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

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HIGHLIGHTS

- A surfactant-free method leads to a clean surface.
- Sodium citrate plays significant role in structure and thus enhanced catalytic performance.
- AuPd NWs show high activity and duration towards ethanol electrooxidation.
- 49% of the initial current intensity (1.41 A/mg_{Pd}) remained after 4000s i-t test.

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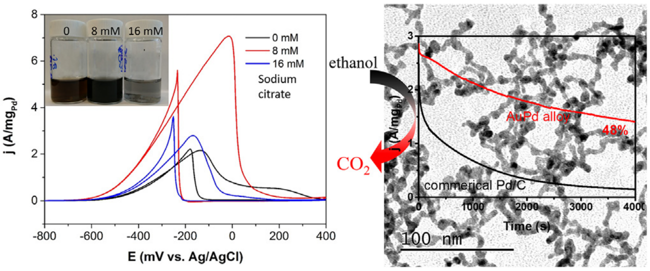
GRAPHICAL ABSTRACT



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 A/mg_{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.

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

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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-nano-raspberries 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 Au_1Pd_1 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%, $HAuCl_4 \cdot 3H_2O$), 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 MΩ 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 Cu Kα radiation ($\lambda = 0.154$ 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 $NaBH_4$ 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 $AuPd_0$, $AuPd_8$ and $AuPd_{16}$. The ratios of Au/Pd were also optimized by changing the volume of $HAuCl_4$ (0, 25 or 100 μL) in the aqueous solution containing 50 μl H_2PdCl_4 and 8 mM SC. Hereafter, the AuPd nanoparticles (Au_0Pd_1, $Au_{0.5}Pd_1$, Au_1Pd_1, and Au_2Pd_1 NWs) were prepared from $HAuCl_4/H_2PdCl_4$ 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 $Au_{0.5}Pd_1$, Au_1Pd_1, and Au_2Pd_1 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 μm Al_2O_3 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 μL 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 N_2-saturated 1 M KOH-1 M ethanol until stable CVs were obtained. Durability tests were performed in N_2-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

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 3–8 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-G) 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