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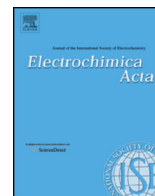


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# Quinary PdNiCoCuFe Alloy Nanotube Arrays as Efficient Electrocatalysts for Methanol Oxidation



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## ABSTRACT

Multi-metallic alloy nanotube arrays are highly favorable for superior electrocatalytic performance and efficient utilization of catalyst because of the special characteristics of alloys, hollow nanotubes, and array nanostructures. Here we firstly prepared the quinary PdNiCoCuFe alloy nanotube arrays (NTAs) by template-assisted electrodeposition method. The inner diameters, wall thicknesses, and lengths of PdNiCoCuFe alloy nanotubes are 300~400 nm, 150 nm, and 1.8  $\mu$ m, respectively. Because of the high specific surface area, hollow nanotube arrays, and synergistic effects of various elements, the quinary PdNiCoCuFe alloy NTAs as efficient electrocatalysts showed superior catalytic activity and long-term cycle stability for methanol electrooxidation. The combination of compositionally and geometrically favorable factors provides a new method to design the novel catalysts with excellent electroactivity and durability.

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## 1. Introduction

Platinum (Pt) has been widely recognized as the best electrocatalyst for the oxidation of small organic molecules for direct alcohol fuel cells (DAFCs) that are especially ideal for portable applications, but its high cost and low content in the Earth have severely limited its wider adoptions. [1–3] So it is desirable to find new low-cost catalysts with high performance to replace the expensive and scarce Pt. Among the various metals, palladium (Pd) has attracted great interest because it is similar to Pt (e.g., same group in the periodic table, same fcc crystal structure, and similar atomic size) while being less expensive and more abundant than Pt. [4,5] Recently, Pd-based materials have been studied intensively as one of the most promising Pt-free catalysts because of their high catalytic performance in basic media, especially for the electrooxidation of small organic molecules. [6,7]

Due to the structural and electronic changes caused by alloying Pd with transition metals (TMs), the Pd alloys show better catalytic performance than the pure Pd. [8–10] In addition, the formation of alloys also can be adopted as a strategy to overcome the drawbacks of Pd. For example, the cost-issues can be addressed by adding economical metals, and the cycle stability can be enhanced by the incorporation of robust metals. [11–13] On the other hand, it

was also found that the surface morphology of nanocrystals (NCs) plays significant roles in catalytic activity and catalyst durability. [14] For example, it has been reported that the tetrahedral Pd NCs exhibited higher catalytic performance than Pd black. [15] In order to minimize the utilization of precious metal and further enhance the catalytic performance, it is therefore highly interesting to “transfer” the idea of shape-controlled Pd nanostructures into its multi-component systems. [16–21] Among various nanostructures, the nanotube arrays (NTAs) are particularly attractive because of their unique hollow morphology and high surface to volume ratio, which can obviously promote catalytic properties. Accordingly, the NTAs consisted of multiple metallic components are a promising platform for catalyst applications. However, up to now, the fabrication of multi-component Pd-based alloy NTAs is still a huge challenge because of the difficulties involved in controlling the nucleation and growth of nanostructures in the presence of different metal precursors with various reduction kinetics.

Here we devote our attention to the synthesis of quinary Pd-TM alloy NTAs because of their special electronic and structural effects. The quinary Pd-TM alloy NTAs are characterized by the uniquely hollow nanostructures, anisotropic natures, and multicomponent effects, which will impart many advantageous factors, such as large surface area, high transport rate of electroactive species, high utilization rate of electrocatalysts, low precious metal loading, and synergy effects among the various elements. In addition, the well-aligned alloy NTAs will also provide the continuous charge carrier transport pathways. Based on the above considerations, here the

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quinary PdNiCoCuFe alloy NTAs with low Pd content were synthesized by a facile template assisted electrodeposition method, which shows following merits: (i) the multiple metallic alloys are easily formed; (ii) the hollow NTAs can be well fabricated; (iii) the PdNiCoCuFe alloy NTAs can directly grow on conductive substrate in a good solid contact that can largely enhance conductivity. Unlike the seeded-growth method or metallic-precursor reduction for the synthesis of heterostructure nanoparticle materials, which requires a mass of surfactants that will hinder the catalytic activity of metal surface, [22] this strategy just uses water as a solvent and does not need surfactant. To the best of our knowledge, this is the first report on the synthesis of quinary Pd-based alloy NTAs for methanol electrooxidation. These fabricated PdNiCoCuFe alloy NTAs exhibit superior electrocatalytic activity and durability because of the compositional (i.e. multi-component alloy) and geometrical (i.e. hollow nanotube array) properties of the materials.

## 2. Experimental Section

**Synthesis of PdNiCoCuFe alloy nanotube arrays (NTAs):** All chemical reagents were analytical (AR) grade. Electrochemical deposition was carried out in a simple three-electrode electrolytic cell via galvanostatic electrodeposition, and the graphite electrode was used as a counter electrode (spectral grade,  $1.8\text{ cm}^2$ ). A saturated calomel electrode (SCE) was used as the reference electrode that was connected to the cell with a double salt bridge system. All potentials used in electrodeposition were the values vs SCE. A pure Ti plate (99.99%,  $1.0\text{ cm}^2$ ) was used as working electrode. Before electrodeposition, Ti substrate was cleaned ultrasonically in 0.1 M HCl, distilled water, and acetone and then rinsed in distilled water again. The PdNiCoCuFe alloy NTAs were fabricated by the procedures shown in Scheme 1 in paper, and the details of fabrication are described as follows:

- (1) ZnO nanorod arrays (NRAs) templates were electrodeposited on Ti substrate in solution of  $0.01\text{ M Zn(NO}_3)_2 + 0.05\text{ M NH}_4\text{NO}_3$  at current density of  $0.5\text{ mA cm}^{-2}$  at  $70^\circ\text{C}$  for 90 min.
- (2) ZnO@PdNiCoCuFe core-shell NRAs were fabricated by electrodeposition of PdNiCoCuFe alloys on the surfaces of ZnO nanorods in solution of  $0.00157\text{ M PdCl}_2 + 0.00833\text{ M FeCl}_2 + 0.01667\text{ M CoCl}_2 + 0.00833\text{ M CuCl}_2 + 0.01667\text{ M NiCl}_2$  (pH value was controlled to 4.0 by adding  $\text{NH}_3\cdot\text{H}_2\text{O}$ ) with current density of  $0.15\text{ mA cm}^{-2}$  at  $70^\circ\text{C}$  for 15 min. The ZnO@Pd core-shell NRAs were prepared in solution of  $0.00157\text{ M PdCl}_2$
- (3) The fabricated ZnO@PdNiCoCuFe NRAs and ZnO@Pd core-shell NRAs were immersed in  $2.0\text{ M NaOH}$  solution for 4 h to completely remove ZnO NRAs, and accordingly the PdNiCoCuFe NTAs and Pd NTAs were fabricated.

**Structural Characterization:** The surface morphologies of the fabricated PdNiCoCuFe NTAs were characterized by field emission scanning electron microscopy (FE-SEM, JSM-6330F) and transmission electron microscope (TEM, JEM-2010HR). The fabricated nanomaterials were also characterized by energy-dispersive X-ray spectroscopy (EDX, INCA 300) to determine the compositions. Chemical state analysis of the fabricated nanomaterials was carried out by X-ray photoelectron spectroscopy (XPS) using an ESCALAB 250 X-ray photoelectron spectrometer. All XPS spectra were corrected using the C 1s line at  $284.6\text{ eV}$ . Curve fitting and background subtraction were accomplished.

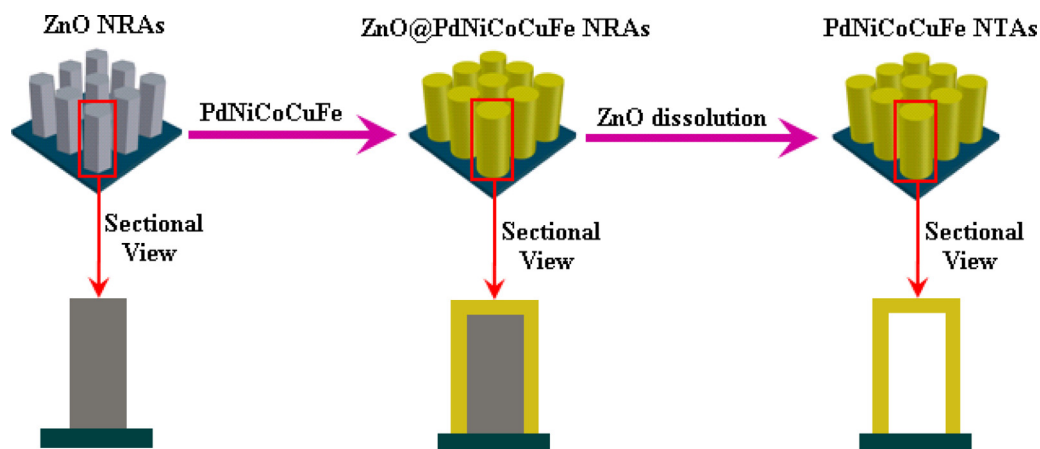
**Electrochemical Characterization:** The electrochemical properties of the prepared electrocatalysts were studied in a standard three-electrode electrolytic cell. The PdNiCoCuFe NTAs or Pd NTAs grown on Ti substrate served as working electrode. A Pt foil served as the counter electrode. A Ag/AgCl was used as the reference

electrode. All potentials were the values vs Ag/AgCl. Cyclic voltammetry (CV) and chronoamperometry measurements were carried out on a CHI 660D electrochemical workstation (CH instruments, Inc.). Before the electrochemical measurements, the surface of electrocatalyst was covered by  $10\text{ }\mu\text{L}$  Nafion (5 wt%) solution. CV curves were recorded between  $-0.80\text{ V}$  and  $0.20\text{ V}$  vs Ag/AgCl at a scan rate of  $50\text{ mV s}^{-1}$ . Chronoamperometry curve for methanol oxidation at  $-0.20\text{ V}$ . For CV and chronoamperometry measurements of ethanol oxidation reactions, an aqueous solution of  $0.5\text{ M CH}_3\text{OH} + 0.5\text{ M NaOH}$  was utilized. Prior to all experiments, the electrolyte solution was purged with high purity nitrogen gas for 10 min. All electrochemical measurements were carried out at room temperature.

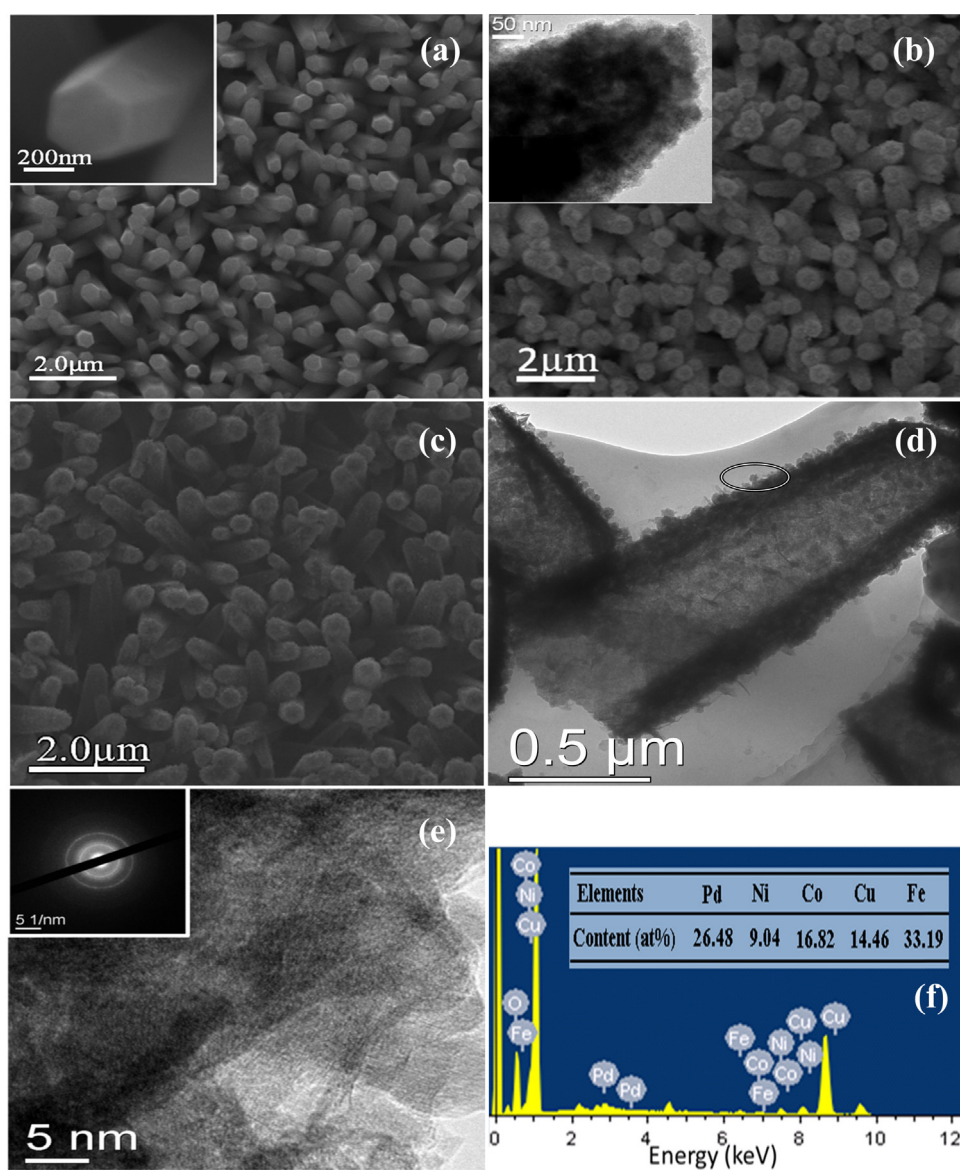
## 3. Results and Discussion

The procedure used to fabricate PdNiCoCuFe alloy NTAs is shown in Scheme 1. The details of the fabrication are described in experimental section. ZnO nanorod arrays (NRAs) were firstly synthesized and utilized as templates. SEM image of the synthesized ZnO NRAs is shown in Figure 1a, which shows the diameters of ZnO nanorods are about  $300\sim 400\text{ nm}$  and their lengths are about  $1.8\text{ }\mu\text{m}$ . Then PdNiCoCuFe alloys were electrodeposited on the surfaces of ZnO NRAs that serve as conductive and dispersing supports, and the ZnO@PdNiCoCuFe core-shell NRAs were fabricated. SEM image of the synthesized ZnO@PdNiCoCuFe core-shell NRAs is shown in Figure 1b, which shows the PdNiCoCuFe wraps uniformly dispersing on the surfaces of ZnO nanorods. The core-shell structure is proved by TEM image as shown in inset in Figure 1b. Finally, the PdNiCoCuFe alloy NTAs were fabricated by etching ZnO from ZnO@PdNiCoCuFe core-shell NRAs in  $2.0\text{ M NaOH}$  aqueous solution for 4 h. The typical SEM image of PdNiCoCuFe alloy NTAs is shown in Figure 1c, which indicates the array morphology is well kept after the dissolution of ZnO nanorods. To prove the hollow nanotube structure, the transmission electron microscopy (TEM) measurement is carried out and TEM image is shown in Figure 1d, which shows the hollow structure of PdNiCoCuFe alloy NTAs. The inner diameter, wall thickness, and length of PdNiCoCuFe alloy nanotubes are  $300\sim 400\text{ nm}$ ,  $150\text{ nm}$ , and  $1.8\text{ }\mu\text{m}$ , respectively. In addition, from Figure 1c, it can be clearly seen that the PdNiCoCuFe alloy NTAs separate from each other and there is high void volume among nanotubes, which will provide a three dimensional (3D) space for mass transfer of reactant and resultant molecules. The high resolution TEM image and SAED pattern are also measured and they are shown in Figure 1e, and they both indicate that the fabricated PdNiCoCuFe alloy nanotubes are polycrystalline. The energy dispersive X-ray spectroscopy (EDS) was measured in large scale and in many locations on the surface of PdNiCoCuFe alloy NTAs to determine the compositions. A typical EDS spectrum of PdNiCoCuFe alloy NTAs is shown in Figure 1f. The peaks of Pd, Ni, Co, Cu, and Fe elements are clearly seen in EDS profile, confirming the successfully co-deposition of Pd, Ni, Co, Cu, and Fe. Quantitative analysis shows the compositions of 26.48 at% Pd, 9.04 at% Ni, 16.82 at% Co, 14.46 at% Cu, and 33.19 at% Fe in the PdNiCoCuFe alloy NTAs.

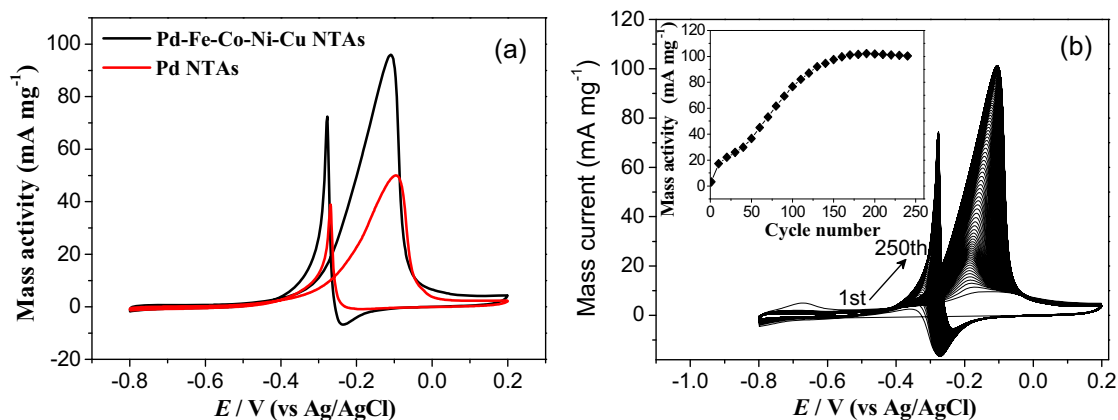
The electrocatalytic activities of the synthesized PdNiCoCuFe alloy NTAs along with Pd NTAs towards methanol electrooxidation were studied in solution of  $0.5\text{ M CH}_3\text{OH} + 0.5\text{ M NaOH}$ . The cyclic voltammograms (CVs) at  $50\text{ mV s}^{-1}$  in Figure 2a show the specific peak current density of forward scan of PdNiCoCuFe alloy NTAs is almost two times higher than that of Pd NTAs (the current densities all are normalized to Pd mass in the catalysts), indicating the specific electroactivity of PdNiCoCuFe alloy NTAs is much higher than that of Pd NTAs. In addition, the onset potential of forward anodic wave of PdNiCoCuFe alloy NTAs is lower than that of Pd NTAs, indicating more favorable for methanol electrodeposition on the PdNiCoCuFe alloy NTAs. On the other hand, in comparison with



**Scheme 1.** Illustration of the fabrication of PdNiCoCuFe alloy NTAs.



**Figure 1.** SEM images of (a) ZnO nanorod arrays and (b) ZnO@PdNiCoCuFe nanorod arrays; (c) SEM image; (d) TEM image; (e) HRTEM image and SAED pattern (inset); (f) EDS pattern of the syn-thesized PdNiCoCuFe nanotube arrays.



**Figure 2.** (a) CVs of PdNiCoCuFe alloy NTAs and Pd NTAs in 0.5 M CH<sub>3</sub>OH + 1.0 M NaOH at 50 mV/s; (b) CVs of PdNiCoCuFe alloy NTAs catalyst from the 1st to the 250th cycle (inset: Change of peak current density of forward scan with increasing cycle number for PdNiCoCuFe NTAs catalyst).

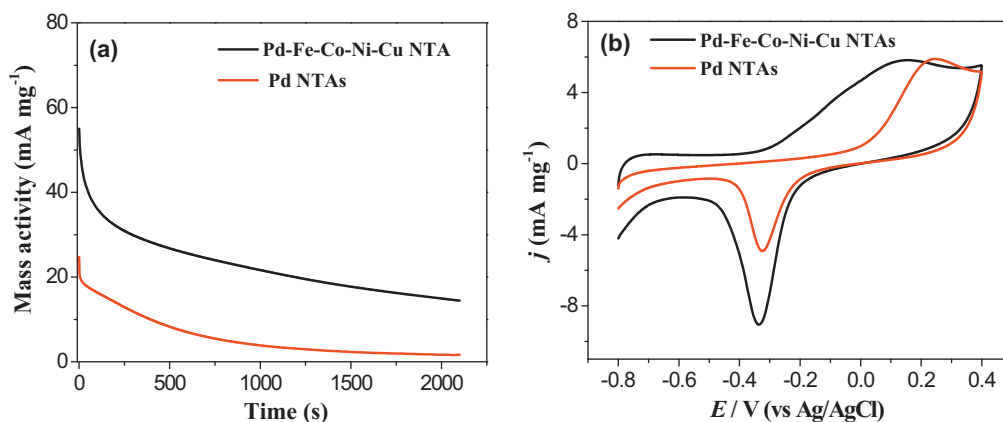
the commercial Pd/C, the well-ordered quinary PdNiCoCuFe NTAs also possess much higher electrocatalytic activity as shown in Figure S1, primarily because of the synergistic effects among various metals and the large surface area of nanotube arrays.

The various CVs of PdNiCoCuFe alloy NTAs with increasing cycle number is shown in Figure 2b, and the corresponding change of peak current density of forward scan is shown in inset. Here we find that the electrocatalytic activity of PdNiCoCuFe alloy NTAs increases drastically during the initial cycles and the maximum peak current density of forward scan appears at the 190th cycle. This observation suggests the active PdNiCoCuFe alloy electrocatalyst is derived through the initial atomic rearrangement process, [23] which would endow the PdNiCoCuFe alloy NTAs with some advantageous material characteristics such as a large proportion of exposed Pd atoms that are desirable for their electrocatalytic activity. After 190 cycles, the peak current density of forward scan almost keeps stability with further increasing cycle number, demonstrating that the PdNiCoCuFe alloy NTAs have strong resistance to the poisoning of carbonaceous species and high cycle stability. The composition and unique structures may be the major factors for the superior performance of PdNiCoCuFe alloy NTAs because the hollow multimetallic nanotubes can lead to the complete electrooxidation of carbonaceous species during backward scan. This is demonstrated by the gradually increased peak current density of back-ward scan in CVs in Figure 2b, which indicates the less carbonaceous species diffusing into electrocatalysts because of the full oxidation of carbonaceous species. The complete oxidation can effectively reduce carbonaceous species "re-occupying" the

active sites and consequently enhance the electrocatalytic activity and durability of PdNiCoCuFe alloy NTAs as shown in inset in Figure 2b.

In order to evaluate the rate of surface poisoning, the chronoamperometry curves of PdNiCoCuFe alloy NTAs and Pd NTAs were measured in solution of 0.5 M methanol + 0.5 M NaOH as shown in Figure 3a. The potential was held at -0.2 V during measurements. It is obvious that the PdNiCoCuFe alloy NTAs exhibit a much slower current decay over time in comparison with the Pd NTAs, indicating a higher tolerance to the carbonaceous species generated during methanol electrooxidation. In addition, these synthesized PdNiCoCuFe alloy NTAs exhibit much higher current densities than Pd NTAs at all time as shown in Figure 3a, indicating that the PdNiCoCuFe alloy NTAs are much higher electroactive than Pd NTAs for methanol electrooxidation. The above results are consistent with the CV results shown in Figure 2a.

The electrocatalytic activity of PdNiCoCuFe alloy NTAs towards CO oxidation was contrasted with Pd NTAs in 0.5 M NaOH electrolyte at room temperature. High purity CO was bubbled into electrolyte solution for 15 min while keeping the electrode potential at 0 V, in order to achieve the maximum coverage of CO at the Pd centers. Subsequently, the undissolved CO was purged out of the electrolyte by bubbling Ar gas for 20 min. CVs were measured for the above catalysts in solution of 0.5 M NaOH between -0.8 and 0.4 V at 50 mV s<sup>-1</sup> as shown in Figure 3b. The onset potential of CO oxidation in forward scan on PdNiCoCuFe alloy NTAs is -0.3 V, which is much more negative than 0.05 V on the Pd NTAs. This result indicates that the PdNiCoCuFe alloy NTAs can obviously lower the



**Figure 3.** (a) Chronoamperometry curves of PdNiCoCuFe NTAs and Pd NTAs in solution of 1.0 M NaOH + 0.5 M CH<sub>3</sub>OH at -0.2 V. (b) CO stripping measurements of PdNiCoCuFe NTAs and Pd NTAs in 0.5 M NaOH at 50 mV/s.



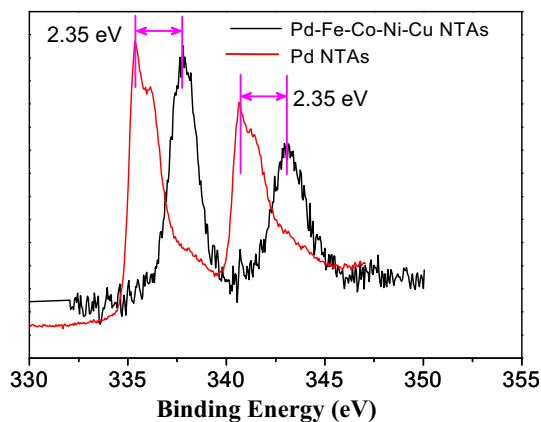


Figure 4. XPS spectrum of PdNiCoCuFe NTAs and Pd NTAs.

adsorption strength of CO on their surfaces and accordingly can facilitate the removal of CO from the surface of catalyst.[24] Therefore, the PdNiCoCuFe alloy NTAs have much stronger resistance to the poisoning of CO than Pd NTAs. In addition, compared with Pd NTAs, the PdNiCoCuFe alloy NTAs also show a much larger CO oxidation peak as shown in Figure 3b, indicating a much larger electro-chemically active surface area of PdNiCoCuFe alloy NTAs than that of Pd NTAs. [25]

Considering identical synthetic route and similar morphology (NTAs), the much higher electrocatalytic activity of PdNiCoCuFe alloy NTAs than Pd NTAs can be ascribed to the synergetic effects among the various elements Pd, Ni, Co, Cu and Fe. The interactions among Pd, Ni, Co, Cu, and Fe can promote the catalytic activity of Pd for C-H cleavage reaction and formation of hydroxyl species at a lower potential and also weaken the bonding intensity of hydroxyl species on the surfaces of PdNiCoCuFe alloy NTAs.[26] The promotive effect of alloys on the electrocatalytic activity and stability is an interesting phenomenon that is highly worthy of investigation. XPS spectra of Pd 3d in Figure 4a shows that the  $3d_{5/2}$  and  $3d_{3/2}$  peaks of PdNiCoCuFe alloy NTAs both shift to higher binding energies (337.73 and 343.06 eV) relative to the  $3d_{5/2}$  and  $3d_{3/2}$  peaks of Pd NTAs (335.38 and 340.71 eV). The positive shifts of Pd are about 2.35 eV in binding energies as shown in Figure 4a, and this confirms the strong electron interactions involving Pd and transition metal atoms within the PdNiCoCuFe alloy NTAs. The strong electron interactions among Pd, Ni, Co, Cu and Fe atoms have obviously altered the electronic states of Pd atoms, making PdNiCoCuFe alloy NTAs have superior electrocatalytic activity, large ECSA, and strong resistance to the poisoning of carbonaceous species as shown in Figures 2 and 3. In addition, the special nanostructures of PdNiCoCuFe alloy NTAs will bring following advantages, such as anisotropic morphology, hollow nanostructure, and large surface area. These advantages will create efficient diffusion paths for active species and significantly enhance the intercalation of active species and utilization rate of electrode material. Therefore, the combination of compositionally and geometrically favorable factors leads to the much enhanced electrocatalytic performance.

#### 4. Conclusions

In summary, we have designed and synthesized the multimetallic PdNiCoCuFe alloy NTAs catalyst by a highly efficient template-assisted electrodeposition route. These synthesized PdNiCoCuFe alloy NTAs possess low content of Pd, but exhibit a markedly enhanced electrocatalytic activity and strong resistance to the poisoning of carbonaceous species relative to Pd NTAs and commercial Pd/C catalysts. The enhanced electrocatalytic performance of PdNiCoCuFe alloy NTAs can be attributed to the combination of

several favorable factors: the multicomponent nature with which different metal elements could work synergistically, the electronic effects associated with alloys, and the unique nanostructure of hollow nanotube arrays. It is highly expected that these quinary PdNiCoCuFe alloy NTAs would be of highly interest for use as low-Pd-content catalysts in DAFCs. The combination of compositionally and geometrically favorable factors provides a new route to design novel electrocatalysts with excellent catalytic activity and durability.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.electacta.2014.02.076>.

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