH_4$ was added dropwise to the abovementioned solution to reduce the Ag ions to metallic Ag. The solution temperature was maintained at 30 °C. After 10 min, Ag nanoparticles were obtained. Then, approximately 2.562 mg of $Pd(NO_3)_2 \cdot H_2O$ was slowly dissolved in 1 mL of 0.1 M HNO_3 to obtain a Pd^{2+} solution, which was used for the subsequent galvanic displacement reaction. Approximately 50 μL of this solution (5.56×10^{-7} mol) was added to 3 mL of a well-stirred solution of Ag nanotemplates at a fixed temperature of 30 °C. After 70 min, the dispersed nanoparticles, in which the Ag/Pd molar ratio was 90:1, were collected. $Ag_{45}Pd_1$ nanoparticles were prepared in a similar manner; however, in this

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case, the concentration of $AgNO_3$ used for the preparation of the Ag nanotemplates was reduced to 2.5×10^{-5} mol. In order to carry out a fair comparison of the optical or catalytic properties, Ag and Pd nanoparticles were produced from the reduction of 5.0×10^{-5} mol of Ag ions and 5.56×10^{-7} mol of Pd ions, respectively, in 0.1 M SDS solution (3 mL). In addition, a Pd/Sn colloidal solution with the same Pd concentration as that used in the nanoparticles was available for comparison.

The prepared nanoparticle solutions were placed on a carbon-coated copper grid and allowed to dry naturally. Then, the characteristic shapes and sizes of the nanoparticles were observed under a transmission electron microscope (TEM; JEOL JEM-3000F) and an energy-dispersive X-ray (EDX) spectroscope. The SPR spectra of the nanoparticles were measured using a UV–vis spectrophotometer (Agilent 8453).

The synthesized hollow $Ag_{90}Pd_1$ and $Ag_{45}Pd_1$ nanoparticles, the solid Ag and solid Pd nanoparticles, and the Pd/Sn colloids were then used as activators for ECD. In order to reduce the interaction of free SDS with the obtained nanoparticles during the ECD reaction, 1 mL of the nanoparticle solution was precipitated by high-speed centrifugation (15,000 rpm) and redispersed in 1 mL of H_2O. This process helped eliminate the free SDS. The ECD bath for the EQCM measurements was prepared from 0.44 M formaldehyde, 0.1 M EDTA, and 0.05 M $CuSO_4$. The pH of the ECD bath was adjusted to 12.3 using NaOH powder. The ECD baths were maintained at 30 °C and bubbled with N_2 for 15 min prior to the measurements. The working electrode used for the EQCM (Autolab PGATAT30 and Seiko QCA922) experiment was prepared by coating 2 μL of the nanoparticle solution or the Pd/Sn colloid solution in a uniform layer over 0.159 cm^2 of the Au surface of the QCM substrate. Au was sputtered on both sides of a Ti film (thickness: 100 Å) on the QCM substrate (Seiko EG&G QA20-A9M-Au), which was connected to an oscillator manufactured in-house. The reference electrode (Hg/Hg_2Cl_2) was separated from the compartment that housed the electrolyte solution by a Luggin capillary filled with saturated KCl solution.

3. Results and discussion

Fig. 1A shows TEM images of the microstructures of the $Ag_{90}Pd_1$ nanoparticles prepared with the abovementioned galvanic displacement method. Some of the hollow nanoparticles were formed after 5.56×10^{-7} mol of $Pd(NO_3)_2$ reacted with the Ag nanoparticles obtained from the reduction of 5×10^{-5} mol of $AgNO_3$. The half-cell reactions and standard reduction potentials (E^0) for this displacement reaction are shown below:

$$\text{Anodic reaction}: \quad Ag \rightarrow Ag^+ + e^-$$

$$E^0 = -0.7996\,V$$

$$\text{Cathodic reaction}: \quad Pd^{2+} + 2e^- \rightarrow Pd$$

$$E^0 = 0.951\,V$$

Hence, the potential corresponding to the net reaction is 0.1514 V. The equlibrium constant (K) calculated using the formula $E_{\text{reaction}} = (RT/nF)\ln K$ is 1.09×10^5. Here, $R = 8.314\,J\,K^{-1}\,mol^{-1}$, $T = 303\,K$, $n = 2$, and F is Faraday's constant. From the value of K and the TEM results, it can be concluded that the displacement reaction readily results in Ag/Pd_{hollow} nanoparticles, even when a low concentration of $Pd(NO_3)_2$ is used. Fig. 1B shows TEM images of the microstructures of the hollow $Ag_{45}Pd_1$ nanoparticles obtained using 2.5×10^{-5} mol of $AgNO_3$. It is evident that these Ag/Pd_{hollow} nanoparticles contain pores at the central location. HR-TEM observations reveal that hollow icosahedral (Fig. 2A) and decahedral (Fig. 2B) nanoparticles with porous {1 1 1} faces are formed from the displacement reaction. Ag nanoparticles synthesized by the displacement reaction using $HAuCl_4$ as the displacing salt are found to have similar morphologies [9].

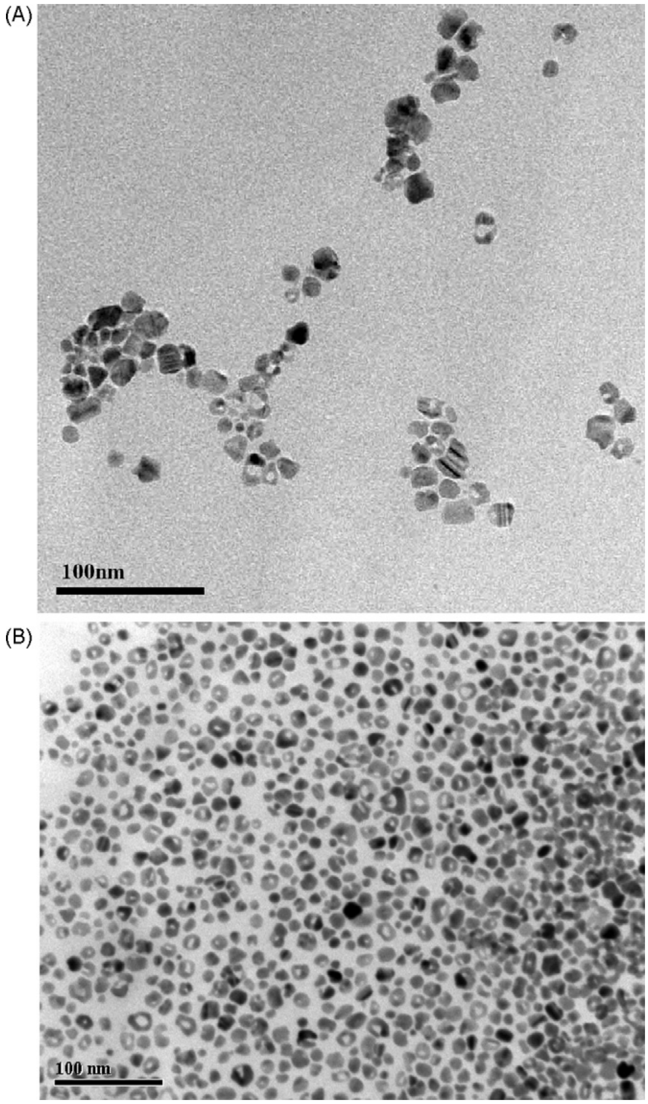

Fig. 1. TEM images of hollow Ag/Pd nanoparticles prepared by the displacement reaction. (A) TEM image of $Ag_{90}Pd_1$. (B) TEM image of $Ag_{45}Pd_1$.

EDX analyses of the synthesized hollow nanoparticles provided information on their architectures, and this information is shown in Table 1. The weight percentages of Pd estimated from the EDX analyses of the $Ag_{45}Pd_1$ and $Ag_{90}Pd_1$ nanoparticles are 15.43% and 10.50%, respectively. The weight percentages of Ag in $Ag_{45}Pd_1$ and $Ag_{90}Pd_1$ are 84.57% and 89.5%, respectively. These results indicate that the nanoparticles prepared by the method described in this paper consist of both Ag and Pd. This confirms the formation of Ag/Pd_{hollow} nanoparticles.

The optical properties of the prepared hollow nanoparticles were determined from their corresponding SPR spectra. Fig. 3 compares the SPR extinction spectra of the cage-like bimetallic nanoparticles, their corresponding Ag nanotemplates, and Pd nanoparticles. A sharp peak at 405 nm was detected in the spectrum of the Ag nanotemplates. However, the SPR peak of the Pd nanoparticles could be detected only in the UV region. Comparison of the spectra of the $Ag_{90}Pd_1$ and Ag nanoparticles revealed a red-shift of the bimetallic SPR peak to 479 nm. Broadening of this peak was observed after Pd was deposited on the Ag templates. How-

Table 1
Comparative EDX and EQCM results of hollow $Ag_{45}Pd_1$ and $Ag_{90}Pd_1$ nanoparticles, solid Ag and Pd nanoparticles, and Pd/Sn colloids.

	Synthesis condition		EDX		EQCM measurement		
	(Ag^+) M	(Pd^{2+}) M	Pd (at%)	Ag (at%)	Ag/Pd (g)	Deposition rate ($\mu g/cm^2$ s)	Activity ($\mu g/\mu g$ cm^2 s)
Hollow $Ag_{45}Pd_1$ nanoparticles	8.197×10^{-3}	1.823×10^{-4}	15.43	84.57	6.67×10^{-6}	0.04	5×10^{-3}
Hollow $Ag_{90}Pd_1$ nanoparticles	1.64×10^{-2}	1.823×10^{-4}	10.5	89.5	6.44×10^{-6}	0.018	2.795×10^{-3}
Ag nanoparticles	8.197×10^{-3}				1.88×10^{-6}	0	0
Pd nanoparticles		1.823×10^{-4}			6.33×10^{-6}	0	0
Pd/Sn colloids		1.823×10^{-4}			2.36×10^{-6}	0	0

ever, no such broadening of the SPR peak was observed in the case of solid Ag/Pd nanoparticles prepared via the chemical reduction method [1]. The optical change observed in the present study was possibly due to the formation of the hollow nanoparticles, as confirmed by the TEM images shown in Fig. 1A. It is noteworthy that the SPR peaks of the $Ag_{45}Pd_1$ nanoparticles broadened to a greater extent than those of the $Ag_{90}Pd_1$ nanoparticles. Thus, it would be reasonable to conclude that the concentration of the Ag/Pd_{hollow} nanoparticles formed increases with the concentration ratio of Pd to Ag.

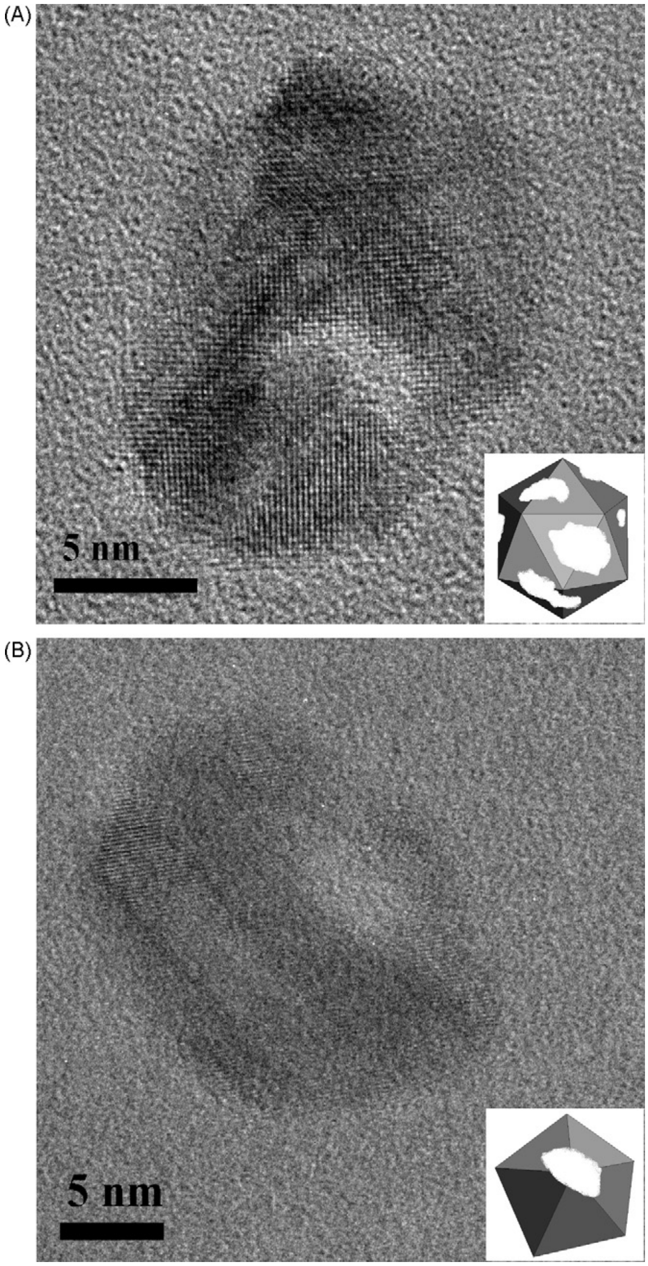

Fig. 2. HR-TEM images of hollow Ag/Pd nanoparticles prepared by the displacement reaction. (A) Hollow icosahedral nanoparticle. (B) Hollow decahedral nanoparticle.

The prepared Ag/Pd_{hollow} nanoparticles were tested for their effectiveness as activators for ECD. Fig. 4A shows the comparative results of EQCM analyses carried out after *in situ* measurements of the catalytic activities, while Fig. 4B shows the open circuit potentials of the Ag/Pd_{hollow}, Ag, and Pd nanoparticles, as well as the Pd/Sn colloids in the ECD bath. The deposition rates shown in Fig. 4A were recalculated from the changes in the electrode frequency using Sauerbrey's equation [12]. The results of these calculations are summarized in Table 1. Ag nanoparticles obtained from the reduction of an 8.197×10^{-3} M solution of Ag ions and Pd nanoparticles and Pd/Sn colloids obtained from the reduction of a 1.823×10^{-4} M solution of Pd ions were found to be inactive for ECD. The average ECD deposition rates observed during the preparation of the hollow Ag_{90}/Pd_1 and Ag_{45}/Pd_1 nanoparticles were approximately 0.018 $\mu g/cm^2$ s and 0.04 $\mu g/cm^2$ s, respectively. These values indicate that the Ag/Pd_{hollow} nanoparticles prepared by this method could be successfully employed as catalysts for ECD. The catalytic activity of the nanocatalysts was calculated according to the following relation:

$$\text{catalytic activity} = \frac{\text{deposition rate}}{\text{weight of the alloy catalyst}}.$$

The catalytic activities of the $Ag_{90}Pd_1$ and $Ag_{45}Pd_1$ nanoparticles were 2.795×10^{-3} $\mu g/\mu g$ cm^2 s and 5×10^{-3} $\mu g/\mu g$ cm^2 s, respectively. Thus, it is evident that the electroless deposition rate and the catalytic activity are enhanced by the more hollow nanoparticles.

As can be seen in Fig. 4B, a steady-state reaction potential (SRP) is observed after the ECD reaction is triggered by the nanocatalysts. The SRPs measured for the inactive Ag nanoparticles, Pd nanoparticles, and Pd/Sn colloids were −0.355 V, −0.409 V, and

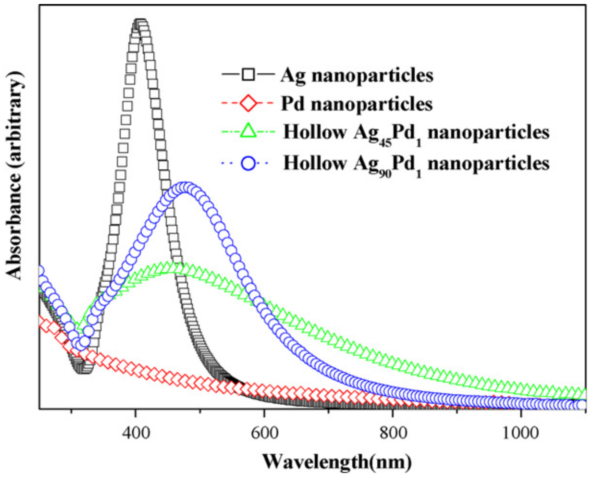

Fig. 3. Comparative SPR spectra of hollow $Ag_{90}Pd_1$ and $Ag_{45}Pd_1$ and solid Ag and Pd nanoparticles.

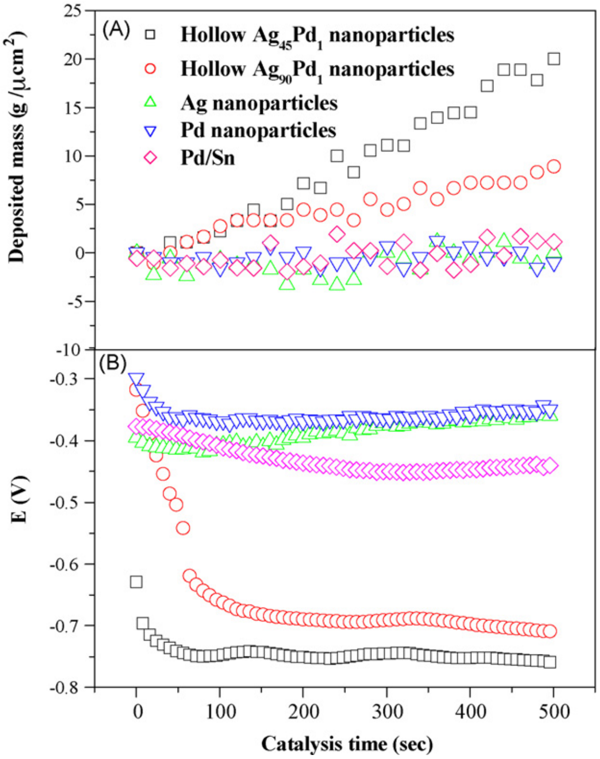

Fig. 4. Comparative EQCM curves of ECD kinetics catalyzed with hollow $Ag_{90}Pd_1$ and $Ag_{45}Pd_1$ nanoparticles, solid Ag and Pd nanoparticles, and Pd/Sn colloids. (A) Deposition rate. (B) ECD reaction potential.

−0.450 V, respectively. The SRPs of the Ag/Pd_{hollow} nanoparticles, which could catalyze ECD, were more negative than those of the Ag and Pd nanoparticles, which were unable to catalyze ECD. The SRPs of the hollow Ag_{90}/Pd_1 and Ag_{45}/Pd_1 nanoparticles reached approximately −0.680 V and −0.750 V, respectively. Thus, it may be concluded that the ECD rate increases as the SRP becomes more negative.

4. Conclusions

Hollow Ag/Pd nanoparticles with different alloy ratios were successfully prepared by a galvanic displacement reaction, in which a small amount of $Pd(NO_3)_2$ was allowed to react slowly with previously synthesized Ag nanoparticles that acted as templates. The resulting hollow Ag/Pd nanoparticles were icosahedral and decahedral in microstructure and showed better catalytic activities for ECD than did the Ag nanoparticles, Pd nanoparticles, and Pd/Sn colloids. In addition, the catalytic activities of these Ag/Pd nanoparticles in the ECD bath could be controlled by suitably tuning their alloy ratios. These Ag/Pd_{hollow} nanoparticles thus constitute a novel class of catalysts for ECD.

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