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One-pot synthesis of PdAu bimetallic composite nanoparticles and their catalytic activities for hydrogen peroxide generation

Xiangyun Xiao*,‡, Tae-Uook Kang,***,‡, Hyobin Nam****,*****,‡, Suk Ho Bhang******, Seung Yong Lee****,*****,†, Jae-Pyung Ahn***,†, and Taekyung Yu*,†**

*Department of Chemical Engineering, Kyung Hee University, Yongin 17104, Korea
**Department of Material Science & engineering, Korea University, Seoul 02841, Korea
***Advanced Analysis Center, Korea Institute of Science and Technology, Seoul 02792, Korea
****Materials Architecturing Research Center, Korea Institute of Science and Technology, Seoul 02792, Korea
*****Department of Nanomaterials Science and Engineering, Korea University of Science and Technology, Daejeon 34113, Korea
******School of Chemical Engineering, Sungkyunkwan University, Suwon 16419, Korea
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Abstract−We report a facile one-pot aqueous-phase synthesis of PdAu bimetallic nanoparticles with different Pd/Au ratio. The synthesis was conducted by co-reduction of Pd and Au precursor using ascorbic acid as a reducing agent and in the presence of polyallylamine hydrochloride (PAH). By high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive X-ray spectrometry (EDS) analyses, we found that the synthesized nanoparticles had an onion-like core/shell/shell/shell structure with Au-rich core, Pd-rich shell, Au-rich shell, and Pd shell, respectively. We also investigated the catalytic performance of the synthesized PdAu nanoparticles toward hydrogen peroxide generation reaction.

Keywords: PdAu Nanoparticles, Core/Shell, Bimetallic, One-pot Synthesis, Hydrogen Peroxide Generation

INTRODUCTION

Bimetallic nanoparticles have attracted considerable attention owing to their specific catalytic, optical, and magnetic properties compared to monometallic counterparts [1-8]. Among the numerous bimetallic nanoparticles, palladium-gold (PdAu) bimetallic nanoparticles are of great interest because of their effective properties for various catalytic reactions, including hydrodesulfurization of thiophene [9], oxidation of alcohols to aldehydes [10], and hydrogen peroxide (H_2O_2) direct synthesis from hydrogen (H_2) and oxygen (O_2) [11]. There have been PdAu bimetallic nanoparticles with various structures including alloy, bimodal, and core/shell structures [12-15].

To synthesize core/shell nanoparticles, a two-step method, known as seed mediated growth, is typically used [16]. A two-step method has an advantage of precisely controlling the morphology of core/shell nanoparticles and shell thickness, but it suffers from long and tedious synthetic process and low concentration of the product [17]. Compared with the two-step method, a one-pot synthesis greatly simplifies the reaction process, but it requires strictly controlling the reaction conditions according to the reaction kinetics. In the synthesis of metal/metal core/shell nanoparticles using a one-pot method, the difference in standard reduction potentials between the two metals plays a crucial role [18]. When two metal cations are simultaneously reduced by a reducing agent having an appropriate reducing power at the same time, a metal having a high standard reduction potential is located in the core, and a metal having a low standard reduction potential is later reduced to be mainly distributed in the shell. Park and co-workers reported Au/Pd core/shell nanoparticles with high-index facets by a simple one-pot synthesis [19]. They kinetically controlled the co-reduction rate of Au and Pd precursor at the room temperature in an aqueous solution and successfully produced the Au/Pd core/shell nanoparticles with an unusual truncated shape without pre-synthesized seeds. However, a one-pot process for preparing core/shell nanoparticles having two shell layer or more complex structures in an aqueous-phase has not been reported yet. Ferrer et al. synthesized three-layer core/shell/shell nanoparticles with a AuPd alloy core, a Au-rich middle shell, and a Pd-rich outer shell; however, they used successive polyol method which needs the addition of the reagents continuously during the reaction [20]. In this paper, we first report a facile one-pot synthesis of onion-like Au/Pd/Au/Pd core/shell/shell/shell bimetallic nanoparticles with controllable Pd/Au composition in an aqueous-phase. This synthesis was conducted by co-reduction of Pd and Au precursor using ascorbic acid in the presence of polyallylamine hydrochloride (PAH). In addition, we also investigated the catalytic performance of the synthesized onion-like PdAu bimetallic nanoparticles toward the H_2O_2 synthesis.

EXPERIMENTAL SECTION

1. Materials

Poly(allylamine hydrochloride) (PAH, MW: 50000), L-ascorbic

†To whom correspondence should be addressed.
E-mail: tkyu@khu.ac.kr, jpahn@kist.re.kr, patra@kist.re.kr
‡These authors contributed equally to this work.

acid (AA), sodium tetrachloropalladate(II) (Na_2PdCl_4) and gold(III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$) were purchased from Aldrich and used without further purification.

2. Synthesis of Onion-like Au/Pd/Au/Pd Core/Shell/Shell/Shell Bimetallic Nanoparticles

In a typical synthesis, 8 ml of an aqueous solution containing PAH (40 mg) and L-ascorbic acid (50 mg) was heated to 80 °C under magnetic stirring (800 rpm). After 20 min, 3 mL of an aqueous solution containing Na_2PdCl_4 and $HAuCl_4 \cdot 3H_2O$ was then added into the reacting solution. The amount of Na_2PdCl_4 and $HAuCl_4 \cdot 3H_2O$ was 21.38 mg/9.53 mg for Pd/Au molar ratio of 3/1, 19 mg/12.7 mg for 2/1, and 14.25 mg/19.05 mg for 1/1, respectively. The total number of moles of Pd and Au was maintained at 0.097 mmol. The resulting solution was heated at 80 °C for 3 h, and cooled to room temperature. The products were collected by centrifugation and washed with deionized (DI) water three times.

3. Measurement of Catalytic Performance

The direct synthesis of H_2O_2 was in a 24 well-plate. The reaction medium (2 mL) was composed of ethanol and water (ethanol : water volume ratio=1 : 4) with 0.9 mM sodium bromide (NaBr) and 0.02 M phosphoric acid (H_3PO_4). The amount of used PdAu nanoparticles was 0.0015 mmol. H_2/Ar (4 : 94) gas flow was 50 mL/min and O_2 gas flow was 20 mL/min, respectively. The total volumetric flow rate of the reactant gas stream was 70 mL/min ($H_2 : O_2$ volume ratio= 1 : 10). The reaction was performed at 300 K and 1 atm for 1 h. After the reaction, the concentration of H_2O_2 was calculated using 2,9-dimethyl-1,10-phenanthroline (DMP) method [21].

4. Characterization

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were captured using a JEM-2100F microscope operated at 200 kV. Inductively coupled plasma spectrometer (ICP) was used to determine the elements' distribution in PdAu

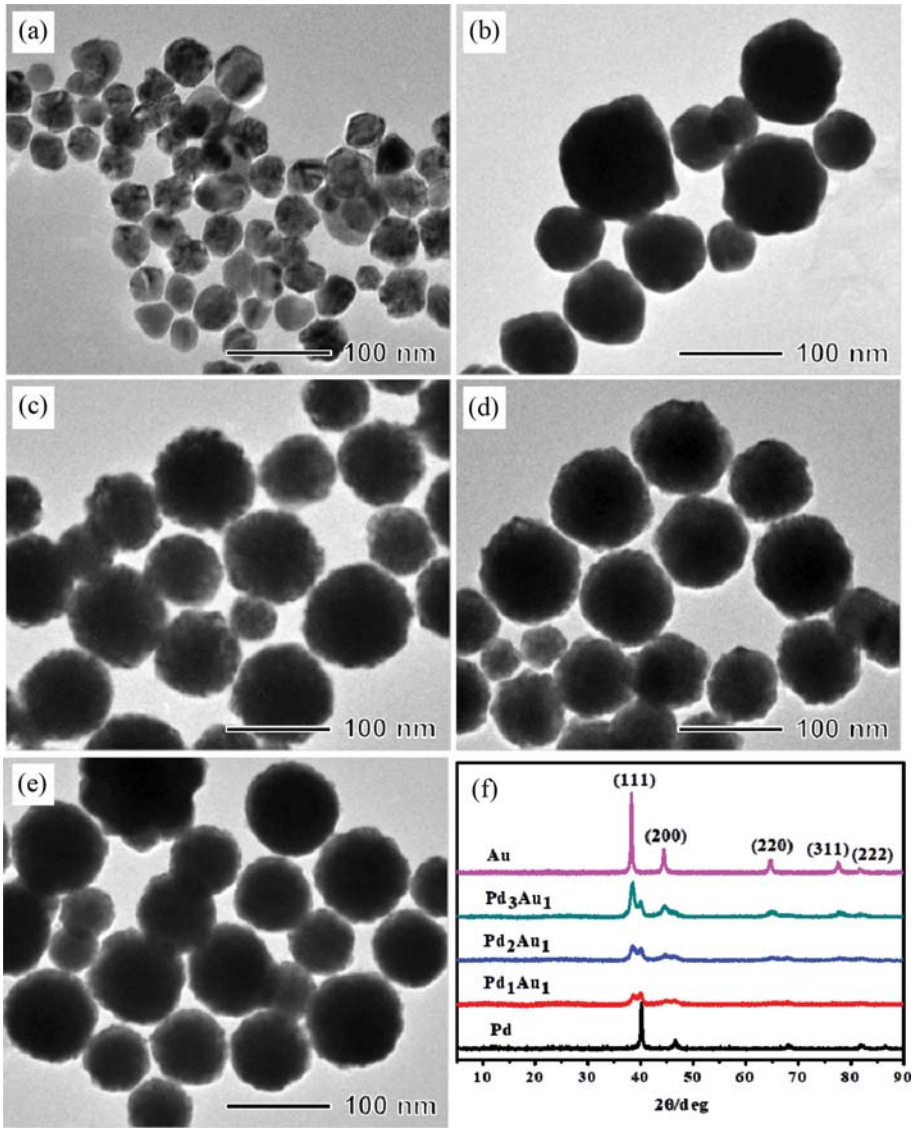

Fig. 1. (a) and (b) TEM images of (a) Pd and (b) Au nanoparticles. (c) to (e) TEM images of PdAu bimetallic composite nanoparticles with different Pd/Au ratio. The Pd/Au ratio of the nanoparticles was (c) 3/1, (d) 2/1, and (e) 1/1, respectively. (f) XRD patterns of Pd, Pd/Au, and Au nanoparticles.

bimetallic composite nanoparticles. The X-ray diffraction (XRD) patterns were obtained using a Rigaku D-MAX/A diffractometer at 35 kV and 35 mA. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive X-ray spectrometry (EDS) operated at Thermo Scientific™ Talos™ 200 kV analytical FEG S/TEM.

RESULTS AND DISCUSSION

The PdAu bimetallic composite nanoparticles were synthesized by co-reduction of a mixture of Na_2PdCl_4 and $HAuCl_4 \cdot 3H_2O$ with L-ascorbic acid in the presence of PAH. Pd and Au nanoparticles were also prepared by the same process in the presence of only Pd and Au precursor, respectively. In this synthesis, PAH was considered as a stabilizing agent for forming nano-sized particles [22]. TEM images of the products reveal that the synthesized nanoparticles including Pd, Au, and PdAu (molar ratio of Pd/Au=3/1, 2/1, and 1/1, respectively) had spherical morphology with average size of 39.7, 115.7, 103.9, 104.3, and 128.8 nm, respectively (Fig. 1(a) to (e)). Fig. 1(f) shows the XRD patterns of the products, indicating that the Au and Pd nanoparticles clearly presented five diffraction peaks at about 38, 45, 65, 77, and 82° and 40, 46, 68, 82, and 86°, respectively, corresponding to the (111), (200), (220), (311), and (222) planes of Au and Pd (JCPDS file no. 04-0784 for Au and JCPDS

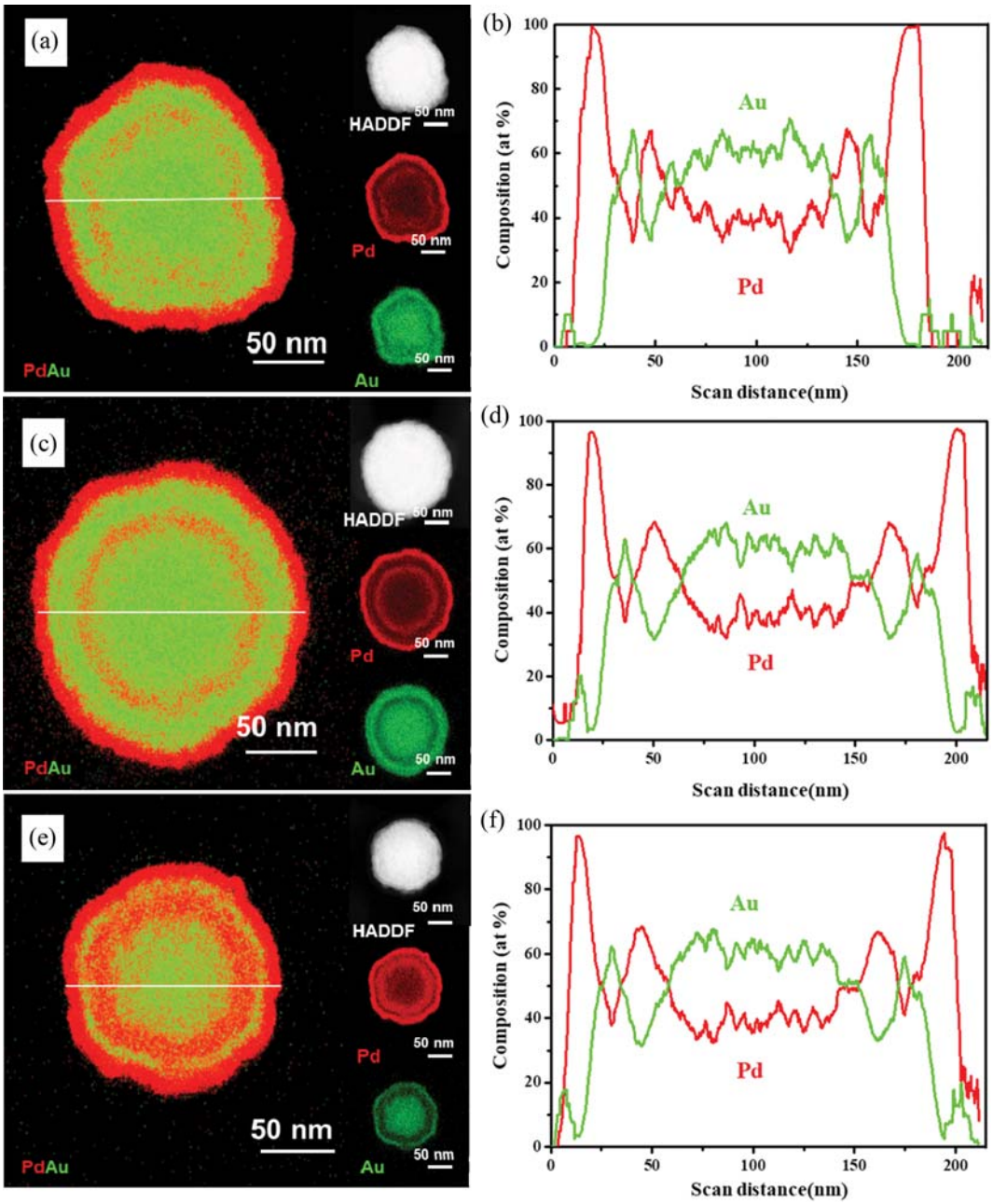

Fig. 2. The HAADF-STEM-EDS mapping ((a), (c), and (e)) and line profile results ((b), (d), and (f)) of the synthesized PdAu bimetallic composite nanoparticles with different Pd/Au ratio. (a) and (b): Pd/Au=1 : 1; (c) and (d): Pd/Au=2/1; (e) and (f): Pd/Au=3/1.

file no. 46-1043 for Pd, respectively). The PdAu nanoparticles with Pd/Au=3/1, 2/1, and 1/1 show the presence of two peaks separated in the middle of monometallic Au and Pd. We think this phenomenon is due to the mixing of the XRD peak for Pd and the XRD peak for Au. In Fig. 1(f), we found that the XRD peaks became closer to Pd as the amount of Pd increased (from Pd/Au=1/1 to Pd/Au=3/1). In addition, ICP results indicate that the Pd/Au ratio of three nanoparticles was 1.2/1 for 1/1, 2.09/1 for 2/1, and 3.02/1 for 3/1, respectively.

The HAADF-STEM-EDS analysis was performed for further confirmation of PdAu bimetallic composite nanoparticles (Fig. 2). The HAADF-STEM-EDS spectrum images of the PdAu nanoparticles with different Pd/Au ratio (Pd/Au=1/1, 2/1, and 3/1) show the synthesized nanoparticles have a core/shell structure with three shells, consisting of a Pd shell, a Au shell, and a Pd shell on the outermost surface in the order of a Au core. Interestingly, EDS mapping data of each element (Au and Pd) and the EDS line scanning analyses exhibited that the core and the inner two shells were composed of mixture of Pd and Au, while the outer shell was composed only of Pd (insets in Fig. 2(a), 2(c), and 2(e), and Fig. 2(b), 2(d), and 2(f)). More precisely, these nanoparticles consisted of a Au-rich core, a Pd-rich shell, a Au-rich shell, and finally a Pd shell. As to why the core/shell structure came out in the one-pot synthesis, we think that the difference in the degree of reduction between Pd and Au precursor may be the reason. However, more research would be needed to understand the formation of core/shell/shell/shell structures rather than Au/Pd core/shell nanoparticles.

The H_2O_2 catalytic performance of the PdAu bimetallic nanoparticles was investigated. Production rates of the PdAu nanoparticles with different Pd/Au ratio were 14.0 mmol/g·h for Pd/Au=1/1, 100.8 mmol/g·h for Pd/Au=2/1, and 145.6mmol/g·h for Pd/Au=3/1, respectively, indicating that the catalytic activity tended to increase as the content of Pd in the nanoparticles increased (Fig. 3). Notably, as the amount of Pd increased, the catalytic activity increased explosively rather than linearly. To illustrate this phenomenon, we focused on the STEM data and found that STEM-EDS mapping results showed that the thickness of the inner Pd shell became thicker as Pd content increased (Fig. 2(a), 2(c), and 2(e)). As a result, the increase of the Pd content increased the thickness of the outer Pd shell, and at the same time, the strain induced in the adjacent Au shell region would affect the H_2O_2 productivity by causing the change of electronic structure.

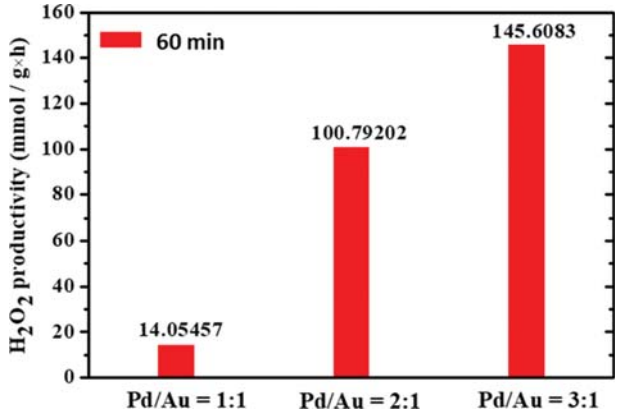

Fig. 3. The H_2O_2 productivity of the catalysts of PdAu bimetallic composite nanoparticles with different Pd/Au molar ratio.

CONCLUSION

In the typical synthesis of core/shell nanoparticles, multiple-step synthesis has been commonly used. In this research, we have demonstrated that core/shell structure could be synthesized by a one-pot reaction using the difference in reactivity of two metal precursors. We expect that this method can be used to make a variety of different metal core/shell nanoparticles. Currently, we are conducting studies to control the reactivity of a metal precursor by attaching an agent to it. If the reactivity of the metal precursor can be controlled, it is thought that we could manufacture from alloy nanoparticles to core/shell nanoparticles at one time.

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