Sodium citrate assisted facile synthesis of AuPd alloy networks for ethanol electrooxidation with high activity and durability

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Abstract

The direct ethanol fuel cell is an emerging energy conversion device for which palladium is considered as the one of the most effective components for anode catalyst, however, its widespread application has been still limited by the activity and durability of the anode catalyst. In this work, AuPd alloy networks (NWs) are synthesized using H_2PdCl_4 and HAuCl_4 as precursors reduced by NaBH_4 in the presence of sodium citrate (SC). The results reveal that SC plays significant role in network structure, resulting in the enhanced electrocatalytic activity of the catalyst. This self-supported AuPd NWs catalyst exhibits much higher electrochemical catalytic activity than commercial Pd/C catalyst toward ethanol electrooxidation in alkaline solution. Significantly, AuPd NWs catalyst shows extremely high durability at the beginning of the chronoamperometry test, and as high as 49% of the mass current density ($1.41 \text{ A/mg}_{\text{Pd}}$) remains after 4000 s current-time test at -0.3 V (vs. Ag/AgCl) in N_2 -saturated KOH -ethanol solution. This strategy provides a facile method for the preparation of alloy networks with high electrochemical activity, and can be potentially expanded to a variety of electrochemical applications.

Keywords: sodium citrate; gold-palladium alloy nanowire; ethanol oxidation reaction; high activity; improved durability.

1. Introduction

Alkaline fuel cells (AFCs) have emerged as one of the most promising energy sources [1] since last century because they can directly convert chemical fuels to electricity with high efficiency without pollution [2] and catalyst corrosion [3], among which direct ethanol fuel cells (DEFCs) have attracted increasing attention since ethanol is a non-toxic, cheap, readily available and environmentally benign resource, and possesses a higher specific energy density than methanol [4] and formic acid [5]. Pd-based alloy nanomaterials are considered to be an effective anode catalyst in alkaline solution due to the synergistic effect and electronic effect of their components [3, 6]. It has been proved that rational design of novel metal nanostructures with favorable size, shape, and composition provides wide opportunities to construct advanced catalysts [7-10]. Various kinds of Pd-based alloy nanomaterials have been fabricated to increase electrocatalytic activity by improving mass current density of Pd, such as PdCu [11, 12], PdNi[13, 14], PdAg[15, 16], PdCo[17, 18], PdRh[19, 20] and PdAu[21, 22]. For example, Wang and coworkers reported Pd-Au hetero-nanoraspberries with around 21 nm in diameter for plasmonic controlled electrocatalytic activity towards ethanol oxidation. The hot electrons shift from the Au core into the Pd nanopetals under visible-light irradiation, leading to an improvement of the electrooxidation of ethanol on Au and deterioration on Pd[23]. However, some critical problems, such as polymer surfactant usage, complex procedures, harsh experimental conditions, especially the relative low electrocatalytic activity and poor endurance, have highly affected the spread of Pd catalyst, and further constrained the widespread commercial application of the DEFCs [24, 25]. Therefore, developing a simple method to prepare Pd-based alloy nanomaterials with great activity and high durability is still a great challenge and highly desired [1, 3].

Herein, we reported a facile method to fabricate the self-supported dendritic AuPd alloy networks (NWs) in the presence of sodium citrate (SC) within 5 min at room temperature. SC plays significant role in the nanowire formation and thus enhanced electrocatalytic activity. Transmission electron microscope (TEM) and x-ray diffraction (XRD) spectroscopy reveal the formation of AuPd alloy networks (NWs). Moreover, the electrocatalytic activity of the AuPd with different ratios has been compared using cyclic voltammograms (CVs) and chronoamperometry methods in alkaline solution. The results demonstrate that AuPd NWs with Au/Pd of 1:1 (denoted as Au₁Pd₁ NWs) shows highest electrocatalytic current toward ethanol electrooxidation and largest electrochemical surface area (ECSA). Compared with commercial Pd/C catalyst, optimized AuPd NWs exhibited improved ECSA, high

ethanol electrooxidation peak current and extremely high durability, which makes these prepared dendritic three-dimensional (3D) AuPd NWs great potential in the fuel cells and many other electrochemical applications.

2. Experimental section

2.1 Chemicals

Gold (III) chloride trihydrate (99.9%, $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), palladium (II) chloride (99.9%, PdCl_2), nafion (5 wt.%) solution and commercial Pd/C (10% Pd mass loading) catalyst were obtained from Sigma-Aldrich. Sodium borohydride (NaBH_4), sodium citrate dehydrate (99%, SC) and potassium hydroxide (85%, KOH) were obtained from Alfa Aesar. Ethanol was purchased from Fisher Scientific. All reagents were directly used as received without further purification. Milli-Q water with a resistivity of greater than $18.2 \text{ M}\Omega \cdot \text{cm}$ was used throughout the experiments. All electrochemical experiments were carried out at room temperature.

2.2 Apparatus

Transmission electron microscopy (TEM) measurements were carried out on JEOL 100 CX II operated at 100 kV accelerating voltage. High resolution TEM (HRTEM) and mapping results were obtained from JEM-2100F field emission TEM. X-ray diffraction (XRD) measurement was performed with Bruker AXS D8 Focus powder x-ray diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) at 40 kV accelerating voltage and 40 mA current. Energy dispersive spectroscopy (EDS) was measured on JEOL 7000F Scanning Electron Microscope (SEM) equipped with an Oxford Aztec spectrometer. The electrochemical measurements were performed on an Autolab PGSTA12 electrochemical workstation. A three-electrode system was used throughout this work. The glassy carbon (GC) electrode (3 mm in diameter, BASi), Ag/AgCl (saturated with KCl, BASi) and platinum wire were used as working, reference and counter electrode, respectively.

2.3 Synthesis of AuPd alloy nanoparticles

HAuCl_4 was dissolved into water with a concentration of 0.1 M, and PdCl_2 was dissolved into 1 M HCl to form 0.1 M of H_2PdCl_4 . Firstly, 50 μL of HAuCl_4 and 50 μL of H_2PdCl_4 were added into 10 mL of water containing 8 mM of sodium citrate under vigorous magnetic stirring at room temperature. Then

0.5 mL of fresh prepared 2 mg/mL NaBH₄ solution was quickly injected into the above solution under stirring, and the color of solution changed from light yellow to darkish rapidly. After stirring for 5 min, the solution was centrifuged and washed with water.

The effect of SC on bimetallic nanostructure morphology was investigated by changing the concentration of SC as 0, 8 and 16 mM, and the products are named as AuPd₀, AuPd₈ and AuPd₁₆. The ratios of Au/Pd were also optimized by changing the volume of HAuCl₄ (0, 25 or 100 μ L) in the aqueous solution containing 50 μ L H₂PdCl₄ and 8 mM SC. Hereafter, the AuPd nanoparticles (Au₀Pd₁, Au_{0.5}Pd₁, Au₁Pd₁, and Au₂Pd₁ NWs) were prepared from HAuCl₄/H₂PdCl₄ mixtures with molar ratios of 0:1, 0.5:1, 1:1 and 2:1, respectively. Based on EDS result, the Au/Pd ratios in Au_{0.5}Pd₁, Au₁Pd₁, and Au₂Pd₁ NWs are 38:62, 52:48 and 67:33, respectively.

2.4 Electrocatalytic experiment

The as-prepared AuPd NWs and commercial Pd/C catalysts were dispersed in a mixture (water, isopropanol, and nafion (5%)) with v/v/v = 4/1/0.025) and ultrasonicated to form a well-dispersed suspension with 0.88 mg/mL of Pd. Prior to the surface coating, the GC electrodes were polished carefully with 0.3 and 0.05 μ m Al₂O₃ powder, rinsed with water, and treated with sonication in water and ethanol successively for 3 cycles. Then the electrodes were readily to dry under nitrogen. After that, 3 μ L of prepared slurry was dropped onto the GC disk and dried under ambient condition to obtain the catalyst layer. Before catalytic test, the catalysts were cycled with a scanning rate of 50 mV s⁻¹ in the N₂-saturated 1 M KOH-1 M ethanol until stable CVs were obtained. Durability tests were performed in N₂-saturated 1 M KOH-1 M ethanol mixture at -0.3 V (vs. Ag/AgCl) for 4000 s.

3. Results and discussion

3.1 Characterization of the AuPd NWs.

Fig. 1. Typical TEM images (A and B), HRTEM image (C) and HAADF-STEM (D) and elemental mapping (E, Au-L, F, Pd-L and G, merged image) of Au_1Pd_1 NWs prepared in presence of 8 mM SC.

The structure of the prepared AuPd nanostructure were investigated with transmission electron microscopy (TEM). As shown in Fig. 1, in the present of 8 mM SC, **dendritic three-dimensional (3D) well-dispersed networks** (NWs) were obtained (Au_1Pd_1), which are composed of uniform nanowire building blocks with diameter of 3 to 8 nm. HRTEM image (Fig. 1C) indicates that the AuPd NWs are dominant formation of the face-centered cubic (fcc) (111) lattice image with 0.23 nm lattice spacing. High angle annular dark field scanning TEM (HAADF-STEM) and elemental mapping results (Fig. 1D-1G) show that Au and Pd distributed uniformly in the AuPd NWs. Fig. 2 shows the typically x-ray diffraction (XRD) of AuPd NWs of different Au/Pd ratios. The peaks (red curve) centered at 38.95° , 44.65° and 65.96° are assigned to the (111), (200) and (220) planes of Au_1Pd_1 NWs [26], respectively. As expected, all of these peak positions of Au_1Pd_1 NWs lie between fcc crystal nanostructure of Au (JCPDS no. 04-0784, green) and Pd (JCPDS no. 46-1043, magenta) peaks, indicating the formation of AuPd alloy nanostructure.

Fig. 2. XRD pattern of AuPd NWs with different Au/Pd ratios. JCPDS peak positions for Au (green) and Pd (Magenta), dash lines indicate peaks of Au₁Pd₁ NWs.

3.2 Electrochemical test of AuPd NWs towards ethanol oxidation

The catalytic performance of the AuPd NWs was studied in N₂-saturated 1 M KOH-1 M ethanol mixture. Firstly, the role of SC was investigated by varying the concentrations (0, 8 or 16 mM) of sodium citrate during the preparation. As shown in inset of Fig. 3, AuPd₀ dispersion reveals dark brown. Compared with the nanowire networks of AuPd₈, AuPd₀ are composed of the separated non-uniform nanospheres (Fig. 4A and 4B). However, while the concentration of SC was increased to 16 mM, agglomerates can be clearly observed during the fabrication process (inset of Fig. 3), and the TEM result reveals the AuPd₁₆ shows similar structure as AuPd₈ NWs (Fig. 1), but with larger building blocks (6 to 13 nm, Fig. 4C and 4D), which might lead to reduced electrochemically active surface area and this is adverse to the electrochemical catalysis. This phenomenon may result from the following reasons: citrate ions often serve as capping agent to fabricate uniform metal nanoparticles and prevent them from aggregation [13, 27-29]. However, large amount of ions often lead to aggregation of nanoparticles and larger size nanocrystals by collapsing electric double layer because of high ion strength[30].

Fig. 3. CV curves of Au1Pd1 prepared in the presence of 0, 8 and 16 mM SC, respectively. Inset is the digital photograph of the three kinds of samples.

The corresponding ethanol electrooxidation catalytic activity of AuPd NWs prepared with different concentrations of SC was further determined in N_2 -saturated 1 M KOH-1 M ethanol with cyclic voltammograms (CVs). As expected, the AuPd₈ shows most negative onset potential and largest peak current than that of AuPd₀ and AuPd₁₆ in the forward scan (Fig. 3), indicating that AuPd₈ NWs possess the highest ethanol oxidation reaction (EOR) activity. Therefore, the introduction of certain amount of SC in our strategy plays a critical role in formation of nanowire networks and thus improved the catalytic activity of AuPd nanostructures.

Fig. 4. TEM images of AuPd in the absence (A and B) and presence (C and D) of 16 mM SC.

3.3 Effect of Au/Pd ratio

To investigate the optimum ratio of Au/Pd with the best catalytic capability, Au/Pd with various ratios were prepared in the presence of 8 m SC. From the TEM images shown in Fig. S1-S3, we can see that these nanostructures also exhibit similar morphology and structure, 3D dendritic networks. As shown in Fig2, all XRD peak positions of Au_1Pd_1 NWs are located between corresponding peaks of Au_2Pd_1 (black curve) and Au_1Pd_2 NWs (blue curve), confirming the well-structured AuPd alloy. The electrocatalytic performance of these AuPd NWs toward ethanol electrooxidation was further examined. Fig. 5A shows typical CVs of these catalysts towards ethanol oxidation in N_2 -saturated 1 M KOH-1 M ethanol solution. The CV curves show different peaks for different Au/Pd ratio. This phenomenon has been reported in previous work[23], which is often attributed to the morphology and the surface coverage of the different metal, since ethanol oxidation on Au and Pd takes place in the different potential ranges. Instead of two distinct peaks[23], the alloy nanowires in this work show single forward scan peak due to relatively homogeneous distribution of Au and Pd atoms on the surface of alloy rather than hetero-nanoparticles[31]. Of these kinds of AuPd alloy nanomaterials, Au_1Pd_1 possessed the highest

peak current and displayed a less positive anodic onset potential and high mass current density (summarized in Table 1). In detail, the peak of current density of the Au_1Pd_1 (7.06 A/mg_{Pd}) was 4.08, 1.49, 1.48 and 2.22 times higher than those of the Au_0Pd_1 (1.73), $\text{Au}_{0.5}\text{Pd}_1$ (4.73), Au_2Pd_1 (4.75) and commercial Pd/C (3.18), respectively. In addition, Au_1Pd_1 NWs possessed the lowest onset potential at -0.50 V, which is more negative than that of the Au_0Pd_1 (-0.45 V), $\text{Au}_{0.5}\text{Pd}_1$ (-0.48 V), Au_2Pd_1 (-0.46 V) and commercial Pd/C catalyst (-0.48 V). Interestingly, the onset potential of the backward scan positively shifted with the increasing proportion of Au in the alloy NWs, which might be result from the introduction of less active Au into the alloy nanocatalysts [32].

Fig. 5. (A) CV curves of the AuPd NWs with different Au/Pd ratios and commercial Pd/C catalyst in N_2 -saturated 1 M KOH-1 M ethanol, at a scan rate of 50 mV/s. (B) Chronoamperometric curves of various catalysts in N_2 -saturated 1 M KOH-1 M ethanol mixture at -0.3 V (vs. Ag/AgCl).

Table 1. Electrochemical properties of different electrocatalysts based on Fig. 5A and Fig. S4.

Catalysts	Onset potential (V)	Current density		ECSA (m ² /g _{Pd})
		A/mg _{Pd}	mA/cm ² _{Pd}	
Au_0Pd_1	-0.45	1.73	27.07	6.39
$\text{Au}_{0.5}\text{Pd}_1$	-0.48	4.73	18.93	24.99
Au_1Pd_1	-0.50	7.06	26.28	26.86
Au_2Pd_1	-0.46	4.75	43.14	11.01
Pd/C (sigma)	-0.48	3.18	13.00	24.45

The typical CVs of Au_0Pd_1 , $\text{Au}_{0.5}\text{Pd}_1$, Au_1Pd_1 , Au_2Pd_1 and commercial Pd/C in N_2 -saturated 1 M

KOH are shown in Fig. S4. The reduction peaks of metal oxides in AuPd alloy NWs were presented in the range of -0.20 to -0.30 V in the negative scan, which is positive than Au_0Pd_1 NWs and commercial Pd/C. It is worth mentioning that because of introduction of Au, AuPd alloy nanostructures were formed, and the reduction peak of the AuPd NWs shifted positively with the increasing amount of Au in AuPd nanostructures, in detail, -0.343 , -0.302 , -0.248 and -0.211 V for Au_0Pd_1 , $\text{Au}_{0.5}\text{Pd}_1$, Au_1Pd_1 , and Au_2Pd_1 , respectively. Moreover, the ECSA of these five kind of catalysts were calculated [16, 33], which dominates the electrochemical activity of the catalysts [6]. As shown in Table 1, the ECSA of the Au_0Pd_1 , $\text{Au}_{0.5}\text{Pd}_1$, Au_1Pd_1 , Au_2Pd_1 and commercial Pd/C are 6.39, 24.99, 26.86, 11.01 and $24.45 \text{ m}^2/\text{g}_{\text{Pd}}$, respectively. This indicates that the Au_1Pd_1 dendritic nanostructures possess highest ECSA value than AuPd NWs with other Au/Pd ratios, and even higher than the commercial Pd/C catalyst ($24.45 \text{ m}^2/\text{g}_{\text{Pd}}$), which would probably increase the active sites for the ethanol electrooxidation. Moreover, the specific activity of the Au_1Pd_1 is twice larger than that of Pd/C, but it is smaller than Au_0Pd_1 and Au_2Pd_1 , which is because of the small ECSA of these two nanomaterials. It can be concluded that introduction of Au is critical to the formation of nanowire networks structures and enhanced electrocatalytic activity of AuPd NWs towards ethanol electrooxidation.

3.4 Electrochemical surface area (ECSA) measurement

Table 2. The electrochemical parameters of kinds of Pd-based catalysts toward ethanol electrooxidation in KOH/NaOH-ethanol solution.

Catalysts	method	Peak current ^a (A/mg _{Pd})	i-t potential ^a (V)	Duration (s)	Mass current density ^b at the end of test (A/mg _{Pd})	Reference
AuPd	NaBH ₄ /SC	7.06	-0.3 (Ag/AgCl)	4000	1.41	this work
PdAg	NaBH ₄	1.97	-0.3 (Ag/AgCl)	2000	~ 0.5	[16]
PdAu	NaBH ₄ /KBr/PVP	10.8	-0.1 (Ag/AgCl)	6000	0.2	[26]
PdCu/C	hydrazine hydrate	<1.5	-0.4 (Hg/HgO)	7200	< 0.005	[11]
PdCo/rGO	SnCl ₂ /heat	~ 0.5	-0.25 (SCE)	3600	< 0.1	[34]
PdPt	NaBH ₄	~ 1.6	0.85 (RHE)	2000	~ 0.5	[35]
PdNi/CNF	NaBH ₄	~ 0.45	-0.5 (Hg/HgO)	1800	~ 0.15	[36]
PdAg/rGO	GO/heat	0.7	-0.3 (Hg/HgO)	2100	0.4	[37]
PdCu	NaHB ₄	6.16	-0.3 (Ag/AgCl)	3000	0.25	[38]
PdCoNTs/CFC	Electrodeposition	1.5	0.77 (RHE)	600	0.2	[18]

^aThe electrochemistry tests were performed at a scan rate of 50 mV/s, ^bthe mass current density at the end of i-t test, CNF (carbon nanofiber), rGO (reduced graphene oxide), PVP (polyvinylpyrrolidone), NTs (nanotubes), CFC (carbon fiber cloth), SCE (saturated calomel electrode), RHE (reversible hydrogen electrode).

In addition to the high catalytic activity, excellent durability is crucial for the fuel cells as well. The electrocatalyst durability of Au₁Pd₁ NWs and commercial Pd/C toward ethanol electrooxidation was investigated with chronoamperometric tests. As shown in Fig. 5B, all the catalysts present a clear declining current density at the very beginning, and the current decay of Au_{0.5}Pd₁, Au₁Pd₁, Au₂Pd₁ NWs is much slower than that of commercial Pd/C and Au₀Pd₁ NWs. It can be concluded that introduction of Au improves the stability of the catalysts by forming the self-supported alloy networks. Furthermore, Au₁Pd₁ NWs possess the highest current density throughout the durability test and remain 1.41 A/mg_{Pd} catalytic activity after 4000 s test, which is much higher than most of the current reports summarized in Table 2. The high stability of Au₁Pd₁ NWs catalysts can be further confirmed by the CVs and TEM compared with commercial Pd/C before and after chronoamperometric tests. As shown in Fig. S5, no obvious change was observed on CVs of Au₁Pd₁ NWs after 4000 s i-t test, whereas that of commercial Pd/C showed evident decrease. Figure S6 shows the TEM images of the AuPd NWs before and after 4000 s endurance test in N₂-saturated 1 M KOH-1 M ethanol solution. The AuPd NWs show average diameter of 3.3-8.5 nm (close to the size before endurance test) and almost unchanged morphology with little aggregation because of the drying process. However, the Pd nanoparticles on the carbon aggregate together after the test (Figure S6D). All these results demonstrated the higher durability of the AuPd NWs than that of the commercial Pd/C catalyst. This improved stability of Au₁Pd₁ NWs is likely due to the introduction of Au and high structural stability of nanowire [39], which keeps the nanowire structure from dissolution and Ostwald ripening.

4. Conclusions

A facile and fast (within 5 min) strategy for three-dimensional (3D) AuPd alloy networks (NWs) synthesis was reported by co-reduction of HAuCl₄ and H₂PdCl₄ in aqueous solution using NaBH₄ as reducing reagent in the presence of sodium citrate (SC) at room temperature. SC plays crucial role for nanowire network formation and thus enhanced ethanol electrocatalytic activity of the AuPd catalyst. The AuPd NWs show composition-dependent activity and durability of EOR in alkaline solution, and Au₁Pd₁ NWs exhibit most efficient EOR catalytic activity with mass current density of 7.06 A/mg_{Pd}. Significantly, 49% of the mass current density (1.41 A/mg_{Pd}) on Au₁Pd₁ NWs can be remained after 4000 s i-t test. This facile synthesis and improved electrocatalysis make AuPd NWs nanostructure a promising catalyst for DEFCs and other electrocatalytic applications.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://>

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Figure Captions

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Fig. 5. (A) CV curves of the AuPd NWs with different Au/Pd ratios and commercial Pd/C catalyst in N₂-saturated 1 M KOH-1 M ethanol, at a scan rate of 50 mV/s. (B) Chronoamperometric curves of various catalysts in N₂-saturated 1 M KOH-1 M ethanol mixture at -0.3 V (vs. Ag/AgCl).