Supporting Information

Strained Lattice Platinum-Palladium Alloy Nanowires for Efficient Electrocatalysis

Mengyun Ren[a#], Fangfang Chang[a#,*], Ruifang Miao[a], Xianhong He[a], Lin Yang[a]*, Xiaolei Wang[b] and Zhengyu Bai[a*]

EXPERIMENTAL SECTION

Chemical Reagents. Platinum (II) acetylacetonate (Pt $(acac)_2$, 97%), Palladium (II) acetylacetonate ($Pd(acac)_2$, potassium hydroxide (KOH, 85+ %), ethylene glycol anhydrous (EG, 99.8%), *N*, *N*- dimethylformamide (DMF, 99.8%) and Nafion (5wt%) were obtained from Aldrich. Vulcan XC-72 Carbon black was purchased from Cabot. The E-tek Pt/C catalyst (20.0 wt% metal loading) was purchased from Strem Chemicals. AMillipore Milli-Q water system was used to purify deionized water (DI water). All gases such as oxygen, nitrogen were obtained from Airgas.

Prepration of Pt_xPd_{100-x} catalysts Pt_xPd_{100-x} alloy nanowires with tunable compositions were synthesized by following a protocol reported previously.[1] 92.6 mg Pt$(acac)_2$ and 61.8 mg $Pd(acac)_2$ were added to the mixture solution containing 24.0 mL EG and 36.0 mL DMF. After Pt$(acac)_2$ and $Pd(acac)_2$ were completely dissolved, 5.0 g KOH was added to the above solution. The compositions of the Pt_xPd_{100-x} NWs were tuned by the metal precursor molar ratio. After stirring for the whole night, the resultant homogeneous solution was transferred into a Teflon-lined stainless steel autoclave with a capacity of 100.0 mL. The autoclave was cooled to room temperature after keeping 8 h at 180 ℃. The resulting Pt_xPd_{100-x} NWs were collected by centrifugation four times with ethanol and then loaded on carbon for future use. Briefly, a certain amount of XC-72 carbon was dispersed in deionized water and ultrasonicated for 30 min to obtain well-dispersed carbon suspension. The controlled amount of Pt_xPd_{100-x} NWs was added the above carbon suspension and vigorously stirred for 30 min, followed by 150 ml ethanol to remove amines and deposit Pt_xPd_{100-x} nanowires on carbon to form Pt_xPd_{100-x}/C NWs catalyst. The catalysts with tunable compositions was collected by centrifugation and dried in oven at 70 ºC overnight. The thermogravimetric analysis (TGA) performed on a PerkinElmer Pyris 1-TGA was used to obtain the mass loading of Pt_xPd_{100-x}/C NWs catalysts.

Characterization The PerkinElmer 2000 DV ICP-OES instrument was used to determine the compositions of the Pt_xPd_{100-x} NWs. The morphology of Pt_xPd_{100-x} NWs catalysts were determined by transmission electron microscopy scanning TEM performed on FEI Titan G2 80-200 Chemi-STEM electron microscopes at 200 kV. The structures of Pt_xPd_{100-x}/C were measured by A Bruker D8 ADVANCE X-ray diffraction (XRD) assembled with a Cu K a radiation source (k = 0.15406 nm) and X-ray photoelectron spectroscopy (XPS) operated in a Thermo Scientific Escalab 220i-XL.

Electrochemical Measurements 4.0 mg catalyst of Pt_xPd_{100-x}/C was suspended into a mixture (2.0 mL) of deionized water, isopropanol and Nafion (5%) (19:1:0.015, v/v/v), and then ultrasonicated for 50 min to form a homogeneous catalyst ink (2.0 mg mL^{-1}). The catalyst suspension (10.0 μL) was dropped to the surface of the polished glassy carbon working electrode (diameter 5 mm, area 0.196 cm^2) and dried in air, which was polished by 0.005 um alumina powder and rinsed by sonication in ethanol and deionized water.[2] The electrocatalytic activity of the Pt_xPd_{100-x}/C for methanol and ethanol was evaluated by cyclic voltammetry (CV) in the electrolyte containing 0.1 M $HClO_4$ and 0.5 M CH_3OH or CH_3CH_2OH at a scan rate of 50 mV s^{-1}, which were performed at room temperature in a three-electrode cell on a computer-controlled electrochemical analyzer (CHI760e, CH Instruments). The measurements were performed in a three-electrode electrochemical cell using a glassy carbon electrode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a 1 cm^2 platinum foil as the counter electrode. Before CV measurements, the electrolytic solution (0.1 M $HClO_4$) was de-aerated with high purity nitrogen. The potentials are given with respect to reversible hydrogen electrode (RHE).

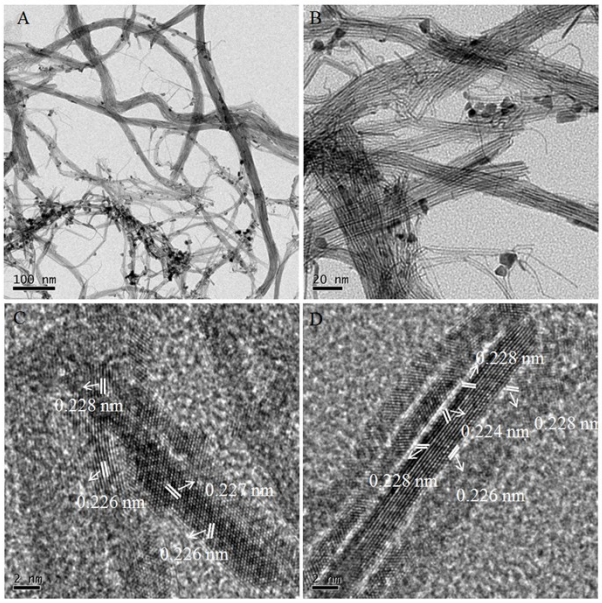

Figure S1 TEM images (A and B) and HR-TEM images (C and D) of Pt NWs/C

Table S1. Summary of Particle Sizes and Lattice Constants for Pt_xPd_{100-x}/C Catalysts

Catalysts	NWs size (nm)	Metal loading (% wt)	Lattice parameter (nm)	Scherer size (nm)
$Pt_{12}Pd_{88}$/C	2.3±0.5	13.0%	0.3895	2.4±0.4
$Pt_{35}Pd_{65}$/C	2.0±0.2	15.0%	0.3903	2.1±0.3
$Pt_{62}Pd_{38}$/C	1.9±0.2	15.0%	0.3909	2.0±0.2
$Pt_{78}Pd_{22}$/C	1.8±0.3	17.0%	0.3915	1.9±0.2
Pt/C	1.5±0.5	15.0%	0.3923	1.7±0.3

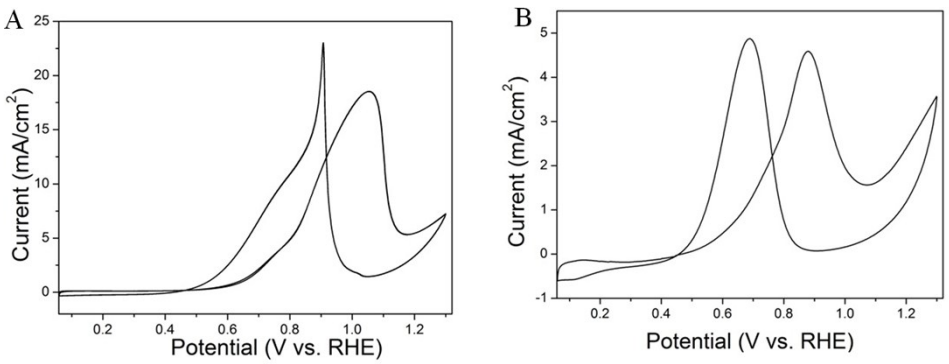

Figure S2. CV curves of (A) Pt NWs/C and (B) commercial Pt/C in 0.1 M $HClO_4$ + 0.5 M CH_3OH solution purged with N_2 at a scan rate of 50 mV s^{-1}

Table S2. Summary of electrochemical parameters of methanol oxidation for Pt_xPd_{100-x}/C Catalysts

Catalysts	anodic peak current (mA/cm^2)	ECSA (m^2/g_{Pt+Pd})	MA (A/mg_{Pt+Pd})	SA (mA/cm^2)
$Pt_{12}Pd_{88}$/C	2.8	48	0.24	0.5
$Pt_{35}Pd_{65}$/C	11.5	65	0.87	1.34
$Pt_{62}Pd_{38}$/C	33.0	50	1.21	1.46
$Pt_{78}Pd_{22}$/C	17.5	80	1.15	1.95

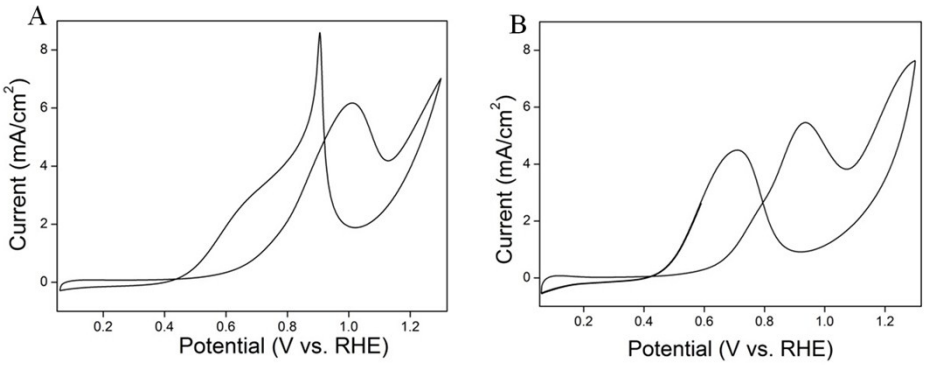

Figure S3. CV curves of (A) Pt NWs/C and (B) commercial Pt/C in 0.1 M $HClO_4$ + 0.5 M C_2H_5OH solution purged with N_2 at a scan rate of 50 mV s^{-1}

Table S3. Summary of electrochemical parameters of ethanol oxidation for Pt_xPd_{100-x}/C Catalysts

Catalysts	anodic peak current (mA/cm^2)	ECSA (m^2/g_{Pt+Pd})	MA (A/mg_{Pt+Pd})	SA (mA/cm^2)
$Pt_{12}Pd_{88}$/C	2.9	48	0.23	0.48
$Pt_{35}Pd_{65}$/C	5.0	65	0.40	0.62
$Pt_{62}Pd_{38}$/C	9.0	50	0.66	0.80
$Pt_{78}Pd_{22}$/C	8.0	80	0.58	0.98

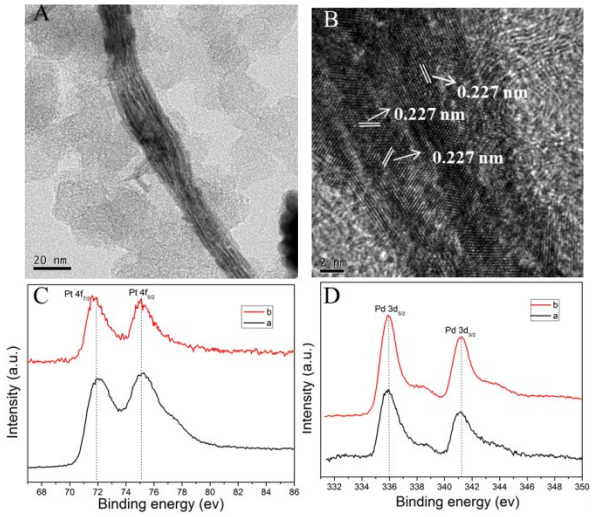

Figure S4. (A) TEM images after chronoamperometry measurement (2.3±0.5 nm); (B) HR-TEM image, the lattice fringes for

(111): 0.227 nm; (C) Pt 4f and (D) Pd 3d (a: before; b: after chronoamperometry measurement). The international standard (C 1s) was used to calibrate the peak position.

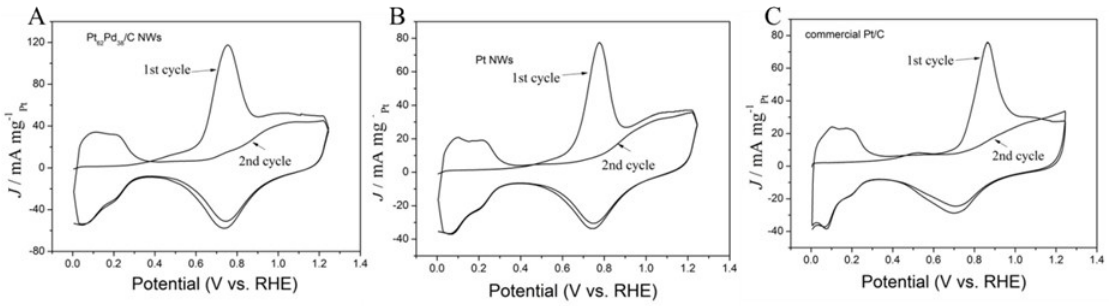

Figure S5. CO stripping curves (A) $Pt_{62}Pd_{38}$/C NWs, (B) Pt NWs and (C) commercial Pt/C in 0.1 M $HClO_4$ solution at a scan rate of 50 mV s^{-1}.

References

1 F. -F. Chang, S. -Y. Shan, V. Petkov, S. Zakiya, A. -L. Lu, J. Ravid, J. -F. Wu, J. Luo, G. Yu, Y. Ren, C. J. Zhong, Composition tunability and (111)-dominant facets of ultrathin platinum-gold alloy nanowires toward enhanced electrocatalysis, *J. Am. Chem. Soc.*, 2016, 138, 12166-12175.

2 Y. Liao, G. Yu, Y. Zhang, T. -T. Guo, F. -F. Chang, C. -J. Zhong, Composition-tunable PtCu alloy nanowires and electrocatalytic synergy for methanol oxidation reaction, *J. Phys. Chem. C.*, 2016, 19, 10476-10484.