Synthesis, characterization, and electrochemical behavior of Au@Pd core shell nanoparticles

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Abstract. Au@Pd core shell nanoparticles (Au@Pd CSNPs) were successfully synthesized using a seed-mediated growth method. Firstly, a pale pink gold seed solution was used to produce a pale purple gold nanoparticles (AuNPs) core solution. Then, three series of Pd shell thickness using 20µ, 100 µL, and 500 µL of PdCl$_2$ produced purple, brown, and deep brown of Au@Pd CSNPs respectively. A strong absorbance UV-Visible spectrum with peaks at 285 nm and 535 nm was identified for AuNPs formation. The disappearance of the peak at 535 nm was indicated the Au@Pd CSNPs formation. The electrochemical properties were examined in phosphate buffer pH 7 using cyclic voltammetry technique with boron-doped diamond (BDD) as working electrode showed a couple oxidation and reduction peak of gold at 0.67 V and at 0.33 V, respectively. The Au@Pd CNPs will be used for modification of BDD electrodes.

1. Introduction
A core shell structure bimetallic nanoparticles (BNPs) are a heterogeneous nanomaterial which have unique catalytic, magnetic, and optical properties, that are very dissimilar from their monometallic nanoparticles constituents [1, 2]. These superior properties are related to their electronic effect and or geometric effect [3]. Interaction between heterometallic (core and shell) surface atoms can modify the surface electronic structure of the BNPs [4]. Hereby, BNPs in the form core shell frequently perform a better catalytic activities compared to their monometallic nanoparticles mixtures or to alloyed counterparts [5, 6]. One of the most fascinate BNPs are gold-palladium core shell nanoparticles (Au@Pd CSNPs), which have been reported to be useful for electrocatalyst of selective oxidative of benzyl alcohol [7], oxygen reduction reaction [2], hydrogen production [8, 4], formic acid oxidation [9], and methanol electro-oxidation [10].

In this work, we reported the synthesis of Au@Pd CSNPs and its characterization using a UV-Visible spectroscopy and their electrochemical properties.

2. Materials and methods

2.1. Chemicals and reagents
Chloroauric acid (HAuCl$_4$·3H$_2$O), palladium (II) chloride (PdCl$_2$), Cetyltrimethylammonium bromide (CTAB), sodium borohydride (NaBH$_4$), Potassium hydrogen phosphate (K$_2$HPO$_4$), Potassium dihydrogen phosphate (KH$_2$PO$_4$), and ascorbic acid (AA) were purchased from Wako Pure Chemical Industries, ltd, while Hydrochloric acid (HCl) was supplied from Merck.
2.2. Preparation of gold core nanoparticles (AuNPs)
AuNPs were synthesized based on modified seed-mediated grow method reported by Sau et al. [11]. Briefly, a 10 mL aqueous solution consists of CTAB 75 mM and HAuCl₄ 0.25 mM was mixed. Then, a 0.6 mL of 10 mM NaBH₄ fresh-cold solution was quickly added with vigorous stirring to the mixture, followed by slow stirring at 35°C for 3 hour, generating a light brown solution. A volume of 2 mL of this solution was diluted to 50 mL of water to produce a seed solution. Then, 2 mL of the seed solution was immediately added to a 25 mL solution containing 0.1 mL 10 M of HAuCl₄, 2 mL of 0.2 M CTAB, and 1.5 mL of 0.1 M AA. The mixture was then stirred slowly at 308 K for 8 h until produced light purple of AuNPs. Then, the AuNPs were characterized using UV-Visible Spectrophotometer in a wavelength of 200-800 nm.

2.3. Preparation of gold-palladium core shell nanoparticles (Au@Pd CSNPs)
Au@Pd CSNPs were synthesized based on the method of Fan et al. [12]. A solution of 10 mM H₂PdCl₄ was prepared from 44.5 mg of PdCl₂ dissolved into 25 mL of 20 mM HCl in a boiling water bath. To control the Pd shell, a 20 mL of the prepared AuNPs was then added by 20 µL, 100 µL, and 500 µL of H₂PdCl₄, to produce one atomic layer, several layers, and nanocubes, respectively. Finally, several brown solutions of Au@Pd CSNPs were observed. Characterization was performed using UV-Visible Spectrophotometer in a wavelength of 200-800 nm.

2.4. Electrochemical study of Au@Pd CSNPs at Boron Doped Diamond (BDD) electrodes
A volume of 2 mL of Au@Pd CSNPs was diluted in 2 mL of 0.1 M phosphate buffer solution (PBS). Then, cyclic voltammetry technique was performed in a potential range of -1 to 1.75 V with a scan rate of 100 mV/s to evaluate the oxidation and reduction properties of Au@Pd CSNPs in compare to AuNPs.

3. Results and discussion
3.1. The formation of Au@Pd CSNPs
Figure 1a show the photograph of a light brown Au seed solution which was produced from the reduction of HAuCl₄ by NaBH₄ using CTAB as the stabilizing agent. CTAB is one of cationic surfactant that usually use as stabilizing and shape-directing agent in the particle synthesis [13]. A strong absorbance of UV-Visible spectrum at 285 nm and an intense Surface Plasmon resonance (SPR) band at 535 nm (figure 2a) were identified from the light purple, indicated that the formation of AuNPs with average diameter of 11 nm [1] (figure 2b). AA was used couple with CTAB to control the morphology and dimension of core AuNPs [11]. Figure 2 (d, e, f) show the photograph of Au@Pd CNPs with Pd shell thickness varying with 500, 100, and 20 µL, respectively. The disappearance of the peak at 535 nm and
Figure 2. UV-Visible spectrum of (a) core AuNPs, (b) H$_2$PdCl$_4$, and Au@Pd CSNPs with (c) 500 µL of Pd shell, (d) 100 µL of Pd shell, (e) 20 µL of Pd shell.

Figure 3. The electrochemical properties of Au@Pd CSNPs in 0.1 M PBS pH 7

420 nm were correspondent to the decreasing of core AuNPs and H$_2$PdCl$_4$ characteristics, respectively, and was indicated the Au@Pd CNPs formation [14] (figure 2b and 2c). The increasing of Pd shell thickness decreased of the peak absorbance at 535 nm, it means no SPR band was detected [14] (figure 2c, 2d, 2e).
3.2. The electrochemical properties of Au@Pd CSNPs at boron doped diamond (BDD) electrode

Electrochemical behaviour of the Au@Pd CSNPs was examined in 0.1 M PBS pH 7 using cyclic voltammetry technique. Figure 3 shows a couple reduction and oxidation peaks of gold at +0.67 V and at +0.33 V, respectively, which were identified for both AuNPs and Au@Pd CSNPs. The strong oxidation peak of core AuNPs was identified as the oxidation of $\text{Au}^0$ to $\text{Au}^{3+}$ [15], whereas the absence of the oxidation peak of Au@Pd CNPs indicated that the Pd shell may inhibit the core from the oxidation. However, a unique reduction peak can be exhibited in Au@Pd CNPs, which can be explained due to the effect of lattice strain produced by core shell structure nanoparticle which increased the reduction catalytic activity [2]. This behaviour suggested that Au@Pd CSNPs may be more sufficient as catalyst for reduction reaction.

4. Conclusions

Au@Pd CSNPs were successfully synthesized using a seed-mediated growth method. UV-Vis spectrum of Au@Pd CSNPs shown that core AuNPs have been successfully coated by Pd shell to form Au@Pd CSNPs. The electrochemical examination showed that a better reduction peak was obtained for Au@Pd CSNPs, whereas a better oxidation peak occurred at the AuNPs core.

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