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Short communication

Promising activities of hollow core-shell Pt-Ag nanoparticles with discontinuous shells as activators for catalyzing electroless copper deposition

Yuan-Ping Lyu, Yi-Shan Wu, Chien-Liang Lee*, Huang-Xiang Zhou

Department of Chemical and Materials Engineering, National Kaohsiung University of Science and Technology, Kaohsiung, Taiwan

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ABSTRACT

Hollow core-shell Pt-Ag nanoparticles (NPs) with discontinuous Ag shells were successfully synthesized using a Pt-seed-mediated growth method and used to catalyze electroless copper deposition (ECD). The activities and resulting ECD kinetics of hollow NPs and solid-core Pt-Ag NPs with sizes of 5.9, 9.6, 14.7, and 20.6 nm were compared. The deposition kinetics was investigated using an electrochemical quartz crystal microbalance (EQCM). The induction period for the 7.3 nm hollow NPs, as observed using a potential-deposition time curve, was 5 s, significantly shorter than that of the 5.9 nm solid Pt-Ag NPs (13 s). At a deposition time of 500 s, the mean mass activities in terms of the weight of the catalyst for the hollow NPs and 5.9 nm NPs were determined to be 4.591 and 3.065, respectively. The large hollow NPs with discontinuous Ag shells show a 1.5-fold higher mass activity than that of the 5.9 nm NPs. In a careful comparison based on the same electrochemical surface area (ESA), the specific activities were in the order: hollow NPs > 20.6 nm NPs > 6 nm NPs > 14.7 nm NPs > 9.6 nm NPs, where the hollow NPs show faster deposition (5.88×10^{-9} g m^{-2} s^{-1}) than the 20.6 nm NPs (5.2×10^{-9} g m^{-2} s^{-1}).

1. Introduction

Core-shell metal nanoparticles (NPs) have drawn considerable research interest owing to their activities in catalytic reactions, such as methanol oxidation [1–3] and oxygen reduction [4–6], surpassing those of commercial catalysts. One reason for the excellent activity exhibited by core-shell catalysts is the tunable *d*-band center of the outer metallic shell that arises from electronic interactions between the outer shell and the core metal, e.g., an outer Pt shell interacting with a Pd core [1,7].

Highly active activators are required to improve electroless copper deposition (ECD), in which the activator is responsible for triggering the process, catalyzing formaldehyde oxidation, and promoting electron transfer. Typically, ECD is used for surface treatment [8,9] and circuit fabrication [10–13] in the electronics industry. In the fabrication of printed circuit boards, Pd/Sn colloids are frequently employed as activators to deposit a conductive copper layer onto insulated side walls through holes [10]. Because of the high cost of Pd/Sn activators, Ag-based nanocatalysts including Ag NPs [14,15], Ag nanocubes [16], and Ag/Sn colloids [17–19] have been developed as new activators for ECD. These Ag activators show their unique catalytic ability in the oxidation of formaldehyde [20,21]. However, the rate of ECD activated by Ag NPs is still lower than that by Pd/Sn colloids [20]. Therefore, the development of new catalysts with improved deposition rate is of interest. Herein, hollow core-shell Pt-Ag NPs are synthesized using a seed-growth method in which discontinuous Ag shells grow and surround Ag-covered Pt seeds. These hollow NPs are used as ECD activators, and their deposition kinetics and activities in terms of electrochemical surface area (ESA) or the weight used are studied and compared with those of solid core-shell Pt-Ag NPs.

2. Experimental

The synthesis of hollow Pt-Ag NPs was carried out by a seed-mediated growth method. A Pt seed solution was initially prepared in which 50 μL of a 0.05 M chloroplatinic acid solution was added to 10 mL of a 2.5×10^{-4} M sodium citrate aqueous solution. Then, 25 μL of a 0.02 M $NaBH_4$ solution was added to form a black-yellow Pt seed solution. In a separate vessel, 100 μL of 0.05 M $AgNO_3$ was added to 10 mL of 0.2 M aqueous hexadecyltrimethyl ammonium bromide (CTAB) solution. Next, 1 mL of 0.5 M aqueous ascorbic acid, 15 mL of the Pt seed solution, and 80 μL of 10 M aqueous NaOH were gradually added to the mixture with continuous stirring over 4 min. Finally, a

* Corresponding author.
E-mail addresses: cl_lee@gm.kuas.edu.tw, cl_lee@url.com.tw (C.-L. Lee).

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solution containing hollow core-shell Pt-Ag NPs was obtained. Based on the same method but decrease the amount of added Pt seed solution, the core-shell Pt-Ag NPs with solid interiors were prepared. The 10 and 5 mL of the Pt seed solutions were added and reacted in the $AgNO_3$/CTAB solution for the synthesis of 5.9 and 9.6 nm NPs. The 14.7 nm NPs were obtained if 2.5 mL of the Pt seed solution was used.

The synthesis of 20.6 nm Pt-Ag NPs was also carried out by a seed-mediated growth method combined with the injection of $AgNO_{3(aq)}$ solution using a syringe pump. First, 1 mL of 0.1 M aqueous ascorbic acid, 1 mL of the above-mentioned Pt seed solution, and 80 μL of 2 M aqueous NaOH were added to 20 mL of 0.1 M aqueous CTAB. Next, 2 mL of 2.5 mM aqueous $AgNO_3$ was added using a syringe pump at a rate of 0.85 mL/h under magnetic stirring at 30 °C. A yellow solution containing 20.6 nm NPs was thus obtained.

The various Pt-Ag NPs were used as catalysts for ECD. To reduce the interaction of free CTAB with the NPs during ECD, the prepared Pt-Ag colloidal solution was centrifuged at 17,000 rpm in order to precipitate out the NPs. The obtained NPs were then resuspended in 1 mL of water. Subsequently, these Pt-Ag catalysts were precipitated again by centrifugation at 15,000 rpm to remove impurities from their surfaces.

The Pt-Ag NPs were placed on copper grids, covered with a carbon film, dried in ambient air, and then observed using transmission electron microscopy (TEM; JEOL JEM-2100) and high-angle annular dark-field scanning TEM (HAADF-STEM; JEOL JEM-2100F CS STEM) to characteristic their sizes and morphologies. The crystalline structures of the prepared nanomaterials were revealed by X-ray diffraction (XRD) spectroscopy (Bruker D8; Cu anode; 1.54184 Å).

In order to measure the ESAs of the Pt-Ag NPs, the Pb under-potential deposition (UPD) process was performed using 200 mL 0.1 M aqueous HCl containing 10 mM. $Pb(NO_3)_2$ A three-electrode cell comprising a glassy carbon electrode (GCE; 0.159 cm^2) covered with 4.77 μg Pt-Ag NPs as the working electrode, a Pt counter electrode, and a Hg/Hg_2Cl_2 saturated calomel reference electrode (SCE) was used. The cyclic voltammetry (CV) curves of hollow Pt-Ag NPs and 20 nm Pt-Ag NPs were measured at a fixed scanning rate (50 mV s^{-1}) in 0.1 M NaOH solution that was maintained at 30 °C and bubbled with N_2 for 15 min prior to the measurements.

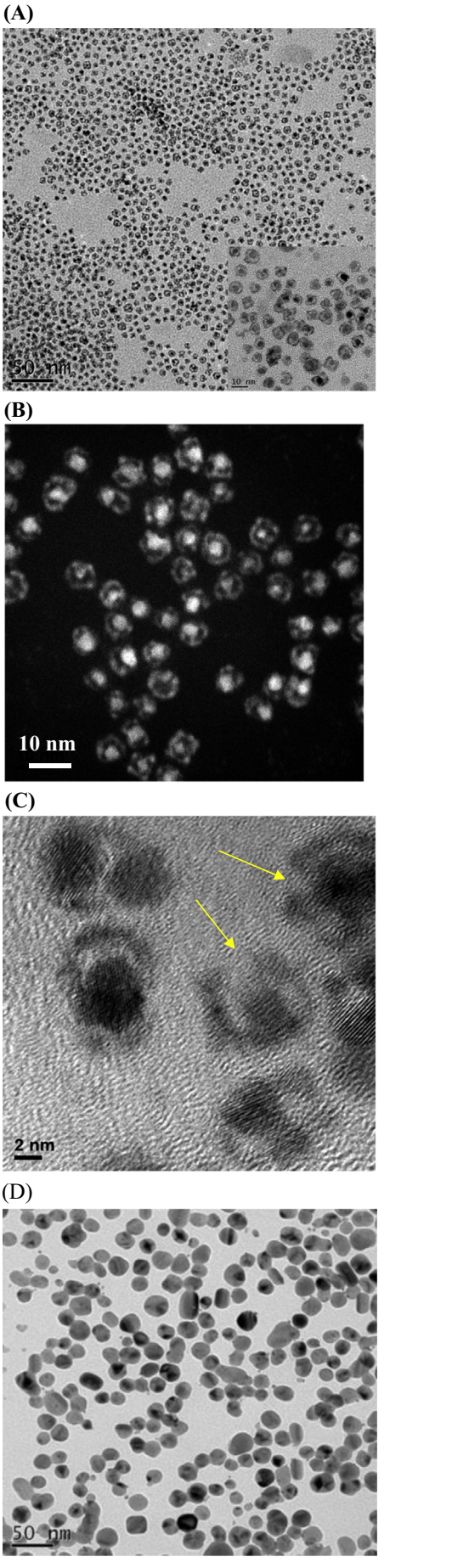
For recording the ECD kinetics, an electrochemical quartz crystal microbalance (EQCM) comprising a potentiostat (Autolab PGATA30) combined with a quartz crystal microbalance (Seiko EG&G QCA 922A; sensitivity: ~1 ng/Hz) and a two-electrode cell composed of an EQCM working electrode and an SCE electrode were used. An activator containing 4.77 μg Pt-Ag NPs was drop-cast onto an Au working electrode (Seiko EG&G QA20-A9M-Au) to obtain a uniform layer upon drying under air at room temperature. Au was sputtered on both sides of a Ti film (0.159 cm^2) on the Si substrate, which was connected to an oscillator. The requirements for the ECD bath for the EQCM experiments are listed in Table 1. The ECD baths were maintained at 30 °C and bubbled with N_2 for 15 min prior to the measurements.

3. Results and discussion

Fig. 1A and the inset show the TEM images of the NPs prepared using 15 mL Pt seed solutions in the seed-mediated growth method. NPs with hollow interiors are obtained in high yields by the growth of Ag

Table 1
Composition of electroless copper deposition for EQCM analysis.

ECD bath for EQCM measurement	
$CuSO_4$	0.05 M
HCHO	0.1 M
Ethylenediaminetetraacetic acid disodium salt	0.1 M
1,10-Phenanthroline (phen)	3.2×10^{-5} M
2,2′-bipyridyl	3.2×10^{-5} M
pH (adjustment with NaOH)	12.3



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