



Synthesis of bimetallic PdAu nanoparticles for formic acid oxidation

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ABSTRACT

In this work, a simple co-deposition strategy for the synthesis of carbon-supported Pd–Au alloy was reported. Our approach involves the co-reduction of Au and Pd ions using ethylene glycol and sodium citrate as the reducing and stabilizing reagents. Both alloy and non-alloy bimetallic Pd–Au nanoparticles are produced using a right rate-limiting strategy. For example, when ethylene glycol and sodium citrate are the limiting reagent with Au and Pd ions in excess, the synthesis environment favors preferential nucleation and growth of Au nanoparticles followed by deposition of Pd either as the shell of Au core or as separate Pd clusters. On the other hand, if the supply of metal ions (not the reducing reagents) limits the reaction, it creates a synthesis condition for Pd–Au alloy particles. The as-prepared Pd–Au alloys exhibit higher Pd-specific activities towards formic acid oxidation compared with the non-alloy counterpart or individual Pd catalyst and an easier removal of adsorbed oxygen species (e.g., O_{ads} or OH_{ads}) was observed from the surface of Pd–Au alloy with a higher content of Au.

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1. Introduction

Structural or electronic properties of binary catalysts could be very different from that of their individual components and enhanced activity or stability of the binary catalysts were often observed [1,2]. Among the various bimetallic materials, Pd–Au system is an interesting one as it shows high activity towards useful chemical reactions (e.g., hydrogenation of 4-pentenotic acid [3], acetoxylation of ethylene to vinyl acetate [4], and oxidation of alcohols to aldehydes [5]) as well as electrochemical reactions (e.g., ethanol oxidation [6], 2-propanol oxidation [7], and formic acid oxidation [8]). Investigations of catalysts for formic acid electro-oxidation have attracted interests due to their use in direct formic acid fuel cell, a promising power device for consumer electronics. $Au_{core}-Pd_{shell}$ structured materials have been reported to show enhanced activity for formic acid oxidation than the well-known Pd [8,9]. Catalytic properties of bimetallic nanoscale catalysts are highly dependent on their structure (e.g., alloy, core-shell structure) and surface composition [10]. Moreover, interesting and unique electrochemical properties of Pd–Au alloys for formic acid oxidation might be explored.

Although efforts have been made to study the synthesis of Pd–Au bimetallic nanocatalysts, preparation of alloy structured Pd–Au nanoparticles is still considered to be a big challenge [11,12]. The synthesis of core-shell structured Pd–Au catalysts can be easily achieved using either sequential [13,14] or co-reduction methods [11,12,15]. To make alloy catalysts, Ksar et al. [6] have reported a

radiolytic reduction method, through which, Pd–Au alloy nanoparticles stabilized by poly(acrylic acid) were achieved. Mejía-Rosales et al. [16] synthesized and characterized Pd–Au nanoparticles passivated with poly(vinylpyrrolidone) (PVP) using a sequential reduction protocol. Using hydrazine as the strong reductant, PVP-protected Pd–Au alloy nanodendrites with an average particle size of 15–26 nm have been synthesized [17].

In this work, we report a simple co-reduction method with ethylene glycol and sodium citrate as the reducing and stabilizing agents to synthesize Pd–Au bimetallic nanoparticles. Traditionally, the formation of Pd–Au alloys through concurrent reduction of Pd and Au ions is not easy because of the vast difference of redox potentials between Au and Pd [15]. At the same reducing environment, Au ions have much higher reduction rate than that of Pd ions. To overcome this limitation, our approach adopts the principle of reaction engineering and rate-limiting strategy to carefully control the synthesis environment that would enable the production of alloy and non-alloy Pd–Au bimetallic nanoparticles. Pd–Au alloy nanoparticles with different metallic compositions were successfully synthesized by this new approach. Electrochemical evaluation suggests that the as-synthesized Pd–Au alloys exhibit higher Pd-specific activities towards formic acid electro-oxidation than Pd/C. Moreover, Pd–Au catalysts consisting of a higher content of Au show an easier removal of adsorbed oxygen species (e.g., O_{ads} or OH_{ads}).

2. Experimental

2.1. Chemicals

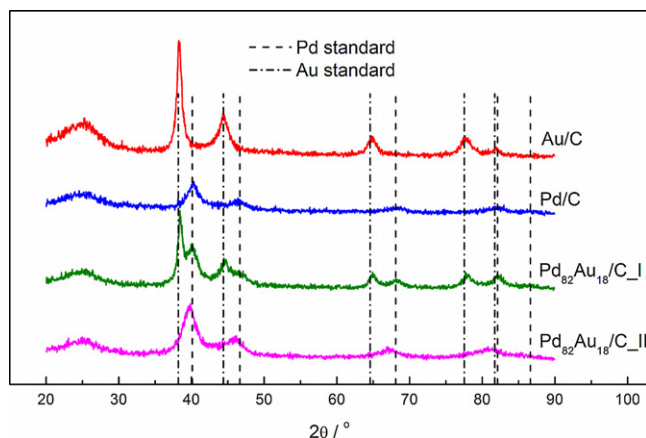
Ammonium tetrachloropalladate ($(NH_4)_2PdCl_4$, 99.995%), hydrogen tetrachloroaurate trihydrate ($HAuCl_4 \cdot 3H_2O$, 99.9%),

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Table 1
Metallic loadings of catalysts based on ICP-AES characterization.

Catalysts	Metallic loadings based on ICP-AES characterization (%)		Atomic ratio (Pd/Au)	
	Au	Pd	Experimental	Precursor
Pd	N/A	12.7	N/A	N/A
Pd ₈₂ Au ₁₈ /C.I	4.8	10.9	81/19	82/18
Pd ₈₂ Au ₁₈ /C.II	4.9	12.8	83/17	82/18
Pd ₆₇ Au ₃₃ /C.II	8.1	8.8	67/33	67/33
Pd ₅₀ Au ₅₀ /C.II	10.3	5.9	51/49	50/50

**Fig. 1.** XRD patterns of Au/C, Pd/C, and Pd₈₂Au₁₈/C (prepared by protocols I and II) catalysts.**Table 2**
Crystal size and lattice parameter of the Pd/C, Au/C and Pd₈₂Au₁₈/C (prepared by protocols I and II) based on XRD characterization.

Catalysts	Crystal size/nm	Lattice parameter/nm
Pd/C (protocol II)	3.6	0.3893
Au/C (protocol II)	7.2	0.4064
Pd ₈₂ Au ₁₈ /C (protocol I)	4.2 (Pd)	0.3890 (Pd)
	6.8 (Au)	0.4054 (Au)
Pd ₈₂ Au ₁₈ /C (protocol II)	3.0	0.3940

ethylene glycol (C₂H₆O₂, 99.5%), perchloric acid (HClO₄, 69%) were purchased from Sigma Aldrich. Sodium citrate (C₆H₅Na₃O₇·2H₂O, 99%) was ordered from BDH. Formic acid (HCOOH, 98%) was ordered from Riedel-de-Haën. Vulcan XC-72 carbon was purchased from E-TEK. Nafion solution (5%) was received from Dupont. Ethanol (C₂H₅OH, 99.5%) was purchased from Merck KGaA.

2.2. Synthesis of catalysts

2.2.1. Synthesis protocol I for Pd₈₂Au₁₈/C catalyst

Firstly, 21.9 mg ammonium tetrachloropalladate ((NH₄)₂PdCl₄) and 0.65 ml hydrogen tetrachloroaurate trihydrate (HAuCl₄·3H₂O) aqueous solution (1 g/100 ml) were dissolved into 48 ml water

Table 3
Atomic compositions of five nanoparticles of the Pd₈₂Au₁₈/C.II catalyst based on EDX characterization.

Nanoparticles	Pd (atom %)	Au (atom %)
# 1	89.30	10.70
# 2	85.81	14.19
# 3	82.38	17.62
# 4	86.35	13.65
# 5	88.50	11.50
Stoichiometric value	82	18

Table 4

Atomic compositions of five nanoparticles of the Pd₈₂Au₁₈/C.I catalyst based on EDX characterization.

Nanoparticles	Pd (atom %)	Au (atom %)
# 1	100	N/A
# 2	87	13
# 3	57	43
# 4	100	N/A
# 5	100	N/A
Stoichiometric value	82	18

to obtain the precursor solution. Then, 48 mg Vulcan XC-72 carbon was poured into the solution to get the precursor suspension, which was stirred and ultrasonically mixed for 2 h. At the same time, 0.283 g sodium citrate was dissolved into 2 ml water + 10 ml ethylene glycol mixture solution to get the sodium citrate water/ethylene glycol solution. After removing air with Ar gas bubbling for 30 min, the precursor suspension was refluxed at 170 °C oil bath for 5 min and then the prepared sodium citrate water/ethylene glycol solution was added into the heated precursor suspension drop by drop. Another 40 ml ethylene glycol was added into the reaction system, which was then continued to be heated for another 2 h. The reaction product was filtered and washed with water and ethanol. The residue was dried at 60 °C oven for 12 h and then grounded in an agate mortar. Catalyst synthesized by this protocol is denoted as Pd₈₂Au₁₈/C.I in the following discussion.

2.2.2. Synthesis protocol II for Pd₈₂Au₁₈/C catalyst

Firstly, 0.283 g sodium citrate was dissolved into 50 ml water/ethylene glycol mixture solution (volume/volume = 1:1), and then 48 mg Vulcan XC-72 carbon was poured into the above solution to obtain the sodium citrate suspension, which was stirred and ultrasonically mixed for 2 h. At the same time, 21.9 mg ammonium tetrachloropalladate ((NH₄)₂PdCl₄) and 0.65 ml hydrogen tetrachloroaurate trihydrate (HAuCl₄·3H₂O) aqueous solution (1 g/100 ml) were dissolved into another 10 ml water/ethylene glycol solution (volume/volume = 1:1) to obtain the precursor solution. After removing air with Ar gas bubbling for 30 min, the sodium citrate suspension was refluxed at 170 °C oil bath. After 5 min heating, the precursor solution was added into the heated sodium citrate suspension drop by drop. Another 40 ml water/ethylene glycol solution (volume/volume = 1:1) was added into the reaction system, which was then continued to be heated for another 2 h. The reaction product was filtered and washed with water and ethanol. The residue was dried at 60 °C for 12 h and then grounded in an agate mortar. Catalyst synthesized by this protocol is denoted as Pd₈₂Au₁₈/C.II in the following discussion.

Protocol II was also used for the synthesis of Pd/C (same palladium/carbon ratio with that in the Pd₈₂Au₁₈/C catalysts), Au/C (same gold/carbon ratio with that in the Pd₈₂Au₁₈/C catalysts), Pd₆₇Au₃₃/C (metal loading of 20 wt% with atomic ratio of Pd to Au being 67:33 in the precursor solution) and Pd₅₀Au₅₀/C (metal loading of 20 wt% with atomic ratio of Pd to Au being 50:50 in the precursor solution).

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