# Supporting information

## Trimetallic Palladium-Copper-Cobalt Alloyed Wavy Nanowires

### Advance Ethanol Electrooxidation in Alkaline Medium

Fengling Zhao<sup>a</sup>, Chaozhong Li<sup>a</sup>, Qiang Yuan<sup>\*a, b</sup>, Fang Yang<sup>a</sup>, Bin Luo<sup>a</sup>, Zixuan Xie<sup>a</sup>,

Xiaotong Yang<sup>a</sup>, Zhiyou Zhou<sup>c</sup> and Xun Wang<sup>\*b</sup>

<sup>a</sup>Department of Chemistry, College of Chemistry and Chemical Engineering, Guizhou

University, Guiyang 550025, People's Republic of China (P. R. China).

<sup>b</sup>Key Lab of Organic Optoelectronics & Molecular Engineering, Department of Chemistry, Tsinghua University, Beijing 100084, People's Republic of China.

<sup>c</sup>State Key Laboratory of Physical Chemistry of Solid Surfaces, College of Chemistry

and Chemical Engineering, Xiamen University, Xiamen 361005, People's Republic of

China.

\*Corresponding author e-mail: qyuan@gzu.edu.cn; wangxun@mail.tsinghua.edu.cn

#### **Experimental section:**

#### Synthesis of pure Pd Nanoparticles

In a typical synthesis, 0.50 mL of 0.1 M Na<sub>2</sub>PdCl<sub>4</sub> was added to 8.8 mL of ethylene glycol containing 0.050g Polyvinyl Pyrrolidone (PVP-8000) and 0.2 mL formamide, and stirred for 30 minutes. Then, the resulting clear solution was transferred to a 15

mL Teflon-lined stainless-steel autoclave. The sealed vessel was then heated at  $150^\circ C$ 

for 8 hours before it was cooled to room temperature. The products were separated several times by centrifugation and washing cycles at 10,000 rpm for 10 minutes with ethanol. The pure Pd nanoparticles was redispersed in ethanol.

### Synthesis of Pd<sub>49</sub>Cu<sub>51</sub> nanowires

In a typical synthesis, 0.25 mL of 0.1 M  $Na_2PdCl_4$ , 0.25 mL of 0.1 M  $CuCl_2$  were added to 8.8 mL of ethylene glycol containing 0.050 g Polyvinyl Pyrrolidone (PVP-8000) and 0.2 mL formamide, and stirred for 30 minutes. Then, the resulting clear solution was transferred to a 15 mL Teflon-lined stainless-steel autoclave. The sealed

vessel was then heated at  $150^{\circ}$ C for 8 hours before it was cooled to room temperature.

The products were separated several times by centrifugation and washing cycles at 10,000 rpm for 10 minutes with ethanol. The  $Pd_{49}Cu_{51}$  was redispersed in ethanol.

### Synthesis of Pd<sub>84</sub>Co<sub>16</sub> nanowires

In a typical synthesis, 0.25 mL of 0.1 M  $Na_2PdCl_4$  and 0.25 mL of 0.1 M CoCl<sub>2</sub> were added to 8.8 mL of ethylene glycol containing 0.050g Polyvinyl Pyrrolidone (PVP-8000) and 0.2 mL formamide, and stirred for 30 minutes. Then, the resulting clear

solution was transferred to a 15 mL Teflon-lined stainless-steel autoclave. The sealed

vessel was then heated at 150°C for 8 hours before it was cooled to room temperature.

The products were separated several times by centrifugation and washing cycles at 10,000 rpm for 10 minutes with ethanol. The  $Pd_{84}Co_{16}$  nanoparticles was redispersed in ethanol.

#### **Characterizations:**

Transmission electron microscope (TEM) was characterized on a Hitachi H-7700 at 100 KV. High-angle annular dark field scanning TEM (HAADF-STEM) and energydispersive X-ray spectroscopy (EDS) element mapping were obtained with Tecnai G2 F20 S-Twin high-resolution transmission electron microscope 200 KV (HRTEM). HRTEM images were obtained with FEI Titan 80 (300 KV). X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8 Advance diffractometer with CuK<sub>a</sub> radiation ( $\lambda$ =1.5418Å) with graphite monochromator (40 KV, 40 mA). X-ray photoelectron spectroscopy (XPS) measurements were performed using a PHI Quantum 2000 Scanning ESCA Microprobe (Physical Electronics, USA), using Al K<sub>a</sub> X-ray radiation (1486.6 eV) for excitation. Binding energies were corrected from charge effects by reference to the C1s peak of carbon at 284.8 eV. The inductively coupled plasma optical emission spectrometry (ICP-OES) analysis of samples was performed on IRIS Intrepid II XSP (ThermoFisher).

#### **Electrochemical experiment:**

All of the electrochemical measurements were performed in a conventional threeelectrode cell equipped with salt bridge using a CHI 760e electrochemical analyzer (CH Instruments, Inc., Shanghai). A Ag/AgCl electrode and platinum black plate were used as reference and counter electrodes, respectively. The working electrode is a glassy carbon (GC, d=5.0 mm) electrode embedded in a Teflon holder. Before the electrochemical test, we use alumina powder of size 1.5, 1.0 and 0.05  $\mu$ m to polish the GC electrode, and clean it in an ultrasonic bath. The suspension of catalysts was spread on the GC electrode. As soon as the electrode was dried under infrared lamp, 4  $\mu$ L Nafion diluents (1.0 wt % Nafion® solution) was coated onto the electrode surface.

For ethanol oxidation reaction (EOR) test, the cyclic voltammograms (CVs) were obtained in nitrogen-saturated 1.0 M KOH solution or 1.0 M KOH+1.0 M C<sub>2</sub>H<sub>5</sub>OH, and the potential was scanned from -0.8 to 0.2 V (vs. Ag/AgCl) at a scan rate 50 mV s<sup>-1</sup>. The scan was repeated several times to ensure that a stable cyclic voltammetry (CV) was obtained.

The electrochemically active surface area (ECSA) tests was estimated by CO stripping test: All electrodes which was made of each sample were carried out by firstly in the a CO-saturated 0.1 M HClO<sub>4</sub> solution electrolytic cell, and let the sample adsorb CO at 0.20 V for 300 sec. Then transfered the electrodes to N<sub>2</sub>-saturated 0.1 M HClO4 solution electrolytic cell to test in the 0 to 1.1 V (Ag/AgCl) at a scan rate of 50 mV s<sup>-1</sup>. The ECSA was calculated from the charge involved in the CO adsorption

processes using the following equation:

$$ECSA = Q/(0.42 \times M),$$

where Q (mC) is the charge for the CO adsorption. 0.42 (mC/cm<sup>2</sup>) is the electrical charge associated with full monolayer adsorption of CO on Pd.

In alkaline solution, the electrochemically active surface area (ECSA) can be calculated from charges changes in the reduction region of Pd-O according to the equation as follow: ECSA =  $Q/(0.405 \times Pd_m)$ , where  $Pd_m$  is associated with the loading of Pd on the GCE electrode, 0.405 mC cm<sup>-2</sup> is a constant assuming that a monolayer of Pd-O was reduced on the Pd surface and Q in mC is the reduction charge of PdO.

In acidic solution, the electrochemical surface area (ECSA) were calculated by the following equation: ECSA =  $Q_H/m \times 210$ , where  $Q_H$  is the charge for Hupd adsorption determined using  $Q_H = 0.5 \times Q$ , m is the Pt loading amount on the electrode, and 210  $\mu$ C cm<sup>-2</sup> is the charge required for the monolayer adsorption of hydrogen on the Pt surface.

Electrochemical in-situ Fourier Transform Infrared (FTIR) reflection spectroscopy measurements were tested on a Nexus 870 spectrometer (Nicolet) equipped with a liquid nitrogen-cooled MCT-A detector. Before in situ FTIR measurement, a particular Infrared cell with a CaF<sub>2</sub> window must be used, and a thin layer (<10  $\mu$ m) between the GCE and CaF<sub>2</sub> window was necessary. The resulting spectra were reported as the relative change in reflectivity and calculated as follows:

 $\Delta R/R = (R(E_s) - R(E_R))/R(E_R)$ 

where  $R(E_S)$  and  $R(E_R)$  are the single-beam spectra collected at sample potential  $E_S$  and reference potential  $E_R$ , respectively.

The electrochemical double-layer capacitance of the catalyst was measured. The traditional cyclic voltammetry is used. The potential of cyclic voltammetry is  $-0.55V \sim -0.45$  V and Ag/Agcl with scanning rates of 20, 40, 60, 80, 100 mV s<sup>-1</sup>. Then, by plotting j= (j<sub>a</sub>- j<sub>c</sub>), the -0.5 V (where j<sub>a</sub> and j<sub>c</sub> are anode and cathode current densities, The scanning rate was compared with Ag/Agcl, and the slope was C<sub>dl</sub>.

Sample	Element	Atomic%	Atomic%
		Feeding radio	(result from ICP-OES)
Pd <sub>36</sub> Cu <sub>60</sub> Co <sub>4</sub>	Pd	33.4	36
	Cu	50	60
	Со	16.6	4
$Pd_{31}Cu_{61}Co_8$	Pd	16.6	31
	Cu	50	61
	Со	33.4	8
$Pd_{30}Cu_{58}Co_{12}$	Pd	12.6	30
	Cu	50	58
	Со	37.4	12
Pd <sub>49</sub> Cu <sub>51</sub>	Pd	50	49
	Cu	50	51
Pd <sub>84</sub> Co <sub>16</sub>	Pd	50	84
	Со	50	16

**Table S1**. The inductively coupled plasma optical emission spectrometry (ICP-OES) results of theas-synthesized PdCuCo wavy nanowires,  $Pd_{49}Cu_{51}$  NWs and  $Pd_{84}Co_{16}$  NWs.



**Fig. S1**. The TEM images of as-prepared  $Pd_{49}Cu_{51}$  NWs (a),  $Pd_{84}Co_{16}$  NWs (b) and pure Pd nanoparticles (c) and XRD spectra (d) of as-prepared pure Pd nanoparticles,  $Pd_{49}Cu_{51}$  NWs and  $Pd_{84}Co_{16}$  NWs. (The size of Pd nanoparticles (a) was uniform, about 4.2 nm and these particles tended to aggregate. ) (The lines on X axial stand for standard peaks of Pd: JCPDS-46-1043 (blue); Cu: JCPDS-04-0836 (green) and Co: JCPDS-15-0806 (pink ).)



**Fig. S2**. The TEM images of as-synthesized products with the same method as  $Pd_{31}Cu_{61}Co_8$  nanoalloys at different reaction times.10 min (a), 2h (b) and 4h (c).



**Fig. S3**. The CVs of the as-prepared PdCuCo NWs,  $Pd_{49}Cu_{51}$  NWs,  $Pd_{84}Co_{16}$  NWs and Pd nanoparticles; Pd black (b); Pd/C (c) in 1 M KOH solution with a scanning rate of 50 mV s<sup>-1</sup>.



**Fig. S4**. The CVs of the as-prepared PdCuCo NWs,  $Pd_{49}Cu_{51}$  NWs,  $Pd_{84}Co_{16}$  NWs and Pd nanoparticles (a); Pd black (b); Pd/C (c) in 0.1 M HClO<sub>4</sub> solution with a scanning rate of 50 mV s<sup>-1</sup>.



**Fig. S5.** CO stripping curves (a) of the as-synthesized pure Pd, (b) of the as-synthesized Pd<sub>36</sub>Cu<sub>60</sub>Co<sub>4</sub>, (c) of the as-synthesized Pd<sub>31</sub>Cu<sub>61</sub>Co<sub>8</sub>, (d) of the as-synthesized Pd<sub>30</sub>Cu<sub>58</sub>Co<sub>12</sub>. (e) of the as-synthesized Pd<sub>49</sub>Cu<sub>51</sub> and (f) of the as-synthesized Pd<sub>84</sub>Co<sub>16</sub>. (Black line is the CO stripping and the red line is base line ).

Sample	Hupd	CO-stripping	PdO
Pd nanoparticles	29.2	29.9	27.2
Pd <sub>36</sub> Cu <sub>60</sub> Co <sub>4</sub>	88.3	89.2	86.5
Pd <sub>31</sub> Cu <sub>61</sub> Co <sub>8</sub>	95.1	97.2	93.1
Pd <sub>30</sub> Cu <sub>58</sub> Co <sub>12</sub>	91.3	92.1	87.7
Pd <sub>49</sub> Cu <sub>51</sub>	61	66.9	59.8
Pd <sub>84</sub> Co <sub>16</sub>	77.7	78.9	62.5
Pd/C	35.0	/	32.0
Pd black	17.1	/	14.6

Table S2. The ECSAs of the as-prepared samples, the commercial Pd/C and Pd black.



Fig. S6. The mass activity CVs of Pd/C (a), current-time curves of Pd/C (b) in 1.0 M KOH+1.0 M  $C_2H_5OH$ .



Fig. S7. The mass activity CVs of the as-prepared samples (a), current-time curves of the samples (b) in  $1.0 \text{ M KOH}+1.0 \text{ M C}_2\text{H}_5\text{OH}$ .



Fig. S8. Linear scanning curves of PdCuCo NWs, Pd nanoparticles and Pd black.



**Fig. S9.** Cyclic voltammograms in the region of -0.55 to -0.45 V vs. Ag/AgCl at various scan rates and the corresponding linear fitting plots of the capacitive currents vs. scan rates to estimate the  $C_{dl}$ . (a) and (b) for  $Pd_{31}Cu_{61}Co_8$ ; (c) and (d) for  $Pd_{49}Cu_{51}$ ; (e) and (f) for  $Pd_{84}Co_{16}$ ; (g) and (h) for pure Pd , (i) and (j) for Pd black ,and the calculated  $C_{dl}$  values are shown in the insets.





**Fig. S10.** TEM images (a) and energy dispersive X-ray spectra (b) of  $Pd_{31}Cu_{61}Co_8$  after current-time test for 30 min.



Fig. S11. The mass activity CVs (a), (b) of  $Pd_{31}Cu_{61}Co_8$  for 100 cycles in 1.0 M KOH+1.0 M  $C_2H_5OH$ .





Fig. S12. TEM images (a) and energy dispersive X-ray spectra (b) of Pd<sub>31</sub>Cu<sub>61</sub>Co<sub>8</sub> after 100 cycles.

(a)

Catalysts	Test Condition	Mass Activity	Reference
		(A/mg )	
PdCu nanocapsules	1.0 M C <sub>2</sub> H <sub>5</sub> OH + 1.0 M	1.14	24
	КОН;		
	Scan rate:50 mV·s <sup>-1</sup>		
	1.0M NaOH +1M C <sub>2</sub> H <sub>5</sub> OH;	6.0045	25
Pu/AG-BP nyoria	Scan rate:50 mV·s <sup>-1</sup>		
Pd nanonetwork	1.0 M C <sub>2</sub> H <sub>5</sub> OH + 1.0 M	2.04	26
	KOH;		
	Scan rate:50 mV-s <sup>-1</sup>		
4H/fcc Au@Pd	1.0 M C <sub>2</sub> H <sub>5</sub> OH + 1.0 M	2.92	27
nanorod	КОН;		
	Scan rate:50 mV·s <sup>-1</sup>		
D4Cu	1.0M KOH +1.0M C <sub>2</sub> H <sub>5</sub> OH;	1.6	28
PaCu <sub>2</sub>	Scan rate:50 mV-s <sup>-1</sup>		
Ordered PdCuCo	1.0 M C <sub>2</sub> H <sub>5</sub> OH + 1.0 M	7.72	29
nanoalloy	NaOH; Scan rate:50 mV·s <sup>-1</sup>		
IM-Pd3Pb NNs	1.0 M C <sub>2</sub> H <sub>5</sub> OH + 1.0 M	3.2	30
	NaOH; Scan rate:50 mV-s <sup>-1</sup>		
v-PdCuCo-AS	1.0 M C <sub>2</sub> H <sub>5</sub> OH + 1.0 M	0.82	32
	KOH; Scan rate:50 mV·s <sup>-1</sup>		
DdCa Nanatuha	1.0M KOH +1M C <sub>2</sub> H <sub>5</sub> OH;	1.48	33
r uCo manotude	Scan rate:50 mV·s <sup>-1</sup>		
Pd <sub>31</sub> Cu <sub>61</sub> Co <sub>8</sub>	1.0 M C <sub>2</sub> H <sub>5</sub> OH + 1.0 M	7.45	This work
NWs	KOH; Scan rate:50 mV·s <sup>-1</sup>		

**Table S3**. Summary of mass activities on typical Pd-based catalysts for EOR in alkaline medium recently.

#### **References:**

- 24 C. Hu, X. Zhai, Y. Zhao, K. Bian, J. Zhang, L. Qu, H. Zhang and H. Luo, Small-sized PdCu nanocapsules on 3D graphene for high-performance ethanol oxidation. *Nanoscale*, 2014, **6**, 2768-2775.
- 25 T. Wu, Y. Ma, Z. Qu, J, Fan, Q. Li, P. Shi, Q. Xu, Y. Min, Black phosphorus–graphene heterostructure-supported Pd nanoparticles with superior activity and stability for ethanol electro-oxidation. *ACS Appl. Mater. Interfaces*, 2019, **11**, 5136-5145.
- 26 H. Begum, M. S. Ahmed and S. Jeon, Highly efficient dual active palladium nanonetwork electrocatalyst for ethanol oxidation and hydrogen evolution. *ACS Appl. Mater. Interfaces*, 2017, 9, 39303-39311.
- 27 Y. Chen, Z. Fan, Z. Luo, X. Liu, Z. Lai, B. Li, Y. Zong, L. Gu and H. Zhang, High-Yield

synthesis of crystal-phase-heterostructured 4H/fcc Au@Pd core-shell nanorods for electrocatalytic ethanol oxidation. *Adv. Mater.*, 2017, **29**, 1701331.

- 28 J. Xue, G. Han, W. Ye, Y. Sang, H. Li, P. Guo and X. Zhao, Structural regulation of PdCu<sub>2</sub> nanoparticles and their electrocatalytic performance for ethanol oxidation. ACS Appl. Mater. Interfaces, 2016, 8, 34497-34505.
- 29 K. Jiang, P. Wang, S. Guo, X. Zhang, X. Shen, G. Lu, D. Su and X. Huang, Ordered PdCubased nanoparticles as bifunctional oxygen-reduction and ethanol-oxidation electrocatalysts. *Angew. Chem. Int. Ed.*, 2016, **55**, 9030-9035.
- 30 C. Zhu, C. Bi, H. Xia, M. H. Engelhard, D. Du and Y. Lin, Intermetallic Pd<sub>3</sub>Pb nanowire networks boost ethanol oxidation and oxygen reduction reactions with significantly improved methanol tolerance. *J. Mater. Chem. A*, 2017, **5**, 23952-23959.
- 32 Y. Zuo, D. Rao, S. Li, T. Li, G. Zhu, S. Chen, L. Song, Y. Chai and H. Han, Atomic vacancies control of Pd-based catalysts for enhanced electrochemical performance. *Adv. Mater.*, 2018, 30, 1704171.

33 A. Wang, X. He, X. Lu, H. Xu, Y. Tong and G. Li, Palladium-cobalt nanotube arrays supported on carbon fiber cloth as high-performance flexible electrocatalysts for ethanol oxidation. *Angew. Chem. Int. Ed.*, 2015, **54**, 3669-3673.