Facile Synthesis of Highly Active PdAu Nanowire Networks as Self-Supported Electrocatalyst for Ethanol Electrooxidation

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S *Supporting Information*

ABSTRACT: In recent years, direct ethanol fuel cells (DEFCs) are attracting increasing attention owing to their wide applications. However, a significant challenge in the development of DEFC technology is the urgent need for highly active anode catalysts for the ethanol oxidation reaction. In this work, a facile and reproducible method for the high-yield synthesis of PdAu nanowire networks is demonstrated. The whole synthetic process is very simple, just mixing Na_2PdCl_4, $HAuCl_4$, and KBr in an aqueous solution and using polyvinylpyrrolidone as a protective reagent while sodium borohydride as a reductant. The whole synthetic process can be simply performed at room temperature and completed in 30 min, which can greatly simplify the synthetic process and lower the preparation cost. Electrochemical catalytic measurement results prove that the as-prepared catalysts exhibit dramatically enhanced electrocatalytic activity for ethanol electrooxidation in alkaline solution. The facile synthetic process and excellent catalytic performance of the as-prepared catalysts demonstrate that they can be used as a promising catalyst for DEFCs.

KEYWORDS: *palladium, gold, nanowire networks, ethanol, electrooxidation*
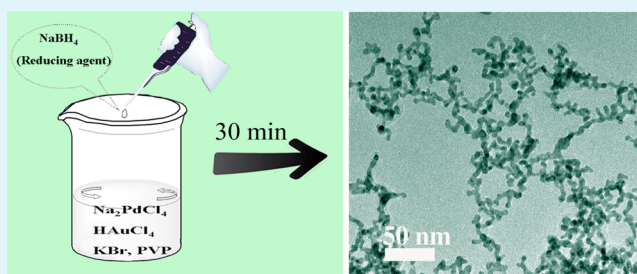
1. INTRODUCTION

In recent years, as one of the promising future candidates for the replacement of the combustion-based energy sources, direct fuel cells (DFCs) have been receiving increasing attention due to their cleanness and high efficiency.[1,2] Among the different types of DFCs, direct ethanol fuel cells (DEFCs), especially DEFCs operating in alkaline conditions, are attracting special attention because of their several unique advantages. Firstly, ethanol has a lower toxicity but possesses a higher theoretical energy density (8.01 kW·h kg^{-1}) than methanol (6.09 kW·h kg^{-1}) and formic acid (1.740 kW·h kg^{-1}).[3,4] Secondly, ethanol is a renewable source that can be easily obtained in large quantities from the chemical industry and fermentation of biomass. Thirdly, DEFCs operating in alkaline conditions can greatly improve the ethanol oxidation kinetics and reduce the risk of corrosion of materials for high durability.[5,6] However, a significant challenge remaining in the development of DEFCs is the relatively low catalytic activity and poor durability of the widely used state-of-the-art commercial Pd/C anode catalyst, which will severely prevent their ultimate commercialization.[7−11] To this end, a wealth of efforts have been devoted to the development of highly active electrocatalysts with long-term stability for DEFCs.[12−14]

On the other hand, the rational design of bimetallic nanostructures has attracted particular interest during the past few years, because these materials are highly promising catalysts.[15−17] Bimetallic nanocrystals often show advanced catalytic activity compared with their monocomponent counterparts, due to the synergistic effect and electronic effect among the different components.[18−20] In comparison with their counterparts Pt, Pd-based catalysts have been proved to be promising candidates for the future anode electrocatalyst for alkaline DEFCs due to their relatively good catalytic activity and relatively lower price.[21−23] Pioneering studies revealed that the shape, size, and composition of the catalysts are the important factors that govern their electrocatalytic performance.[24−28] Therefore, finely manipulating the morphology and composition of Pd-based catalysts can offer a great opportunity to achieve enhanced catalytic performance and higher utilization efficiency of Pd. A prominent example is PdAu bimetallic nanocrystals; recent reports have demonstrated that noteworthy enhancement of electrocatalytic performance for ethanol electrooxidation can be achieved by the incorporation

of Au into Pd and controlling their morphology,[29−31] for example, convex polyhedral Au@Pd core−shell nanocrystals,[29] highly branched concave Au/Pd bimetallic nanocrystals,[30] PdAu bimetallic nanoparticles on graphene,[32] etc. Among these developed materials, one-dimensional nanostructures such as nanowires have received special attention due to their special catalytic performance deriving from their special structure. Wong's group has successfully synthesized PdAu nanowires by using two different methods, and superior electrocatalytic performance for the oxygen reduction has been obtained.[33,34] Dong et al. prepared PdAu nanowires through a hard-template method, which presents superior catalytic activity for ethanol oxidation.[35] Despite these successful demonstrations, it should be pointed out that their mass activity (in terms of Pd) for the ethanol electrooxidation is still not very satisfactory. Furthermore, most of the methods used to prepare these catalysts are relatively complicated. Thus, it is still highly desired and technologically important to develop a simple and practical method for the synthesis of novel Pd-based bimetallic electrocatalysts with high activity and durability for DEFCs.

Herein, we demonstrate a very simple and efficient route to synthesize PdAu bimetallic nanowire networks (NNWs) with high yield in aqueous solution. In a typical synthesis, 30 mg of polyvinylpyrrolidone (PVP), 15 mL of water, 0.2 mL of 0.06 mol L^{-1} Na$_2$PdCl$_4$, 0.12 mL of 0.1 mol L^{-1} HAuCl$_4$, and 0.8 mL of 2.5 mol L^{-1} KBr were mixed together and stirred to form a homogeneous solution. Then, 9 mL of 0.5 mg mL^{-1} freshly prepared NaBH$_4$ aqueous solution was slowly added to the mixture. After reacting for 30 min, the products can be obtained by centrifuging and washing with water several times. The developed nanomaterials can provide better opportunities for their practical application in DEFCs due to their several advantages: (a) The procedure for the synthesis of PdAu NNWs can be performed at room temperature, and the whole process can be simply completed in 30 min, which can greatly simplify the synthetic process and lower the preparation cost. (b) The as-prepared PdAu NNWs can serve as a self-supported electrocatalyst without needing any carbon supports, thus avoiding the corrosion and oxidation of the carbon supports in the harsh operating environment, which would lead to the quick loss of the electrocatalytic activity of the catalysts.[9,11,36−38] (c) The electrocatalytic measurement results prove that PdAu NNWs exhibit significantly enhanced catalytic performance than the commercial Pd/C catalyst toward ethanol electrooxidation in alkaline media.

2. EXPERIMENTAL SECTION

2.1. Materials. Polyvinylpyrrolidone (PVP·K30, molecular weight: 50 000−58 000), chloroauric acid, potassium bromide, and sodium borohydride were obtained from Beijing Chemical Corp (China). Commercial Pd/C (20 wt % on activated carbon), sodium tetrachloropalladate (II), and commercial Pt/C were purchased from Alfa Aesar. All chemicals used were of analytical grade and used without further purification. Milli-Q ultrapure water (Millipore, ≥18.2 MΩ·cm) was used throughout the experiments.

2.2. Apparatus. Transmission electron microscopy (TEM) was performed on a HITACHI H-600 Analytical TEM with an accelerating voltage of 100 kV. High-resolution transmission electron microscopy (HRTEM) measurements, high-angle annular dark-field scanning TEM (HAADF-STEM), and elemental mapping were made on a JEM-2100F high-resolution transmission electron microscope operating at 200 kV. An XL30 ESEM scanning electron microscope (SEM) equipped with an energy-dispersive X-ray analyzer was used to determine the morphology and composition of the as-prepared materials. The exact composition of the as-prepared PdAu NNWs catalyst was determined by an inductively coupled plasma optical emission spectrometer (ICP-OES, X Series 2, Thermo Scientific USA). XRD patterns were recorded on a D8 ADVANCE (BRUKER, Germany) diffractometer using Cu−Kα radiation with a Ni filter (λ = 0.154059 nm at 30 kV and 15 mA). X-ray photoelectron spectroscopy (XPS) measurement was performed on an ESCALAB-MKII spectrometer (VG Co., United Kingdom) with Al Kα X-ray radiation as the X-ray source for excitation. All the electrocatalytic measurements were performed with a CHI 832B electrochemical workstation (Chenhua Instruments Corp, Shanghai, China). A conventional three-electrode cell was used, including a KCl saturated Ag/AgCl electrode as reference electrode, a platinum wire as counter electrode, and a glassy carbon electrode (GCE) with a diameter of 4.5 mm as working electrode, respectively.

2.3. Preparation of PdAu Nanowire Networks. To synthesize PdAu NNWs, 30 mg of PVP, 15 mL of water, 200 μL of 60 mmol L^{-1} Na$_2$PdCl$_4$, 120 μL of 100 mmol L^{-1} HAuCl$_4$, and 0.8 mL of 2.5 mol L^{-1} KBr were mixed together and stirred to form a homogeneous solution. Then, 9 mL of 0.5 mg mL^{-1} NaBH$_4$ was slowly added to the mixture. After reacting for 30 min, the products were collected by centrifugation and washed several times with water. To prepare Pd$_2$Au$_1$ NNWs, HAuCl$_4$ was changed to 60 μL, and the volume of NaBH$_4$ was reduced to 7 mL. Similarly, to prepare Pd$_1$Au$_2$ NNWs, Na$_2$PdCl$_4$ was reduced to 100 μL, and then 4 mL of 1 mg mL^{-1} NaBH$_4$ was added.

2.4. Electrochemical Catalytic Measurements. Before the experiment, the GCE was polished carefully with 1.0, 0.3, and 0.05 μm alumina powder and rinsed with deionized water, followed by sonication in ethanol and Milli-Q ultrapure water successively. For the electrooxidation of ethanol test, commercial Pd/C or as-prepared catalyst solution was dropped on the surface of the GCE and dried with an infrared lamp carefully; the loading mass of Pd of all the prepared PdAu NNWs and commercial Pd/C was 5.1 μg cm^{-2}. Also, the loading mass of Pt for the commercial Pt/C catalyst was 5.1 μg cm^{-2}. Then, 4 μL of Nafion (0.02%) was coated on the surface of the above material modified GCE and dried before the electrochemical experiments. All the electrochemical tests were carried out on a CHI 832B electrochemical workstation, Chenhua Instruments Corp (Shanghai, China).

3. RESULTS AND DISCUSSION

The morphology and structure of the as-prepared samples were initially characterized by transmission electron microscopy (TEM). Figure 1A,B,C shows the typical TEM images of the as-prepared PdAu NNWs with different magnifications, demonstrating that the products consist of uniform nanowire networks with high yield. The average diameter of the PdAu NNWs is about 5 nm, and the length of the prepared NNWs is observed to be several tens of nanometers. The high-resolution TEM (HRTEM) image (Figure 1D) shows that the PdAu NNWs are in the polycrystalline state, of which the d spacing is observed to be 0.23 and 0.2 nm, which can be assigned to the face-centered cubic (fcc) (111) and (200) planes of PdAu alloy, respectively. The nanowire networks' nanostructure was further visualized by high-angle annular dark-field scanning TEM (HAADF-STEM) (Figure 1E). Elemental mapping revealed that Pd and Au elements were uniformly distributed throughout the entire nanostructures, confirming the formation of homogeneous PdAu alloy nanostructures (Figure 1F−H). The energy-dispersive X-ray spectrum (EDS) was used to determine the composition of the prepared products (Figure S1, Supporting Information). The atomic ratio of Pd/Au is determined to be 1:1; the result is in accordance with the inductively coupled plasma optical emission spectrometer (ICP-OES) result as well as the mole ratio of the added
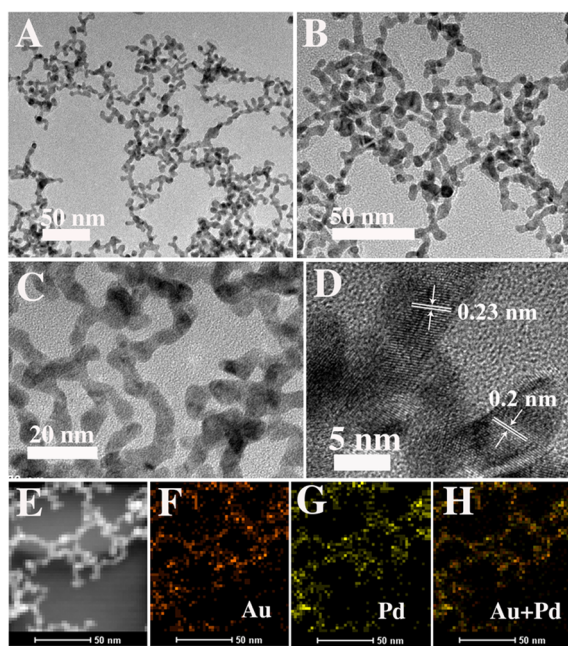
Figure 1. (A, B, C) Typical TEM images of the prepared PdAu NNWs with different magnifications. (D) High-resolution TEM image of PdAu NNWs. (E−H) HAADF-STEM and elemental mapping of the prepared PdAu NNWs.

precursors. Interestingly, two other types of PdAu NNWs with different compositions can also be prepared just by slightly changing the experimental process without deteriorating the nanowire network morphology (Figure 2). The X-ray
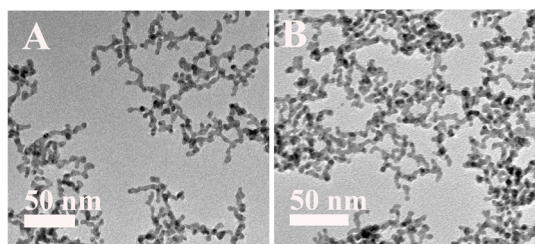

Figure 2. TEM images of the two other types of PdAu NNWs with different compositions: Pd_2Au_1 (A) and Pd_1Au_2 (B).

diffraction (XRD) patterns of the products (Figure 3) further confirmed their alloyed fcc crystal nanostructures. There is only a single phase that can be observed in the XRD pattern and the diffraction peaks of the as-synthesized PdAu nanocrystals are located between the diffraction peaks expected from pure bulk Pd (JCPDS No. 65-2867) and Au (No. 04-0784), which indicates their high degree of crystallinity. The surface chemistry state of as-prepared bimetallic PdAu NNWs was characterized by using X-ray photoelectron spectroscopy (XPS). Figure 4 shows the Pd 3d and Au 4f core-level spectra of the PdAu NNWs. It can be noted clearly that both of the binding energies (BEs) of Pd and Au are shifted to higher values with the Au/Pd atomic ratios increased. This result is consistent with the previously reported observations.[39] The shift of the BE of both Pd and Au in PdAu NNWs indicates the evident changes in the electronic structure; the result may be due to intra-atomic charge transfer or interatomic charge transfer between Au and Pd when they are in the alloyed
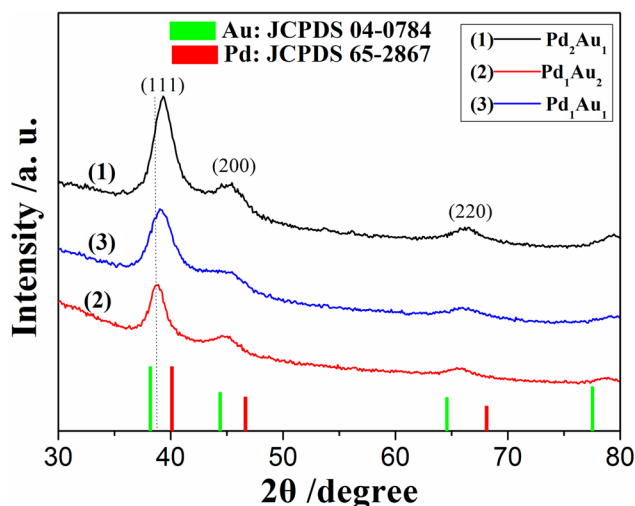

Figure 3. XRD patterns of the PdAu NNWs with different compositions: Pd_2Au_1 (1), Pd_1Au_2 (2), and Pd_1Au_1 (3). The intensity and position for Au and Pd references were taken from the JCPDS database.

structure, which is similar to the observations of the PtAu alloys reported by Aronson's group.[40]

To find the most important factor that influences the morphology of the final products, a set of control experiments were carried out. The appropriate concentration of $NaBH_4$ favors the formation of nanowire networks; when their concentration increased to 1 mg mL^{-1}, the products tended to aggregate, which may derive from the accelerated reaction rate (Figure S2, Supporting Information). Without adding KBr, a mixture containing porous and small nanoparticles can be obtained (Figure S3, Supporting Information), whereas, when the amount of KBr was increased to 4 mL, the products became aggregated (Figure S4, Supporting Information). The result indicates that bromide ions played an important role in the formation of PdAu NNWs, which might be attributed to the following reasons. Firstly, Br^- can serve as a coordination ligand to promote the formation of complexes $[PdBr_4]^{2-}$ and $[AuBr_4]^-$ in aqueous solution, thus reducing the rate of reduction.[41−43] Secondly, as revealed by the previous studies, Br^- can specifically bind onto the (100) facets of fcc nanocrystals, thus leading to the restricted growths of (100) facets, which favors the anisotropic growth,[44−49] while Br^- also has a corrosion effect.[27,46,47] The co-effect of the these factors might ultimately lead to the anisotropic growth of nanowire networks.

Inspired by the attractive nanostructures of the as-prepared PdAu NNWs, we investigated their catalytic activity towards ethanol electrooxidation with an electrochemical measurement system and further compared them with a commercial Pd/C catalyst. Mass activity was used to evaluate the catalytic activity of the prepared catalyst. Electrooxidation toward ethanol was carried out in an aqueous solution containing 1 mol L^{-1} potassium hydroxide and 1 mol L^{-1} ethanol, using a cyclic voltammetry measurement technique, sweeping from −0.8 to 0.4 V at a scan rate of 50 mV s^{-1}. On the basis of the assumption that the charge density for the formation of a fully covered $Pd(OH)_2$ monolayer was 430 μC cm^{-2},[50] the electrochemically active surface area (ECSA) of the catalyst can be estimated. The ECSA of PdAu NNWs is 18 m^2 g^{-1}, lower than 47 m^2 g^{-1} of commercial Pd/C (Figure S5,
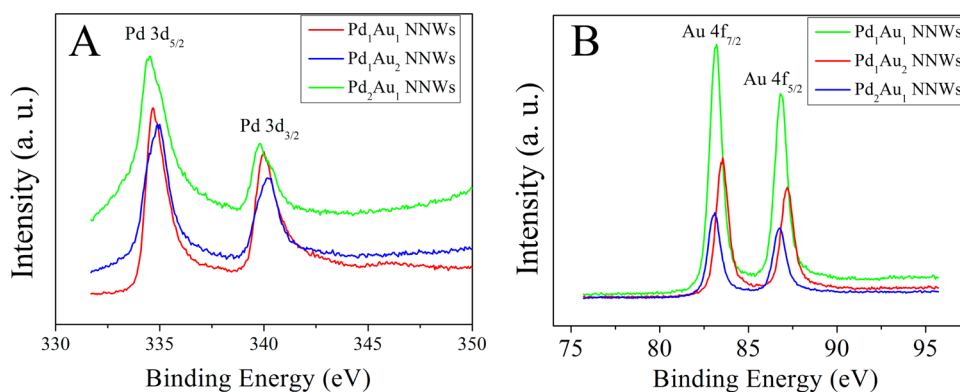
Figure 4. XPS spectra of as-prepared PdAu NNWs: (A) Pd 3d and (B) Au 4f.
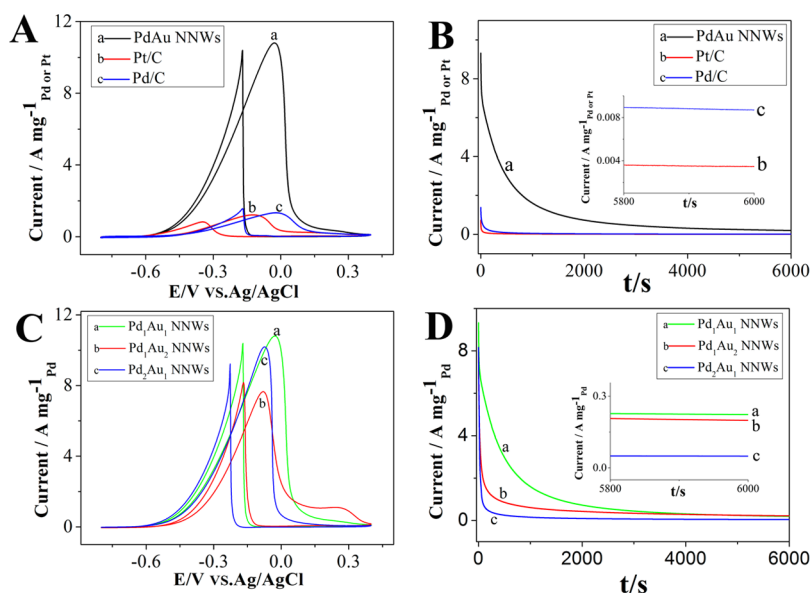

Figure 5. Mass activity of PdAu NNWs, Pd/C, and Pt/C toward ethanol electrooxidation (A), current−time curves of PdAu NNWs, Pd/C, and Pt/C recorded at −0.1 V (B), mass activity of PdAu NNWs with different compositions toward ethanol electrooxidation (C), and current−time curves of PdAu NNWs with different compositions recorded at −0.1 V (D) in a solution containing 1 mol L^{-1} ethanol + 1 mol L^{-1} potassium hydroxide.

Supporting Information). Figure 5A shows the mass activity of the two catalysts toward ethanol electrooxidation. The forward anodic peak value of mass activity for PdAu NNWs is 10.8 A mg^{-1}, which is much higher than 1.5 A mg^{-1} for commercial Pd/C and 1.3 A mg^{-1} (in terms of the Pt mass) for the Pt/C catalyst. The results are also higher than 2.25 A mg^{-1} for Pd$_3$Au$_1$ bimetallic nanoparticle nanotubes,[51] and 3.5 A mg^{-1} for core/shell Ni@Pd nanoparticles supported on carbon nanotubes.[52] Similarly, the backward peak current is also much higher than the commercial Pd/C catalyst. The excellent performance of electrocatalytic oxidation of ethanol by the PdAu NNWs is further evaluated by comparing with other samples reported recently, and the corresponding results are presented in Table S1 (Supporting Information). It can also be noted from Figure 5A that the onset potential toward ethanol electrooxidation of PdAu NNWs is lower than that of the commercial Pd/C, indicating the enhancement in the kinetics of the ethanol electrooxidation reaction.

The stability of PdAu NNWs toward ethanol electrooxidation was investigated by a long-term current−time measurement technique, which was carried out at −0.1 V for 6000 s in a solution containing 1 mol L^{-1} potassium hydroxide and 1 mol L^{-1} ethanol (Figure 5B). As it can be learned from

Figure 5B, the current decay for the reaction on the PdAu NNWs is significantly slower than that on the commercial Pd/C electrocatalyst, indicating its better tolerance toward ethanol electrooxidation. After 6000 s, the residue current of PdAu NNWs is much higher than that of commercial Pd/C. The results from both activity and stability studies indicate that PdAu NNWs possess outstanding catalytic performance for ethanol electrooxidation in alkaline media.

In order to investigate the optimum Pd/Au ratio of PdAu NNWs with the best catalytic activity, we also examined the electrocatalytic activity of two other types of PdAu NNWs with different compositions. Similarly, the ECSA of Pd$_2$Au$_1$ and Pd$_1$Au$_2$ NNWs was calculated to be 28 and 9.1 m^2 g^{-1} respectively, suggesting that the ECSA decreased with an increase of the Au content, which may be due to the lower electrochemical activity of Au than Pd and that the incorporation of Au will lead to the less-exposed surface Pd atoms. The result is in accordance with the reported observations.[53] The electrocatalytic measurement results show that the Pd$_1$Au$_1$ and Pd$_2$Au$_1$ NNWs maintain essentially the same activity in the onset region of the ethanol oxidation curve, and PdAu NNWs possess the highest peak mass activity when the mole ratio between Pd and Au is at 1:1 (Figure 5C), which

is consistent with the previously reported results.[54] It can also be noted from Figure 5D that PdAu NNWs possess the significantly slowest current decay during the first 2000 s when the mole ratio between Pd and Au is at 1:1 (Figure 5C), suggesting that Pd_1Au_1 NNWs possess the best tolerance ability for ethanol electrooxidation. From Figure 5D, it can also be found that Pd_1Au_2 NNWs present higher current decay values than Pd_2Au_1 NNWs. The results may be due to that the resistance ability to the accumulation of poisonous intermediates of Au is stronger than that of Pd. As it was revealed by many previous studies, the electrocatalytic performance of the catalysts depended on their shape, size, and composition.[24−28] Here, the catalytic measurement results proved it again that composition is a very important factor that governs the catalytic performance of the catalyst. The synergetic effect between the different components (Au and Pd) should be responsible for this result.

The excellent electrocatalytic performance of PdAu NNWs for ethanol oxidation should be attributed to the following reasons. (a) The contribution of the special nanostructures: The nanowire networks can possess the advantages of the one-dimensional structure such as improved electron transport characteristics during the catalysis as a result of the path-directing effects of the structural anisotropy.[55,56] Also, the small diameter of the prepared NNWs offers a great opportunity to provide more active sites. What's more, the self-supported materials can avoid the severe corrosion and oxidation of the carbon supports.[9,11,36−38] (b) The important role of Au: A mechanism of the ethanol electrooxidation reaction process on Pd in alkaline media has been proposed by Liang et al.[57] It is believed that a CH_3CO_{ads} intermediate is formed on the Pd catalyst in the alkaline medium, and its reaction with OH_{ads} is the rate-determining step. The co-metals Au on the Pd can provide an opportunity to improve the adsorption of OH_{ads} onto the surface of the catalyst and thus activate the catalyst surface and finally help to enhance the ethanol oxidation process. These facts may can be explained based on the d-band center theory similar to the PdAg alloy, which has been well-studied by Wang's group.[4] That is, because the lattice constant of Pd is smaller than that of Au, the addition of Au to Pd will cause a tensile strain in the structure of surface Pd and shift up the d-band center of Pd. The facts can be supported by the XPS results that the binding energies of Pd shift to higher values with the Au/Pd ratios increased. This effect will improve the adsorption of OH_{ads} onto the surface of the catalyst and weaken the interaction between the adsorbed intermediate species CH_3CO_{ads}, thus improving the ethanol oxidation process.[4,54] The above two important factors should be responsible for the high electrocatalytic performance of PdAu NNWs.

4. CONCLUSION

In summary, we have successfully developed a facile and reproducible method for the high-yield synthesis of bimetallic PdAu nanowire networks with an alloyed structure in aqueous solution. The as-prepared catalysts exhibit dramatically enhanced activity and stability for ethanol electrooxidation in alkaline conditions, demonstrating that they can be used as an effective electrocatalyst for direct ethanol fuel cells. In light of the important role of their special nanostructures in catalysis and their facile synthetic process, the as-synthesized catalysts may also find other applications in fuel cells, such as formic acid oxidation, methanol oxidation, oxygen reduction reaction, etc.

ASSOCIATED CONTENT

Ⓢ Supporting Information

SEM images and EDS of the prepared PdAu NNWs, TEM and optical images of the control experiment results, cyclic voltammetry curves of commercial Pd/C catalyst and PdAu NNWs in H_2SO_4 solution, and ethanol oxidation behaviors of various Pd or Pd-based electrocatalyst modified glassy carbon electrodes, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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