Supporting Information

Noble Metal Nanowire Array as Ethanol Oxidation Electrocatalyst

Zhenhui Lam[a,b,c,‡], Cuicui Liu[b, ‡], Dongmeng Su[b], Huabing Tao[c], Hsin-Yi Wang[c], Jiazang Chen[c], Weichang Xu[b], Liping Zhang[a,c], Yihan Zhu[e], Lingmei Liu[e], Yu Han[e], Hongyu Chen[a,b,d,], Bin Liu[a,c,]**

[a] Energy Research Institute of NTU (ERI@N), Interdisciplinary Graduate School, Nanyang Technological University, Singapore 639798.
[b] Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371.
[c] School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore 637459.
[d] Institute of Advanced Synthesis (IAS), School of Chemistry and Molecular Engineering, Jiangsu National Synergetic Innovation Center for Advanced Materials, Nanjing Tech University, Nanjing 211816, P. R. China.
[e] Advanced Membranes and Porous Materials Center, Physical Sciences and Engineering Division, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia.

‡These authors contributed equally.

*Corresponding Author

E-mail : iashychen@njtech.edu.cn; liubin@ntu.edu.sg

EXPERIMENTAL METHODS

Ascorbic acid (AA), (3-aminopropyl)triethoxysilane (APTES), dimethylformamide (DMF), ethanol (EtOH), chloroauric acid ($HAuCl_4$), chloropalladious acid (H_2PdCl_4), chloroplatinic acid (H2PtCl6), methacrylic acid (MAA), 4-mercaptobenzoic acid (4-MBA), nafion solution (Nafion), polyvinylpyrrolidone (PVP), palladium on activated charcoal (Pd/C, 10% Pd basis, Sigma-Aldrich 75990), sodium borohydrate ($NaBH_4$), sodium citrate tribasic dihydrate, and fluorine doped tin oxide (FTO) glass were all purchased from Sigma-Aldrich. Platinum on Vulcan XC-72 was purchased from Premetek. All chemicals were used as received without further purification.

Synthesis of Au NWs and Au@Pd NWs. Au NW arrays were synthesized following method reported by He, J. T. et al., [20]. Firstly, gold seed (Au NSs) solution was prepared by adding 100 µL of aqueous $HAuCl_4$ solution (17 mg/mL), 160 µL of sodium citrate (1 wt%, H_2O) and 620 µL of $NaBH_4$ (3.8 mg/mL) into 20 mL of deionized H_2O while stirring. Next, FTO glass (around 2 cm^2) was treated in APTES solution (1 µL/mL, EtOH:H_2O = 1:1) for 15 minutes. Then, the FTO glass was washed with H_2O for 5 times, which was then incubated in gold seed solution prepared previously for 1 hour. After that, the gold seed immobilized FTO glass was rinsed in water twice, and then incubated in growth solution for 15 minutes. The growth solution was made up of 150 µL of $HAuCl_4$ (17 mg/mL, H_2O), 600 µL of 4-MBA (10 mM, EtOH), 900 µL of AA (20mM, H_2O) and 2.1 mL of EtOH as solvent. Finally, the FTO glass covered with Au NWs was rinsed with EtOH and H_2O, and then stored for further use. All of the above procedures were carried out at room temperature. Following, Pd was coated by incubating the as-prepared Au NW arrays in MAA solution (1 µL/mL, DMF) at 60 °C for 2 hours, then rinsed with water. Subsequently, the FTO glass with Au NWs was incubated in Pd growth solution at room temperature. The Pd growth solution was made up of 200 µL of

H_2PdCl_4 (20 mM, H_2O), 40 µL of PVP (20 mg/mL, H_2O), 400 µL of AA (10 mM, H_2O) and 2 mL of H_2O as solvent. The synthesized Au@Pd NWs were rinsed with H_2O and stored for further use.

Preparation of Au@Pd NPs electrode. Firstly, gold seed (Au NSs) solution was prepared by adding 100 µL of aqueous $HAuCl_4$ solution (17 mg/mL), 160 µL of sodium citrate (1 wt%, H_2O) and 620 µL of $NaBH_4$ (3.8 mg/mL) into 20 mL of deionized H_2O while stirring. 2 mL of as-synthesized Au NSs solution was concentrated by centrifugation. Next, Au NSs was incubated in Pd growth solution at room temperature. The Pd growth solution was made up of 200 µL of H_2PdCl_4 (20 mM, H_2O), 40 µL of PVP (20 mg/mL, H_2O), 400 µL of AA (10 mM, H_2O) and 2 mL of H_2O as solvent. The synthesized Au@Pd NPs were rinsed with H_2O and stored for further use. After that, FTO glass (around 2 cm^2) was treated in APTES solution (1 µL/mL, EtOH:H_2O = 1:1) for 15 minutes. Then, the FTO glass was washed with H_2O for 5 times, which was then left dried in ambient condition. After that, 7µL of Au@Pd NPs solution was drop cast onto the FTO glass and left dried under vacuum to prevent the prepared electrode from oxidation.

Preparation of Pd/C and Pt/C electrode. First, 2 mg of Pd/C (or Pt/C) was mixed with 1 mL EtOH and H_2O solution (EtOH:H_2O = 1:1). The mixture was sonicated for 30 minutes. Next, FTO glass (around 2 cm^2) was treated in APTES solution (1 µL/mL, EtOH:H_2O = 1:1) for 15 minutes. Then, the FTO glass was washed with H_2O for 5 times, which was then left dried in ambient condition. After that, 7µL of Pd/C mixture was drop cast onto the FTO glass and left dried under vacuum to prevent the prepared electrode from oxidation.

Structural Characterization. The surface morphologies of Au NWs and Au@Pd NWs were characterized by field emission scanning electron microscope (SEM, JEOL JSM-6700F), transmission electron microscopy (TEM, JEOL, operated at 100 kV) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010EX, operated at 200 kV). Atomic resolution scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) experiments were carried out on an FEI aberration-corrected Titan Cubed S-Twin transmission electron microscope (JEOL, JEM-2100F) with high-angle annular dark-filed (HAADF) detector operated at 200 kV. The mass and chemical composition of Au NWs, Au@Pd NWs and were determined using inductively coupled plasma optical emission spectrometry (ICP-OES, PerkinElmer® Optima™ 8300 and PerkinElmer® Avio™ 200).

Electrochemical Characterization. The electrochemical properties were studied in a standard three-electrode cell. The cyclic voltammetry and chronoamperometry measurements were conducted using a CHI 660D electrochemical workstation. The reference electrode used is saturated calomel electrode (SCE) and the counter electrode is Pt foil. As both Au NWs and Au@Pd NWs were growth directly on substrate, no additional treatment was needed when applied as the working electrode. The controls used in this experiment, Pd/C, Pt/C and Au NPs were prepared using drop-cast method, and then were covered with a thin layer of Nafion (5 μL, 5 wt%) before electrochemical measurement. The Pd loading on Au@Pd NWs and Pd/C catalyst were 17.6 μg/cm^2. The Au loading on Au NWs and Au NPs were 13.9 μg/cm^2. The working electrode surface area was limited to 0.28 cm^2. The cyclic voltammograms were measured at a scan rate of 50 mV/s. The chronoamperometry curves for ethanol oxidation were measured at 0.87 V vs. RHE for Pd and 1.07 V vs. RHE for Au. For both cyclic voltammograms and chronoamperometry measurements, the electrolyte used was 1.0 M ethanol with 1.0 M NaOH aqueous solution. The electrolyte was purged with N_2 gas for 30 minutes prior to all electrochemical measurements. All electrochemical measurements were carried out at 25 °C.

SUPPLEMENTARY FIGURES

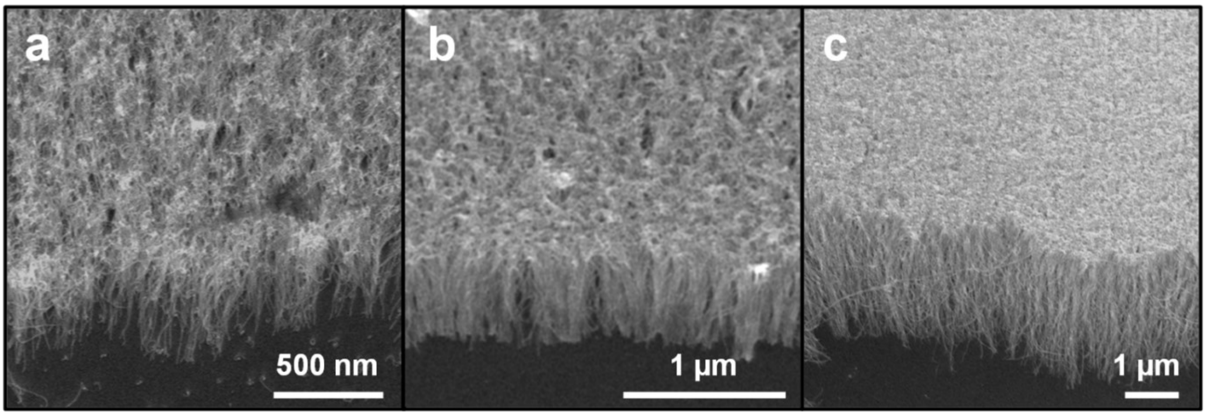

Figure S1. Cross-sectional SEM images of Au NWs with different lengths. The length of Au NWs can be simply controlled by varying the synthesis period.

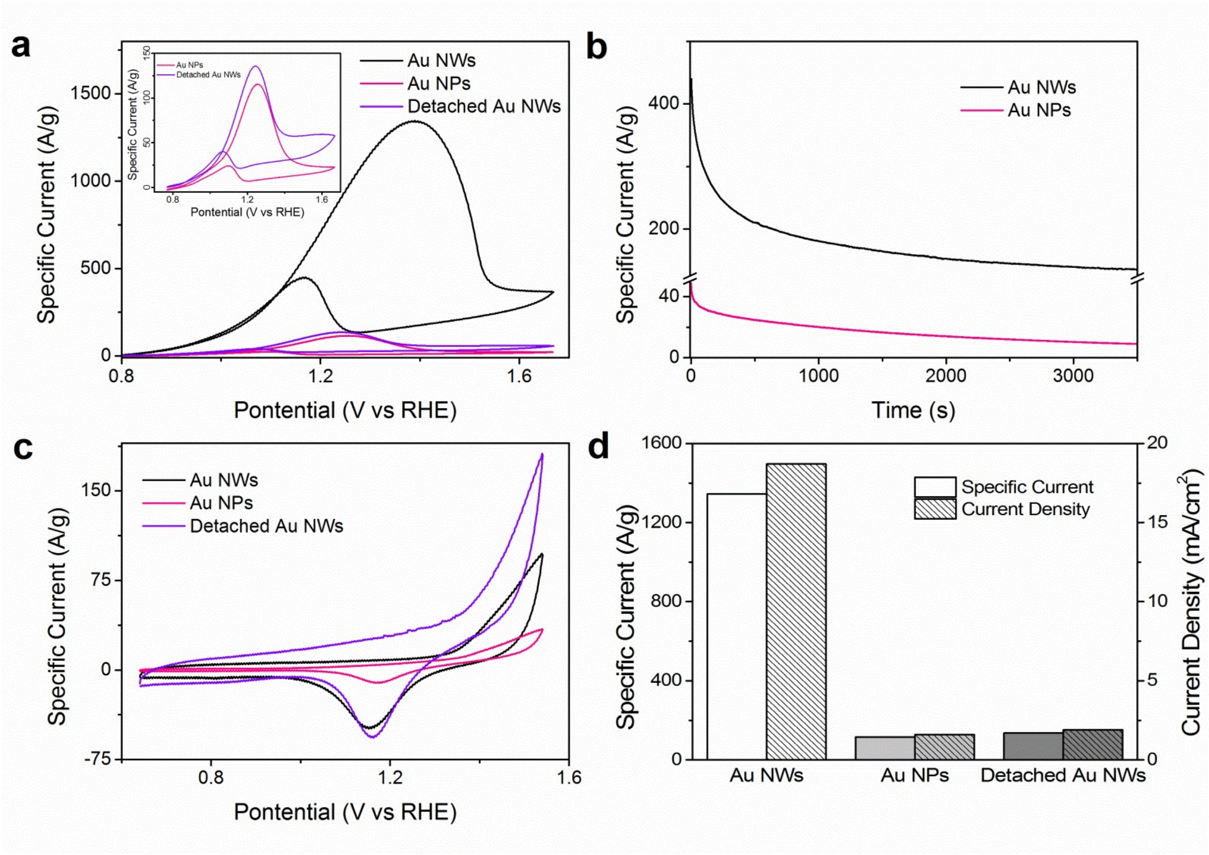

Figure S2. Electrocatalytic properties of Au NWs. (a) CV curves of Au NWs, Au NPs and detached Au NWs catalysts measured in solution of 1.0 M NaOH and 1.0 M ethanol at a scan rate of 50 mV/s. Insert shows the zoom in CV curves of Au NPs and detached Au NWs. (b) Chronoamperometry graph measured at 1.07 V vs. RHE. (c) CV curves of for Au NWs, Au NPs and detached Au NWs measured in solution of 0.5 M H_2SO_4 at a scan rate of 50 mV/s. (d) Specific current and current density comparison of Au NWs, Au NPs and detached Au NWs.

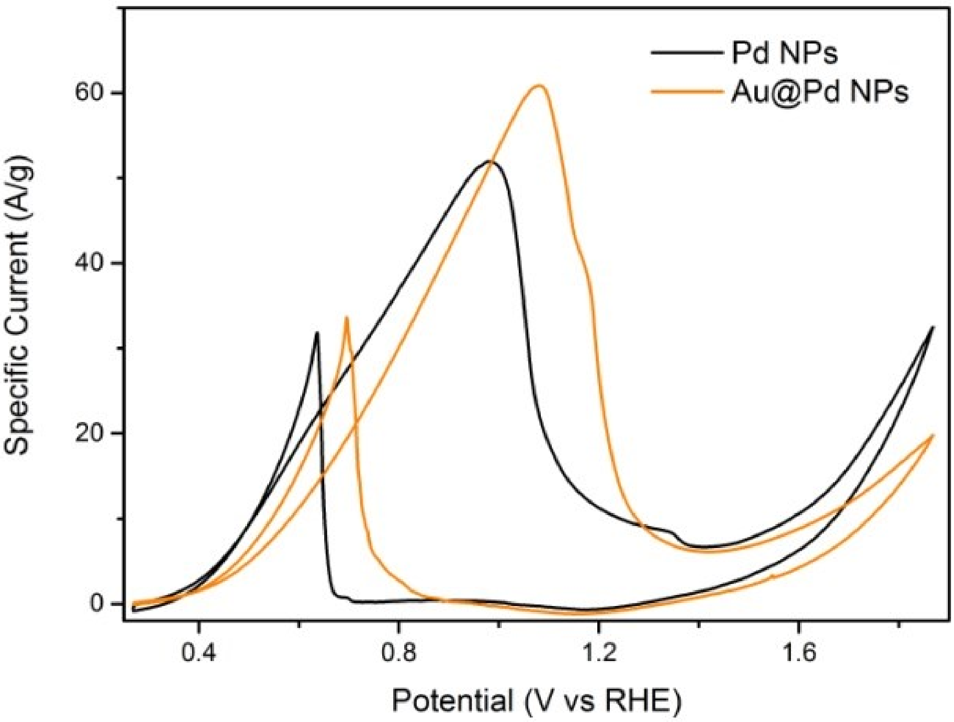

Figure S3. CV curves of Pd NPs and Au@Pd NPs measured in solution of 1.0 M NaOH and 1.0 M ethanol at a scan rate of 50 mV/s. As shown in the CV curves, there is only a slight difference in the specific current for Pd NPs and Au@Pd NPs of the same size, ruling out the enhancement effect from the Au@Pd synergy in our system.

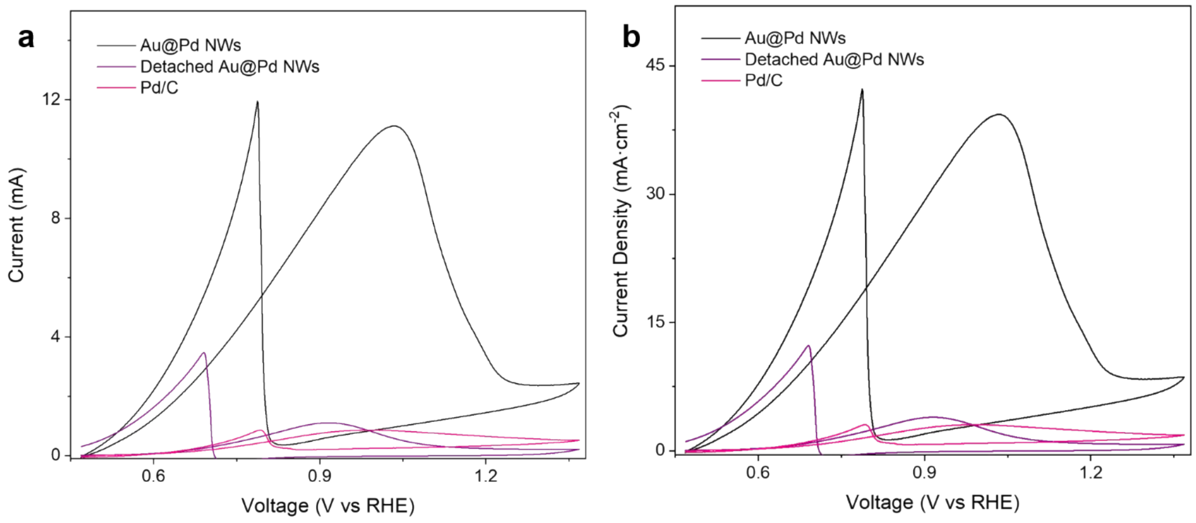

Figure S4. Electrocatalytic properties of Au@Pd NWs. CV curves (a) in raw current and (b) in current density of Au@Pd NWs, detached Au@Pd NWs and Pd/C catalysts measured in solution of 1.0 M NaOH and 1.0 M ethanol at a scan rate of 50 mV/s.

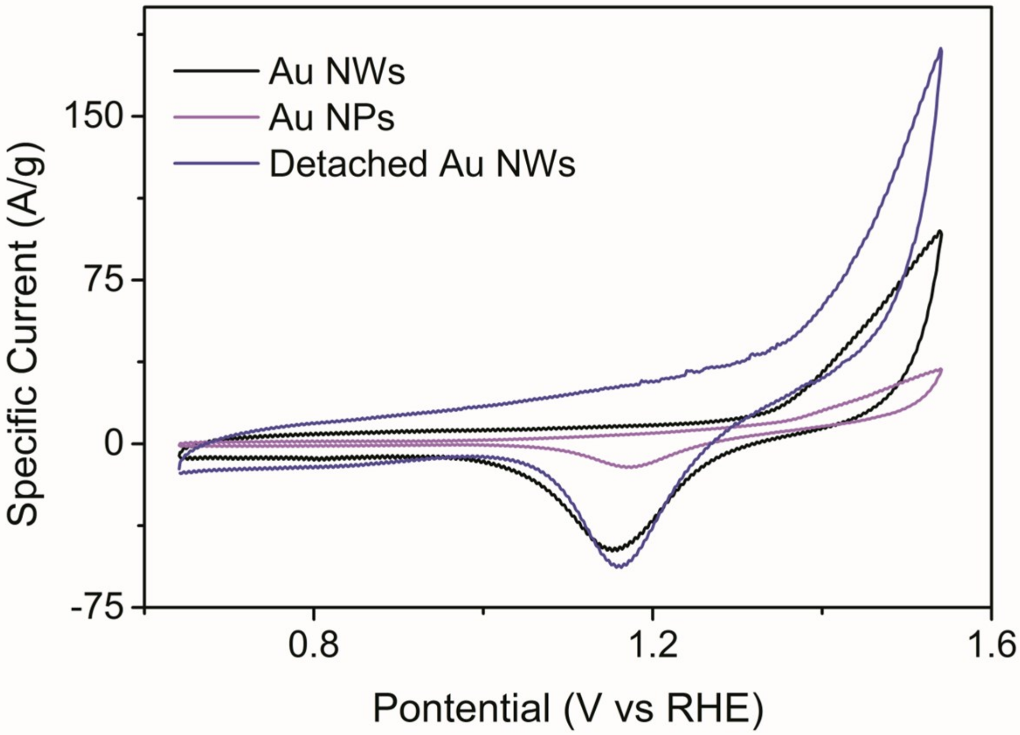

Figure S5. CV curves for Au NWs, Au NPs and detached Au NWs measured in solution of 0.5 M H_2SO_4 at a scan rate of 50 mV/s.

To obtain the electrochemical active surface area (ECSA) of Au NWs and Au NPs, cyclic voltammetry measurements were carried out in 0.5 M H_2SO_4 at a scan rate of 50 mV/s. ECSA was calculated using the following equation:

$$\mathrm{ECSA} = Q_H/0.45*[\mathrm{Au}]$$

where Q_H is the charge resulting from gold oxide (Au_2O_3) reduction (around 1.15 V vs. RHE), 0.45 mC cm^{-2} is the electrical charge associated with Au_2O_3 reduction and [Au] is the loading amount of Au on the working electrode. The ECSA value of Au NWs, Au NPs and detached Au NWs are 50.8 m^2/g, 10.2 m^2/g and 35.6 m^2/g, respectively.

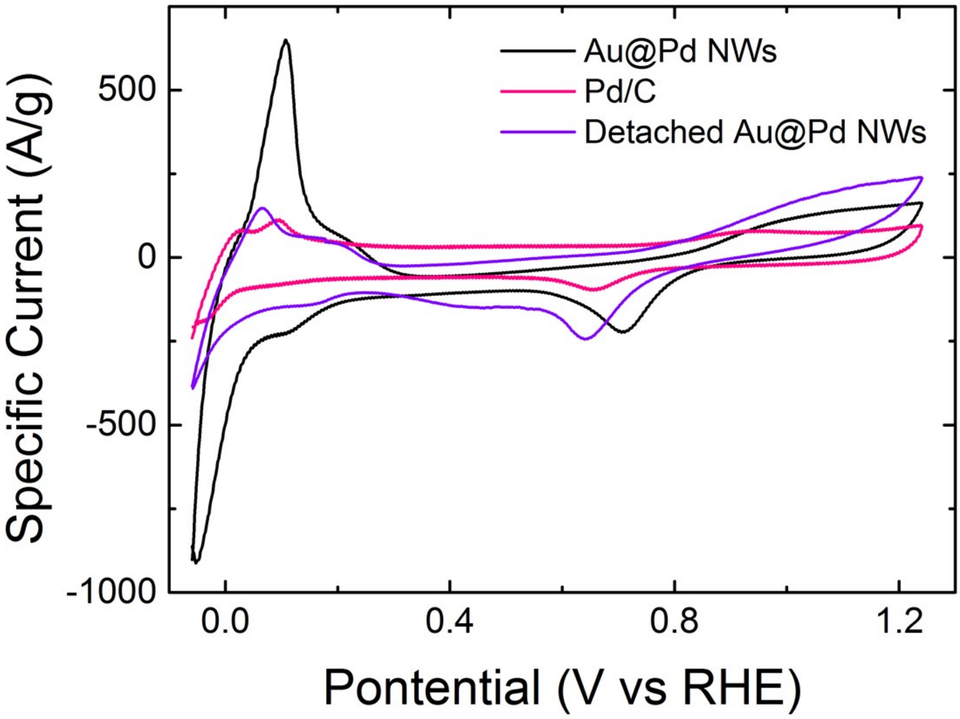

Figure S6. CV curves for Au@Pd NWs, Pd/C and detached Au@Pd NWs measured in solution of 0.5 M H_2SO_4 at a scan rate of 50 mV/s.

To obtain the electrochemical active surface area (ECSA) of Au@Pd NWs and Pd/C, cyclic voltammetry measurements were carried out in 0.5 M H_2SO_4 at a scan rate of 50 mV/s. ECSA was calculated using the following equation:

$$\mathrm{ECSA} = Q_{\mathrm{PdO}}/0.405*[\mathrm{Pd}]$$

where Q_{PdO} is the charge resulting from palladium oxide (PdO) reduction (around 0.70 V vs. RHE), 0.405 mC cm^{-2} is the electrical charge associated with PdO reduction and [Pd] is the loading of Pd on the working electrode. The ECSA value of Au@Pd NWs, Pd/C and detached Au@Pd NWs are 110.1 m^2/g, 43.3 m^2/g and 81.8 m^2/g, respectively.

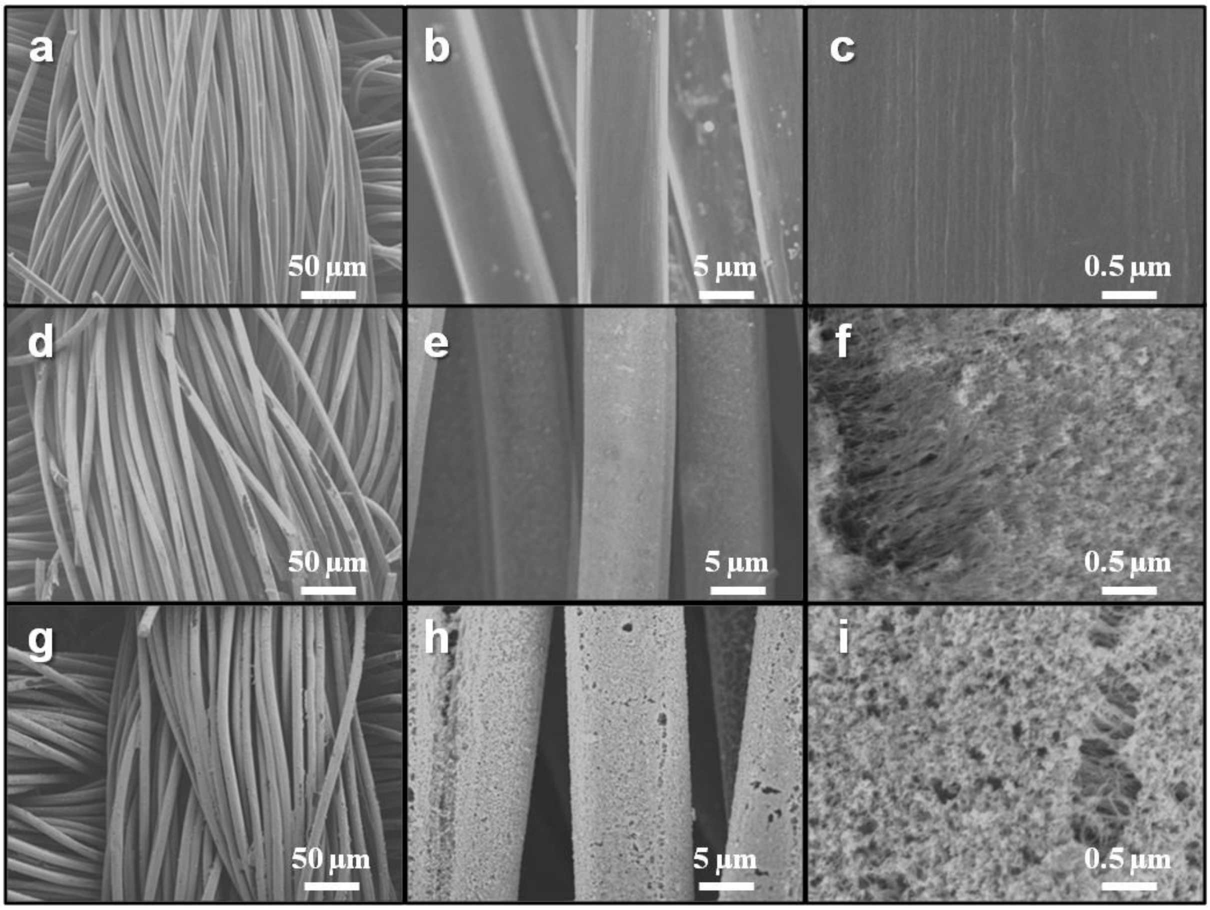

Figure S7. The ability to grow noble metal nanowire forest on three-dimensional conductive electrode was demonstrated on carbon fiber cloth. (a-c) SEM images of bare carbon cloth. (d-f) SEM images of Au NWs grown on conducting carbon cloth. (g-i) SEM images of Au@Pd NWs grown on conducting carbon cloth.

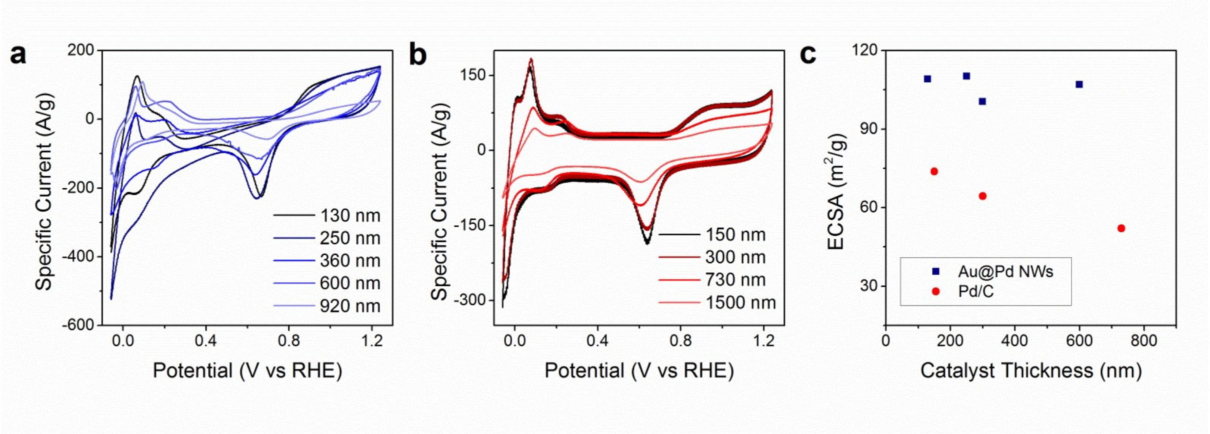

Figure S8. The mass transport of nanowire arrays and nanoparticle catalyst layers were assessed by comparing their electrocatalytic active surface area (ECSA) at different length or thickness. (a) CV curves for Au@Pd NWs and (b) Pd/C of different length or thickness measured in solution of 0.5 M H_2SO_4 at a scan rate of 50 mV/s. (c) A comparison plot of ECSA against thickness of catalyst between Au@Pd NWs and Pd/C.

Table S1. ECSA measured in 0.5 M H_2SO_4 solution for Au@Pd NWs, Pd/C and Au@Pd NPs at different length/thickness.

Au@Pd NWs length (nm)	ECSA (m^2/g)	Pd/C thickness (nm)	ECSA (m^2/g)
130	109.1	150	73.8
250	110.1	300	64.4
360	100.4	730	52.1
600	106.9	1500	28.9
920	37.5		

Assumption The comsumption of reactants (ethanol) on the catalyst surface is instantaneous, reactants will be depleted at the catalyst surface if a potential is suddenly applied and there will be a concentration gradient that drive diffusion of reactants (ethanol molecules) from bulk of solution to the surface of catalyst. In both cases (Au@Pd NWs and Pd/C), the diffusion of ethanol towards the electrode can be divided into two parts: the diffusion of ethanol from bulk to the surface layer of catalyst, and the diffusion of ethanol inside the catalyst layer. The two diffusion steps were lumped together and difficult to be decoupled. Here, we treat both Au@Pd NWs and Pd/C electrodes with same catalyst layer thickess as the planar electrodes, the overall ethanol diffusion coefficeint for the Au@Pd NWs and Pd/C electrodes was estimated using the Randles-Sevcik equation as shown below:

$$I_p = 0.4463\ nFAC(nFvD/RT)^{1/2}$$

where I_p is the peak current, n is the number of electrons involved in ethanol oxidation, F and R is faraday constant and gas constant, respectively, A is the electrode surface area, C is the bulk concentration of ethanol, ν is the scan rate, T is temperature and D is the diffusion coefficient. Following this equation, the diffusion coefficient can be estimated by plotting the peak current against square root of scan rate.

Table S2. Ethanol diffusion coefficient estimated from the Randles-Sevcik method. The length of Au@Pd NWs and thickness of Pd/C were kept to around 200 nm.

Au@Pd NWs			**Pd/C**		
Scan rate, ν (V/s)	**Peak current, I_p (A)**	**Diffusion coefficient, D (cm^2/s)**	**Scan rate, ν (V/s)**	**Peak current, I_p (A)**	**Diffusion coefficient, D (cm^2/s)**
0.001	3.0×10^{-3}	2.8×10^{-14}	0.001	4.9×10^{-4}	2.9×10^{-16}
0.002	5.0×10^{-3}		0.002	4.1×10^{-4}	
0.005	8.0×10^{-3}		0.005	7.8×10^{-4}	
0.010	1.0×10^{-2}		0.010	9.9×10^{-4}	

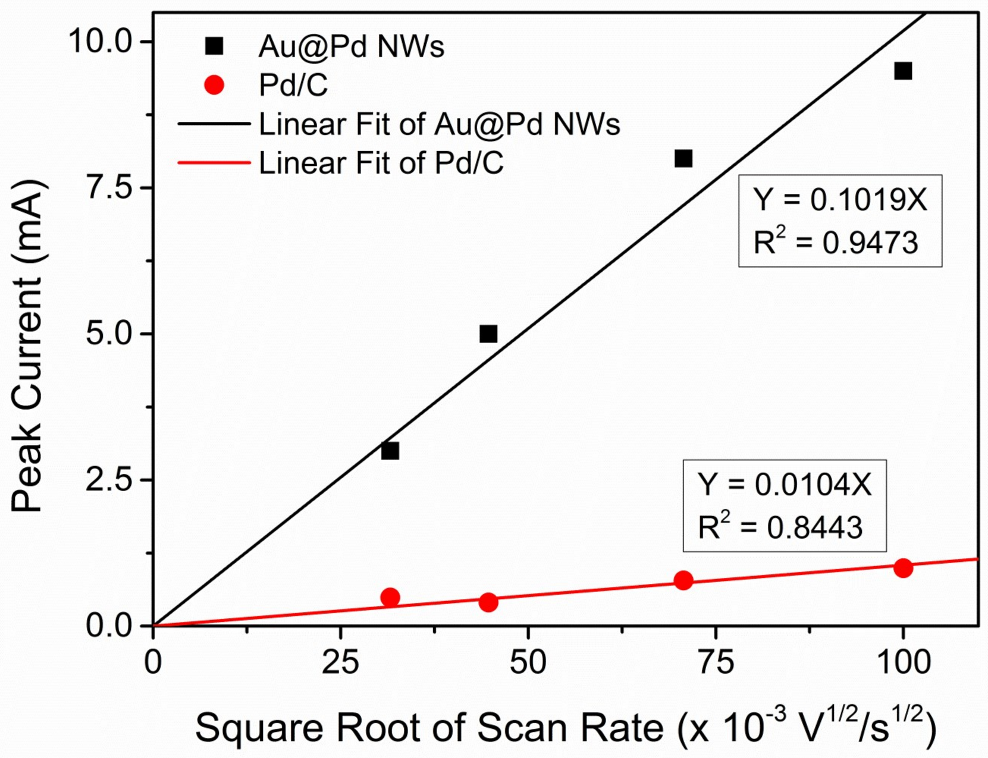

Figure S9. Plot of peak current against square root of scan rate for Au@Pd NWs and Pd/C.

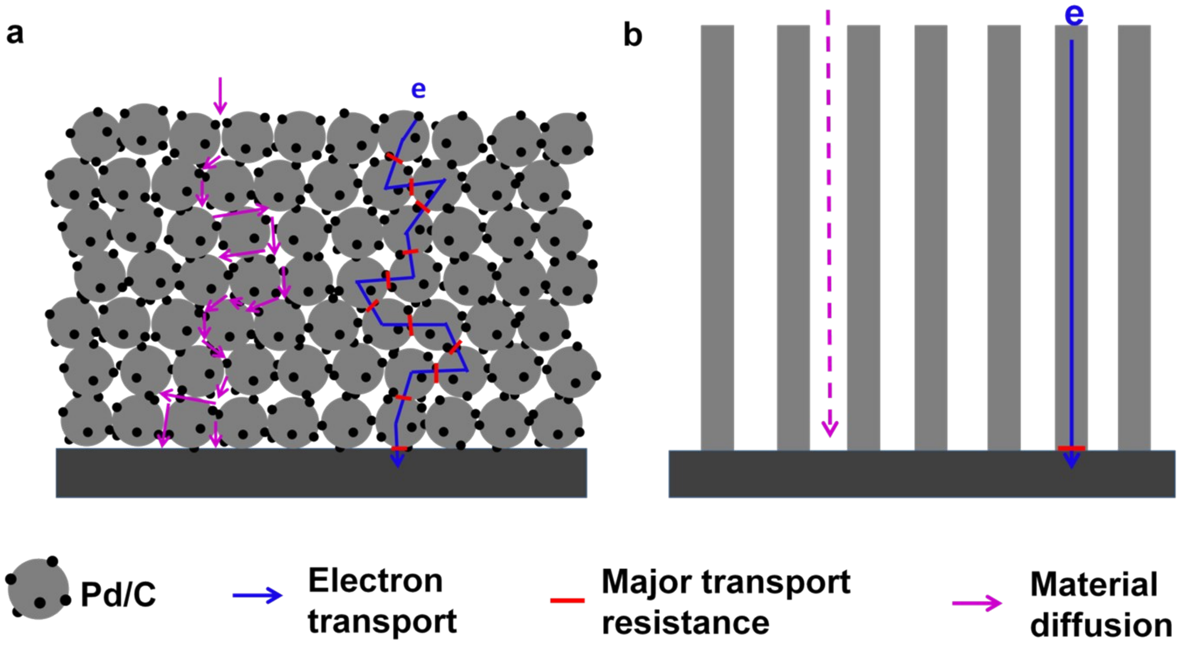

Figure S10. Schematic illustration showing different electron and material transport pathways adopted by nanoparticles and nanowire arrays. (a) Pd/C. (b) Au@Pd NWs.

Table S3. The gold (Au), palladium (Pd) and platinum (Pt) loading amounts of various nanowires on FTO as measured from ICP-OES.

Sample	**Loading amount on FTO (mg/cm^2)**		
	Au	**Pd**	**Pt**
Au NWs	0.019	0	0
Au@Pd NWs	0.018	0.017	0
Au@$Pd_{13.3}Pt_1$ NWs	0.018	0.017	0.001
Au@$Pd_{5.2}Pt_1$ NWs	0.018	0.016	0.003
Au@$Pd_{2.2}Pt_1$ NWs	0.017	0.011	0.005
Au@Pt NWs	0.022	0	0.001

Table S4. The summary of recent achievements in Pd based electrocatalysts for ethanol oxidation reaction.

Electrocatalyst	**Electrolyte**	**Mass Activity (A/g)**	**ECSA (m^2/g)**
Au@Pd NWs (this work)	1.0 M NaOH + 1.0 M ethanol	2237.7	110.1
Au@$Pd_{2.2}Pt_1$ NWs (this work)	1.0 M NaOH + 1.0 M ethanol	6568.1	NA
THH Pd NCs [8]	0.1 M KOH + 0.1 M ethanol	150	8.2
PdNi/C [10]	1 M KOH + 1 M ethanol	1136	NA
Pd-NiO/C [11]	1.0 M KOH + 1.0 M ethanol	316	NA
Pd_4–NiO_1/C [12]	1.0 M KOH + 1.0 M ethanol	246	47
Pd NW [13]	1.0 M KOH + 1.0 M ethanol	1415	12
Pd/PANI/Pd SNTAs [14]	1.0 M NaOH + 1.0 M ethanol	360	3.39
CNT/Pd [15]	1.0 M KOH + 1.0 M ethanol	247.8	NA
Pd/CNTA [16]	1.0 M KOH + 1.0 M ethanol	1484.4	NA
Pd/TiO_2C NT [17]	1.0 M KOH + 1.0 M ethanol	254	NA

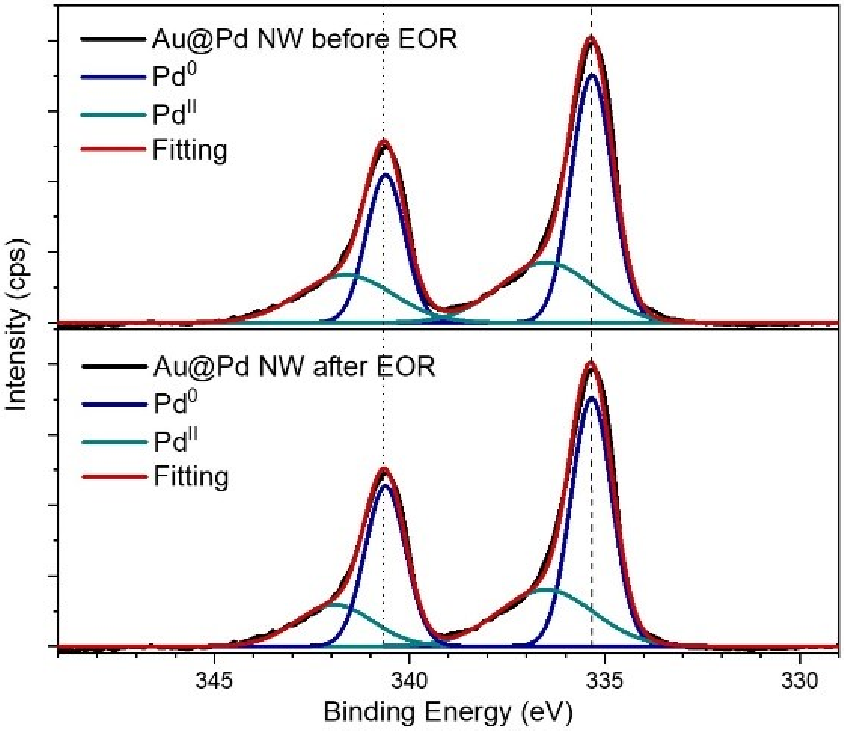

Figure S11. XPS data for the Au@Pd nanowire forest before and after the electrochemical test. It is believed that the Pd remained chemically unchanged after repeated electrochemical tests.