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Simple preparation Au/Pd core/shell nanoparticles for 4-nitrophenol reduction

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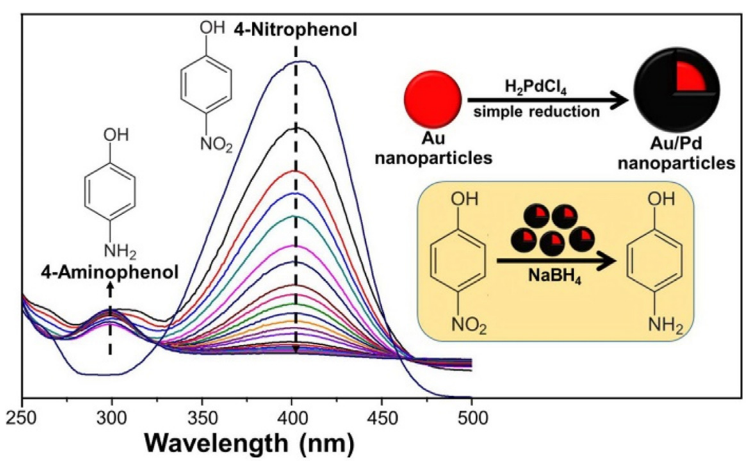
HIGHLIGHTS

- Simple preparation Au/Pd core/shell nanoparticles with various atomic ratios.
- Effect of chemical composition and size of catalysts are reported and compared.
- Highest catalytic activity of bimetallic was obtained from $AuPd_4$ nanoparticles.
- Catalytic activity strongly depend size more than the chemical constituents.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, various sizes and chemical compositions of Au/Pd nanoparticles with core/shell structure were successfully prepared by employing a simple successive reduction method without addition of any stabilizer. The optical properties, morphologies, chemical compositions and crystal structures of the synthesized particles were fully characterized by using a combination of UV–vis spectroscopy, transmission electron microscopy, energy-dispersive X-ray spectroscopy, wavelength-dispersive X-ray spectroscopy, selected area electron diffraction and X-ray diffraction techniques. The catalytic activities of the synthesized Au/Pd nanoparticles for 4-nitrophenol reduction were also investigated and compared with monoatomic Au and Pd nanoparticles. The highest catalytic activity of bimetallic was obtained from $AuPd_4$ nanoparticles. With comparable size, Au/Pd nanoparticles provide better catalytic activity than those of monometallic Au and Pd. However, lower catalytic activities of Au/Pd nanoparticles are shown compared with that of smaller-size Au nanoparticles. This study also reveals that the size effect of catalysts plays important role on catalytic activity more than only changing their chemical constituents.

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1. Introduction

Bimetallic nanoparticles have been intensively investigated since these nanomaterials can provide bi-functional properties generated from each metal constituent or enhanced properties or even new properties with high potential for various applications such as optics, electronics and catalysis [1–3]. Among these issues, recently, one important uses of the bimetallic nanoparticles is as a catalyst in several reactions [3,4]. This kind of catalyst offers better catalytic activity than that obtained from the typical monometallic catalysts [4]. It is well known that the catalytic activity of several nanomaterials depends strongly on their size, shape, structure and chemical compositions [5]. By carefully adjusting these parameters, the desirable catalytic activity of the materials can be achieved. One well-known structure of the bimetallic nanoparticles is named "core/shell structure". This structure can be broadly defined as comprising core and shell of different materials e.g. metal/metal [6], polymer/metal [7], dielectric material/lipid [8], dielectric material/metal [9] or vice versa. This structural type has been interested in the field of catalysis for several chemical reactions [6], due mainly to their unique properties i.e. multiple functionalities, catalytic improvement by synergistic and electronic effect, selectivity and stability [10,11]. In this connection, the Au/Pd bimetallic nanoparticles with core/shell structure have been widely used as catalysts for several important chemical reactions such as hydrogenation of 4-pentenoic acid [12], oxidation of alcohol to aldehyde [13–15] and oxidation of formic acid [16]. Again, interestingly, literature revealed that Au/Pd core/shell catalyst exhibits better catalytic activities than those obtained from the corresponding monometallic nanoparticles [12–16].

Additionally, reduction of 4-nitrophenol (4-NP) has been widely investigated [17–19] due to several points of interest. For example, the 4-NP is considered as a toxic organic pollutant which presents in wastewater generated from several industrial sources [20,21]. The product of reaction, 4-aminophenol (4-AP), is an important compound for preparation of antipyretic and analgesic drugs [20,22]. Moreover, reduction of 4-NP by sodium borohydride ($NaBH_4$) is considered as a model catalytic reaction; yielding a single product in a single reaction at mild condition and no reaction proceeding without catalyst, which has been used to investigate catalytic activity of nanocatalysts [17–20]. Au nanoparticles have been known as an important catalyst for this kind of reaction because Au catalyst is non-toxic and active under mild condition [17]. On the other hand, literature shows that well-stabilized Pd nanoparticles show better catalytic reactivity compared to the typical Au nanoparticles [17,23]. This might be attributed to the fact that Pd is good absorbent for hydrogen [17]. However, suitable stabilizers are needed to prevent aggregate and precipitation of Pd nanoparticles when applying as catalysts. Later, enhancement of catalytic reactivity for reaction has been reported by using bimetallic nanoparticles such as Au@Ag [24] and Au/Pd [25] for reduction of 4-NP. More interestingly, the core-shell Au@Ag nanoparticles show higher catalytic activity than alloy AuAg nanoparticles. So, Au/Pd nanoparticles with core/shell structure are very attractive catalysts for 4-NP reduction. Even though, Au/Pd nanoparticles with core/shell structure have been used as catalysts for several reactions so far, to the best of our knowledge, only few studies have been reported using of core/shell Au/Pd nanocatalysts for this reaction. For example, Shi's group reported synthesis of Au-Pd core-shell nanoparticles stabilized with diblock copolymer; poly(N-isopropylacrylamide)-block-poly(4-vinylpyridine) [26], and tri-block copolymer; poly(ethylene glycol)-block-poly(4-vinlypytidine)-block-poly(poly(N-isopropylacrylamide) [27]. Furthermore, these synthesized nanocomposites were also applied as catalysts for 4-NP reduction. The results show that the bimetallic nanocomposites provide better catalytic activity compared to corresponding monometallic nanocomposites. Also, their catalytic activities can be tuned by changing the weight ratios of corresponding metals. Later, Venkatesan and Santhanalakshmi [28] synthesized core-shell Au-Pd nanoparticles stabilized with cetyl-trimethylammonium bromide and examine the catalytic activity for 4-NP reduction. The enhancement of catalytic activity of bimetallic catalysts over monometallic catalysts was also observed. However, only the catalytic reactivity of Au-Pd with 1:1 atomic ratio was reported whilst these of other Au-Pd compositions are not available. Alternatively, recently, Silva et al. [29] synthesized various chemical composition of Au@Pd core@shell nanoflowers in the present of poly(vinylpyrrolidone) and examine their catalytic activities of 4-NP reduction, compared with hollow AgPd core-shell nanoparticles. They demonstrated that Au core plays important role to enhance catalytic activity of Au@Pd at certain amount of atomic percent of Pd. According to the literatures, it is likely that the core/shell Au/Pd nanoparticles are one of the good catalysts for 4-NP reduction, however, additional stabilizing agents are needed to stabilize core/shell Au/Pd in those studies, as a consequence, several synthetic steps might be involved in the first case. Thus, searching the simple synthetic route for the production of Au/Pd core/shell catalysts is still challenging. Also, the detail investigating of chemical composition effect on the catalytic activity of these nanomaterials is still needed to gain the optimum Au:Pd ratios offering the highest activity. Therefore, this work focuses on the application of simple successive reduction method advocated by Hu et al. [30] for exploring the potential synthesis of core/shell Au/Pd nanoparticles without additional stabilizer. The obtained nanoparticles were characterized by employing several techniques including UV–vis (UV–vis) spectroscopy, transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS), wavelength-dispersive X-ray spectroscopy (WDS), selected area electron diffraction (SAED) and X-ray diffraction (XRD). The catalytic activity of the synthesized Au/Pd for 4-NP reduction was investigated and compared with comparable size of both Au and Pd monometallic nanoparticles. The effects of both size and chemical composition on their catalytic activities were also reported and discussed.

2. Experimental

2.1. Materials

Gold (III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$, 99.999%) was purchased from Sigma-Aldrich. Palladium (II) chloride ($PdCl_2$, 99.99%), ascorbic acid (99%), hydrochloric acid (37%), 4-NP (98%) were obtained from Merck. Sodium citrate tribasic dihydrate ($C_6H_5Na_3O_7 \cdot 2H_2O$, 99%) was purchased from Fluka. $NaBH_4$ (97%) was obtained from APS Chemicals. All chemicals were used as received without further purification.

2.2. Synthesis of Au nanoparticles

The various sizes of Au nanoparticles were synthesized by using Fren's method [31]. Briefly, after a mixture of 1.00 mL of 29.4 mM $HAuCl_4$ solution and 100 mL of deionized (DI) water was heated to boil, a certain amount of 6.8 mM $C_6H_5Na_3O_7$ solution was added into the mixture. The solution was continuously heated for 15 min with vigorous stirring. The red sols were obtained and cooled to room temperature naturally. Various volumes of 6.8 mM $C_6H_5Na_3O_7$ solution (2.5 mL, 1.25 mL and 625 μL) were used to obtain various sizes of Au nanoparticles. The Au nanoparticles were purified by centrifugation technique and washed at least 2 times with DI water. Finally, the volume of Au sols was adjusted to 100 mL with additional DI water.