#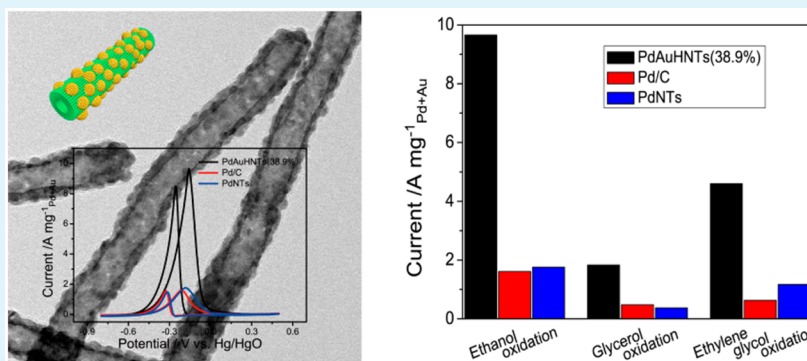 Controlled Synthesis of Au-Island-Covered Pd Nanotubes with Abundant Heterojunction Interfaces for Enhanced Electrooxidation of Alcohol

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S *Supporting Information*

ABSTRACT: Here, we, for the first time, synthesized Pd nanotubes covered by high-density Au-islands, in which abundant exposed Pd−Au heterojunction interfaces are present and the content of element Au can be easily controlled. The optimized nanostructures show remarkably enhanced activity for catalyzing different alcohols in alkaline media than commercial Pd/C. The mass activity is 9.66, 1.83, and 4.60 A mg_{metal}^{-1} toward the electrooxidation of ethanol, glycerol, and ethylene glycol in alkaline media, which is about 6, 4, and 7 times that of Pd/C, respectively. Additionally, a model was proposed to explain the relationship between the structure and the catalytic activity.

KEYWORDS: high-density, heterojunction interface, heterostructure, electrocatalyst, alcohol

■ INTRODUCTION

Developing electrochemical energy conversion devices has become increasingly important for resolving the problems of energy crisis and environment pollution.[1−5] Direct alcohol fuel cells (DAFCs) have received great attention worldwide owing to their high energy density, zero/low environment pollution of alcohol fuel and easy availability and storage.[6−8] For example, ethanol has a considerably high theoretical energy density (8 kW·h kg^{-1}) and can be obtained in large quantity directly from the fermentation of biomass; while ethylene glycol (EG) and glycerol have even higher energy density and availability from biomass, as well as low regulation violation.[9−12]

DAFCs under alkaline condition have significantly improved alcohol oxidation kinetics and reduced risk of catalyst corrosion.[13−15] More importantly, relatively less expensive palladium (Pd) can be used as the leading catalyst for alcohol electrooxidation instead of platinum (Pt) in basic media.[16−18] Even so, further improvement of the catalytic activity and durability of Pd catalyst is still quite critical as metal Pd is also a

rare noble metal and the power density of the current DAFCs still can not meet the practical requirement.[19]

In recent years, numerous studies have been conducted to achieve better catalytic performance through structural design of Pd-based materials. Much work in this area has been focused on heterogeneously structured multimetallic systems, especially core−shell structured materials.[4,7,13] Besides, heterogeneous metal nanocrystals constituted by different metal domains have also attracted considerable attention recently because their unique catalytic properties resulted from the heterojunction interfaces of different metal components.[20,21] Recent studies have shown that the exposed interface between different metals is responsible for the enhancement of catalytic activity.[22−25] However, as far as we know, the so-far reported Pd-based multimetallic systems mostly are of very limited density of heterogeneous metal interface. Therefore, it is highly necessary
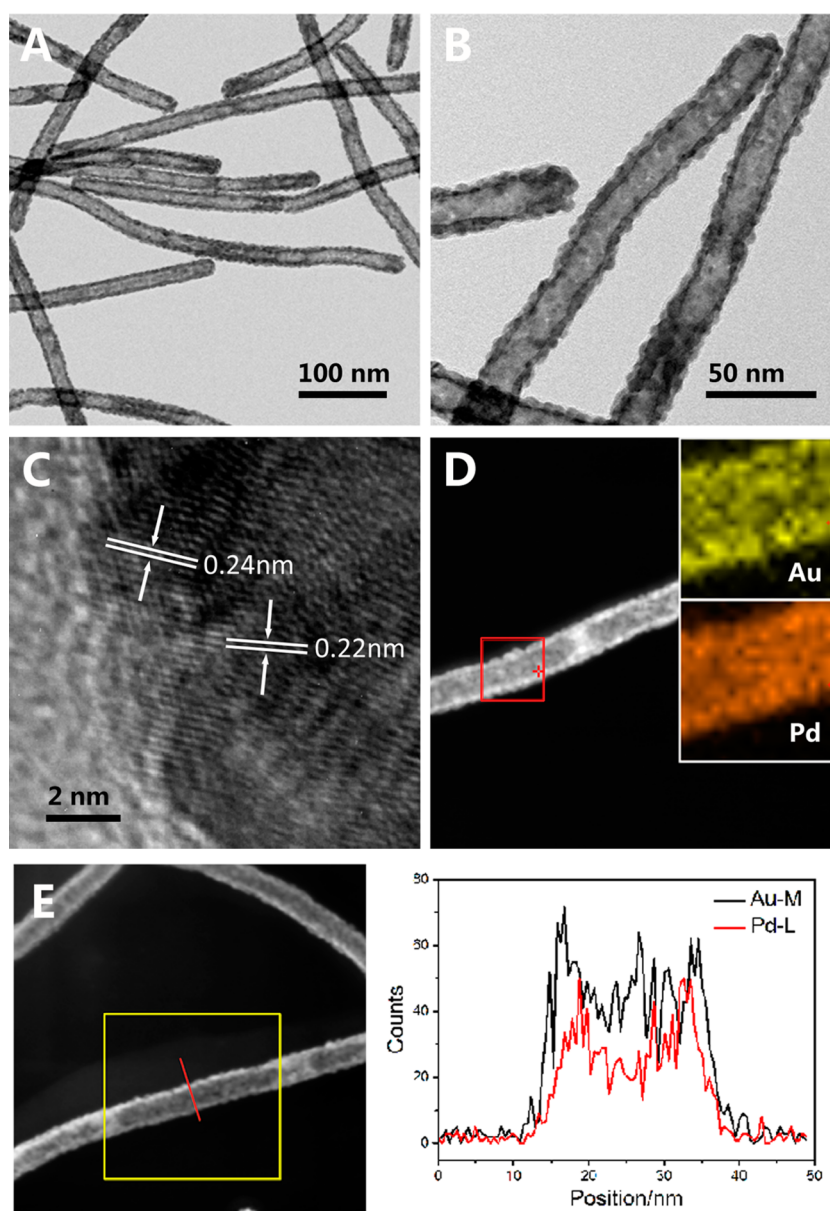
Figure 1. (A, B) TEM images and (C) HRTEM image of PAHNTs. (D) HAADF-STEM-EDX mapping image of PAHNTs (the ratio of Au in weight is 48.5%). (E) The EDX line scanning profiles of the corresponding line in the nanotubes for Pd and Au.

to synthesize new heterostructures with a large number of interfaces to further improve the catalytic activity of Pd-based catalyst.

Here, we report a facile approach to synthesize Pd−Au heterogeneous nanotubes (PAHNTs) using Te nanowires as the template, in which Pd nanotubes are covered by high-density Au nanoislands. It is noteworthy that the structure is different from that of all previously reported materials which used the same template in preparation, including composition and morphology. In the unique structure, nanoislands were designed on one-dimensional nanotubes, which provides the possibility to form rich Pd−Au heterogeneous junctions. Besides, the one-dimensional structure enables the material to be used as a self-supported electrocatalyst to avoid the negative effect from the support.[26−29] By varying the Au/Pd ratio in the precursor, PAHNTs with different Au contents were prepared and the effect of Au content on the electrocatalytic properties for alcohol oxidation was investigated in alkaline media. The

PAHNTs with an Au weight content of 38.9%, at which the largest Pd/Au heterogeneous junction area could be achieved, showed the best electrocatalytic performance for alcohol oxidation, and its mass activity was about 6, 4, and 7 times that of commercial Pd/C for ethanol, glycerol and EG electrooxidation, respectively. Our study not only demonstrates the controllable synthesis of the novel PdAu heterostructures with abundant heterojunctions, but also provides a new route for quantitatively studying the catalytic property of hetero-structures. In addition, the optimized PAHNTs show great application potential for alcohol oxidation in basic DAFCs.

■ EXPERIMENTAL SECTION

Reagents and Materials. Hexadecyltrimethylammonium bromide (CTAB, 99%), nafion (5%), and sodium dodecyl sulfate (SDS, 99%) were supplied by Sigma-Aldrich. Tellurium dioxide (TeO$_2$, 99.99%) was supplied by Aladdin Chemistry Co., Ltd. Potassium hydroxide (85%, GR), hydrazine monohydrate (85%, AR), ethanol (AR),

glycerol (AR), ethylene glycol (EG, AR), polyvinylpyrrolidone (PVP), tetrachloroauric (III) acid hydrate (HAuCl$_4$·4H$_2$O, AR), and palladium(II) chloride (PdCl$_2$, AR) were provided by Sinopharm Chemical Reagent Co., Ltd. The commercial Pd/C catalyst (20 wt %) from BASF was used as the reference sample. Ultrapure water using in the experiment having a conductivity of 18.25 MΩ cm, and all chemicals using in the experiments without further purification.

Characterization. Transmission electron microscopy (TEM) images were obtained by a JEM-2100F high-resolution transmission electron microscopy. A FEI TECNAIF-30 microscope with a high-angle annular dark field (HAADF) function was used for acquiring elemental maps and cross-sectional line profiles. All nanostructures samples dispersing in aqueous solution were deposited a single drop on copper grids for TEM analysis. X-ray diffraction (XRD) characterization was carried out by a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) measurement was performed by a Thermo Fisher ESCALAB 250Xi spectrophotometer with Al Ka radiator, and the data were fitted using the software XPSPEAK.

Synthesis of Pd−Au Heterogeneous Nanotubes (PAHNTs). First, Te NWs were synthesized through a previous method reported by Chang et al.[30] Then, Te NWs (∼10 umol) from the previous experiment were dispersed in 10 mL PVP solution (1 mg mL^{-1}) under constant magnetic stirring at 25 °C. After 15 min, PdCl$_2$ solution (5 mM, 0.4 mL) was added to the solvent containing Te NWs. The color of the solution changed from blue to gray-black. After another 15 min, a certain amount of HAuCl$_4$ solution (5 mM) was added to the solvent, which was centrifuged after 10 min. When the amounts of HAuCl$_4$ solution used in the synthesis were 20, 40, 60, and 80 mL, PAHNTs (14.8%), PAHNTs (25.9%), PAHNTs (38.9%), and PAHNTs(48.5%) were obtained, respectively.

Electrochemical Measurements. The glassy carbon (GC) electrode was polished carefully using 1.0, 0.3, and 0.05 μm alumina powder successively before the electrochemical test, then ultrasonic and rinsed with deionized water. For all the electrochemical tests, aqueous solution containing catalysts with a metal load of 0.36 μg was dropped on the electrode. After drying at room temperature, 3 μL of 0.1% Nafion was dropped on each electrode and dried before electrochemical experiments. All electrochemical tests were operated in a three-electrode cell containing a platinum wire counter electrode, a Hg/HgO reference electrode, and a GC electrode (5 mm in diameter).

■ RESULTS AND DISCUSSION

The transmission electron microscope (TEM) image of Te NWs is shown in Figure S1. The diameter and the length are about 16 and 420 nm, respectively. Pd NTs could be obtained when no Au precursor was used in the reaction. The TEM image of Pd NTs (Figure S2) shows that they have a similar size with Te NWs. A typical TEM image of PAHNTs is shown in Figure 1A. Obviously, the centers of them are brighter than the edges, implying that the PAHNTs are hollow structures. The magnified TEM image in Figure 1B shows that the shell of the nanotubes is covered by a lot of dense and regular particles, and there are at least 80 particles in a length of 100 nm. High-resolution TEM (HRTEM) image (Figure 1C) of the structure demonstrates that the adjacent lattice fringes of the edged particles and the inner part are approximately 0.24 and 0.22 nm, which correspond to the lattice spacing of (111) planes of face-centered-cubic (fcc) Au and Pd, respectively. Figure 1D shows the high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) of the structure. The elemental mapping shows an extensive distribution of Au and Pd. Additionally, the energy-dispersive X-ray spectrum (EDS) performed on the structure (Figure S3) shows that they are composed of Pd and Au basically. The cross-sectional line profiles (Figure 1E) of the structure demonstrate that it is a

hollow tube and element Au is distributed on the surface of Pd nanotube.

The X-ray diffraction (XRD) patterns of the products (Figure 2) further confirms their fcc Pd and Au crystal
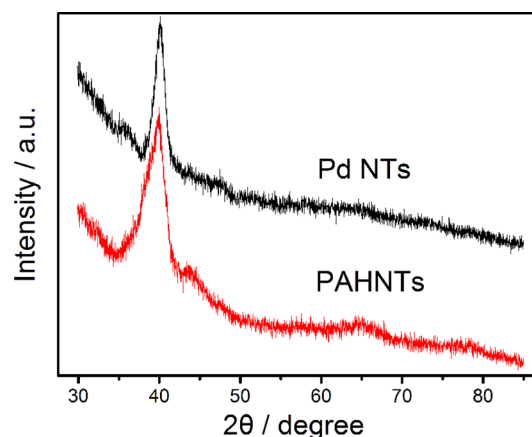

Figure 2. XRD of PAHNTs and Pd NTs.

nanostructures. Compared with Pd NTs, the PAHNTs display an asymmetrical and broader diffraction peak resulted from the accumulation of the peaks of crystal Au and Pd, revealing that they are not alloy. The nonalloy nature of the PAHNTs is also suggested by the X-ray photoelectron spectroscopy (XPS) results shown in Figure S4. The binding energies of Pd in the PAHNTs and Pd NTs are very close, which is obviously different from that in the PdAu alloy.[31]

By controlling the amount of the precursors in the synthesis, we obtained four types of PAHNTs with different ratios of Pd and Au, and their TEM images are shown in Figure S5. The XPS spectra of Pd 3d for PAHNTs and Pd NTs are shown in Figure S6, which are divided into two curves. The peaks observed at relatively lower binding energies represent Pd^0 species and those at relatively higher binding energies represent Pd^{II} species. Obviously, Pd^0 is the predominant species and its ratio becomes larger with the increase of Au ratio. Inductively coupled plasma optical emission spectrometer (ICP-OES) analysis shows that the ratios of Au in weight in the four PAHNTs are 14.8%, 25.9%, 38.9%, and 48.5%, respectively. These samples are designated as PAHNTs(14.8%), PAHNTs(25.9%), PAHNTs(38.9%), and PAHNTs(48.5%) hereafter.

The electrocatalytic activities of the four PAHNTs were assessed by cyclic voltammetry (CV) from −0.8 to 0.5 V in 1.0 M potassium hydroxide at first. Commercial Pd/C and Pd NTs were tested under the same conditions for comparison. All electrode surfaces have a metal loading of 1.84 ug cm^{-2} in the test. Figures S7 and S8 show the typical CV curves of them in N$_2$-saturated 1.0 M KOH solution with a scan rate of 50 mV s^{-1}. PAHNTs present reduction in the peaks of palladium oxides, which are between −0.3 and −0.2 V in the negative scan.

We then investigated their electrocatalytic activity toward ethanol oxidation in alkaline media. Mass activity was used to evaluate their catalytic activities in the study. Figure 3A shows the cyclic voltammograms (CV) of the four PAHNTs in 1.0 M KOH and 1.0 M ethanol at a scan rate of 50 mV s^{-1}. The result shows that PAHNTs (38.9%) possess the best activity (9.66 A mg$_{Pd+Au}$$^{-1}$). As shown in Figure 3B, the mass activities of
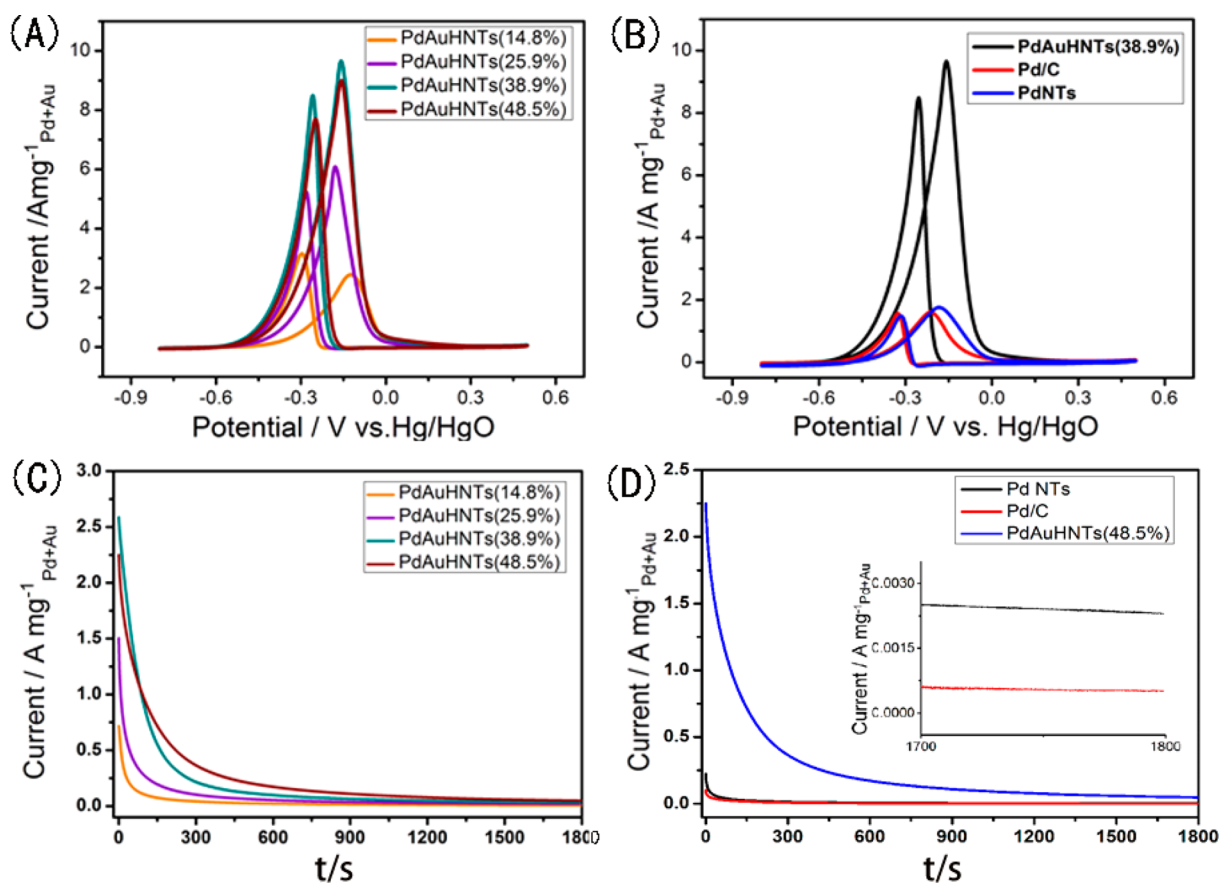
Figure 3. CV curves of (A) PAHNTs with different contents of element Au, (B) PAHNTs (38.9%), commercial Pd/C and Pd NTs for ethanol electrooxidation. Current−time curves of (C) PAHNTs with different contents of element Au, (D) PAHNTs (38.9%), commercial Pd/C and Pd NTs recorded at −0.2 V. The inset is the magnified image of the final test range. All the measurements were conducted in 1.0 M KOH + 1.0 M ethanol.

commercial Pd/C and Pd NTs are 1.61 and 1.76 A mg_{Pd}^{-1}, respectively. All the PAHNTs have higher activities than commercial Pd/C and Pd NTs, though the activities of other PAHNTs in the study are obviously lower than that of PAHNTs (38.9%). Particularly, the activity of PAHNTs (38.9%) is 6 times that of Pd/C and the onset potential in the forward scan exhibits a negative shift for PAHNTs (38.9%).

The stability of these PAHNTs was investigated by chronoamperometric experiments. Figure 3C and 3D show the current−time curves of the four different PAHNTs, Pd/C, and Pd NTs, which were obtained at −0.2 V for 1800 s in a solution containing 1.0 M KOH and 1.0 M ethanol. PAHNTs (48.5%) shows the best stability in the study even though the catalytic activity of PAHNTs (38.9%) is higher than that of others. This result demonstrates that a higher Au content contributes to a better stability of bimetallic electrocatalyst and all the PAHNTs have a better stability than monometallic catalysts, including commercial Pd/C and Pd NTs.

To further study the performance of the PAHNTs for other alcohols, we examined their catalytic properties toward glycerol and EG electrooxidation. Figure 4A shows the CVs of the four PAHNTs in a solution containing 1.0 M KOH and 0.1 M glycerol with a scan rate of 50 mV s^{-1}. Similar results were obtained about their activities: PAHNTs (38.9%) has the best activity (1.83 A mg_{Pd+Au}^{-1}). Figure 4B shows the CVs of PAHNTs (38.9%), Pd/C and Pd NTs. The result indicates that PAHNTs (38.9%) possesses a much better activity than Pd/C and Pd NTs. In the experiment, Pd/C exhibits a better

performance than Pd NTs, which is different from the result in the ethanol solution. Even so, the bimetallic catalysts have a better activity than Pd/C. Among the PAHNTs, PAHNTs (38.9%) exhibits a higher mass activity, which is 3.8 times that of commercial Pd/C and much higher than that of self-supported Pd$_x$Bi catalysts.[32] Figure 4C compares the CVs of the PAHNTs, commercial Pd/C and Pd NTs in a solution containing 0.5 M KOH and 0.5 M EG with a scan rate of 50 mV s^{-1}. The result shows that the mass activity of the PAHNTs is 4.6 A mg_{Pd+Au}^{-1}, which is about 7.3 and 3.9 times that of Pd/C and Pd NTs, respectively. Besides, the activity is also better than that of bimetallic PdPt nanowire network reported very recently.[8] In Figure 4D, the activities of different materials for different alcohols are summarized, clearly showing the great advantage of the optimal PAHNTs to be used as electro-catalysts for alcohol oxidation in alkaline media.

We propose a model illustrated in Figure 5 to explain the effect of Au content on the electrocatalytic activity of PAHNTs. When the density of Au islands on Pd nanotubes is low, the increase of Au content would increase the total area of the Pd−Au interface. As the density of Au islands increases to some critical value, further increase of Au content could lead to the overlap of interface areas among adjacent Au islands, or even aggregation of Au islands; the total interfacial area thus would decrease with the increase of Au content. Since the Pd atoms in the junction areas possess enhanced activity,[24,25] the PAHNTs with an optimal Au content thus present the best activity. The present results provide further evidence for the fact that
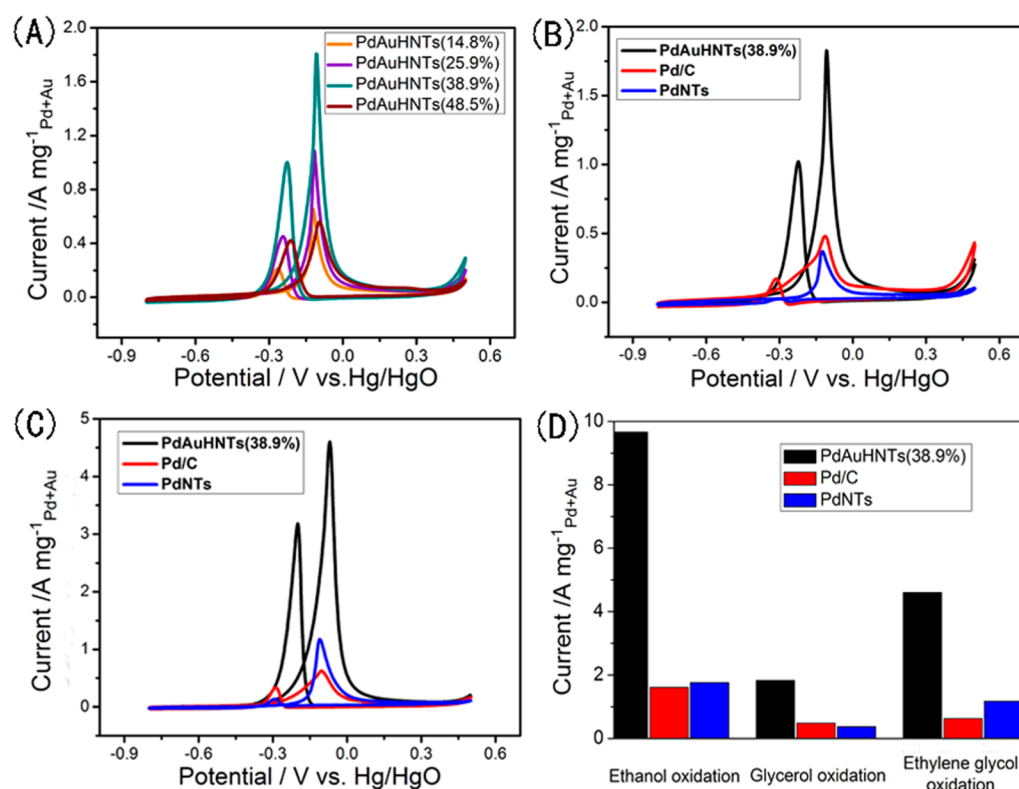
Figure 4. CV curves of (A) PAHNTs with different contents of element Au, (B) PAHNTs (38.9%), commercial Pd/C and Pd NTs for glycerol electrooxidation. (C) CV curves of PAHNTs (38.9%), commercial Pd/C and Pd NTs for EG electrooxidation. (D) Summary of mass activities of PAHNTs (38.9%), commercial Pd/C and Pd NTs for ethanol, glycerol and EG electrooxidation.
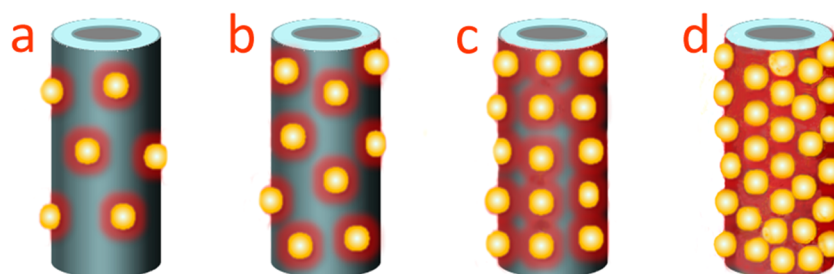

Figure 5. Representation of the variation of PAHNTs with the increase of element Au content from a to d.

heterogeneous metal junctions positively contribute to the catalytic performance of metals.

CONCLUSIONS

In summary, we have demonstrated a facile strategy for the synthesis of novel Pd−Au heterogeneous nanotubes which possess abundant exposed Pd−Au heterojunction interfaces. By regulating the amount of the precursors, the Pd−Au junction area can be easily controlled. At an optimal Au content of 38.9% in weight, the PAHNTs exhibit the best electrocatalytic activity toward alcohol electrooxidation under alkaline condition. The study demonstrates the effectiveness of the interface-abundant heterogeneous metal nanocrystals in boosting the catalytic activity of noble metals, and accordingly saving their use in various catalytic applications. In particular, the optimized PAHNTs show a great prospect to be used as electrocatalysts for alcohol electrooxidation in basic DAFCs. Because of the importance of the Pd-based materials in many fields, such as the formic acid oxidation and many organic reactions, the as-synthesized novel Pd−Au heterogeneous

nanotubes may be of prominent properties for a number of applications.

ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b02099.

> TEM images of Te NWs, Pd NTs, and PAHNTs with different ratio of Au and Pd, EDS and XPS spectra of PAHNTs, and CV curves of all materials (PDF)

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Notes

The authors declare no competing financial interest.

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