Rich grain boundaries endow networked PdSn nanowires with superior catalytic properties for alcohols oxidation

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1. Experimental Section

1.1. Chemicals

Palladium (II) acetylacetonate ($Pd(acac)_2$, 99%), N, N-Dimethylformamide (DMF) were purchased from Sigma-Aldrich. Tin oxalate (SnC_2O_4, 98%) was purchased from Aladdin. Polyvinylpyrrolidone (PVP, K30), Ammonium chloride (NH_4Cl, G.R. grade, 99.8%), and Ethylene glycol (EG, 99%) were purchased from Sinopharm Chemical Reagent Co.Ltd. (Shanghai, China). Water (H_2O) with a resistivity of 18MΩ/cm was used in this work.

1.2. Preparation of electrocatalysts

To synthesize PdSn networked nanowires (NNWs)-1 nanocatalysts, 7.6 mg of $Pd(acac)_2$, 1.7 mg of SnC_2O_4, 100 mg PVP, and 15 mg NH_4Cl were dissolved in 10 mL EG. After ultrasonic treatment for 10 min to obtain a homogeneous solution, the mixture was heated to 180 ℃ in an oil bath and kept for 1 h. Then the PdSn NNWs-1 were collected after centrifugation and washed with ethanol three times. The synthesis of PdSn NNWs-2/PdSn NNWs-3 was similar to that of PdSn NNWs-1, except that 8 mL of EG +2 ML DMF/5 mL of EG + 5 ML DMF substituted for 10 mL EG.

1.3. Physical Characterizations

To study the crystal and structural properties of PdSn NNWs, X-ray diffraction patterns (XRD) were carried out by an X'Pert-Pro MPD diffractometer. X-ray

photoelectron spectroscopy spectra (XPS, VG Scientific ECSALab 220 XL electron spectrometer) were used to analyze the chemical compositions and elemental valences of PdSn NNWs. The structural and compositional properties of PdSn NNWs were examined by the transmission electron microscope (TEM, HT-7700) and high-resolution TEM (HRTEM, F20, operating voltage: 200 kV). The compositions of PdSn NNWs were performed by Scanning electron microscope energy-dispersive X-ray spectroscopy (SEM-EDS, HITACHI S-4700, and operation voltage: 15 kV).

1.4. Preparation and electrochemical measurements

A standard three-electrode system was used to evaluate the electrochemical performance, in which a platinum wire and a saturated calomel electrode (SCE) were used as a counter electrode and a reference electrode, respectively. The working electrode was prepared by loading PdSn NNWs/C ink on the glass carbon electrode (GCE, Diameter: 5 mm). The preparation steps of PdSn NNWs/C ink are as follows: first load PdSn NNWs on Vulcan XC72R carbon black; then, disperse it into 1 ml isopropanol (containing 5 μL Nafion) to make 0.4 $mg_{Pd}mL^{-1}$ ink. After that, 5 μL of uniformly dispersed ink was dropped on the GCE and dried naturally to make a working electrode for testing.

2. Figures and Tables

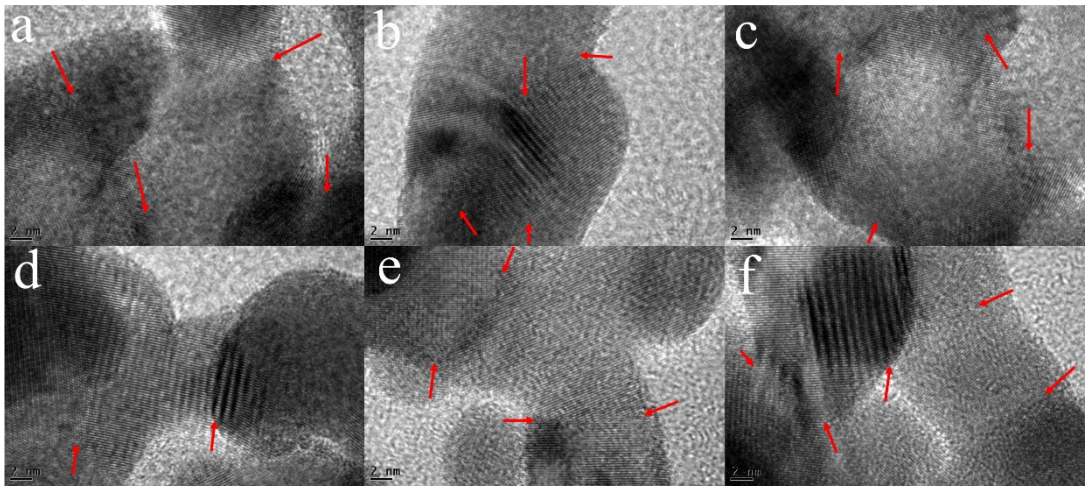

Fig S1 HRTEM images of PdSn NNWs-3.

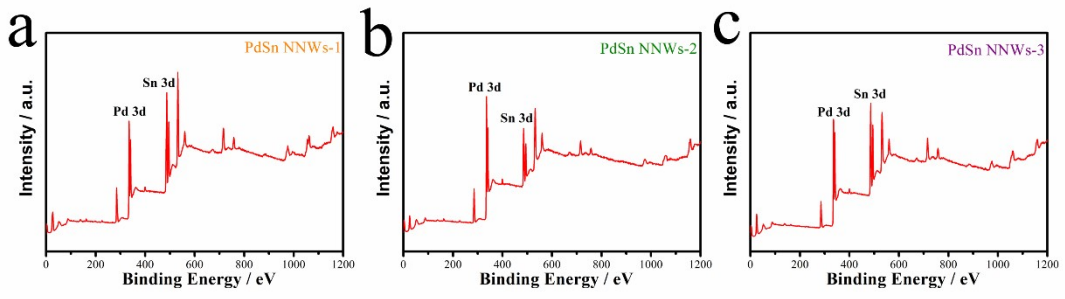

Fig S2 The XPS analysis of survey spectrum of (a) PdSn NNWs-1, (b) PdSn NNWs-2, and (c) PdSn NNWs-3.

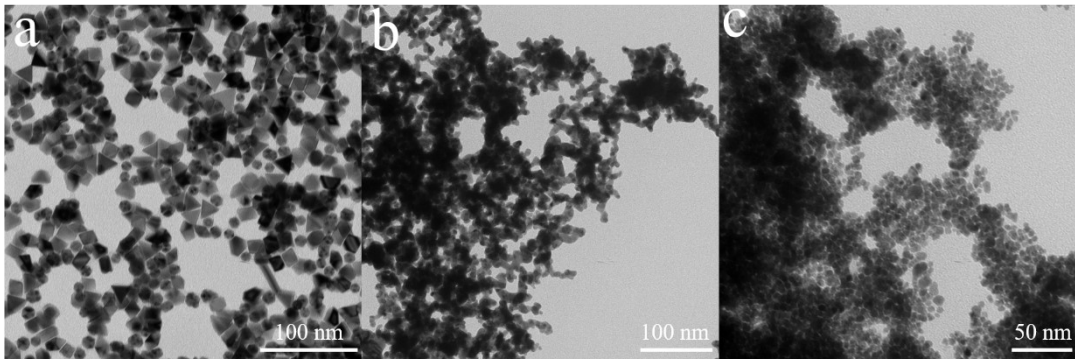

Fig S3 TEM images of the products with the same reaction conditions as that of PdSn NNWs-3 except that (a) without the addition of SnC_2O_4, the amount of SnC_2O_4 change to (b) 3.4 mg and (c) 5.1 mg.

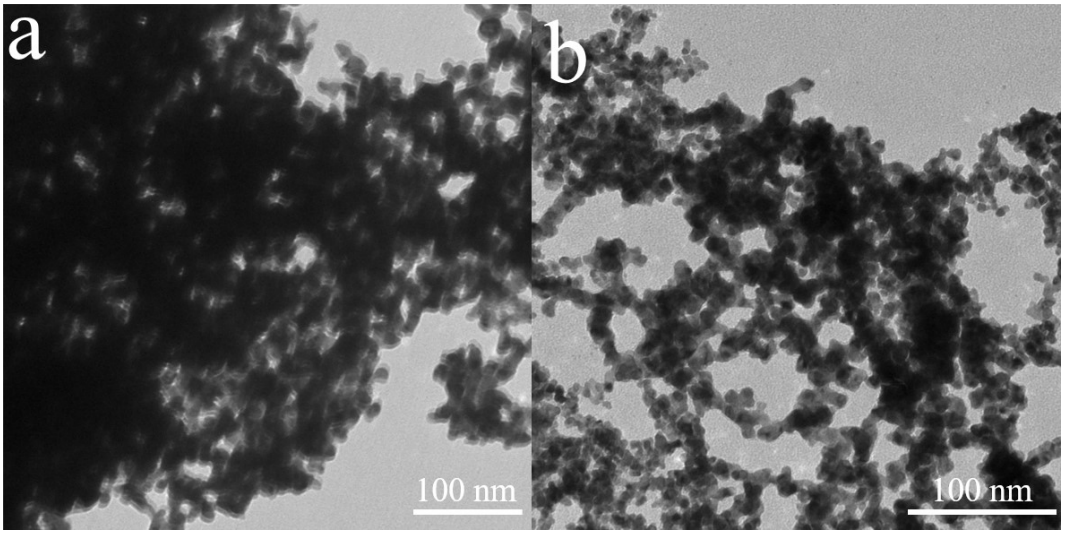

Fig S4 TEM images of the products with the same reaction conditions as that of PdSn NNWs-3 except that (a) without the addition of NH_4Cl, (b) the amount of NH_4Cl change to 30.0 mg.

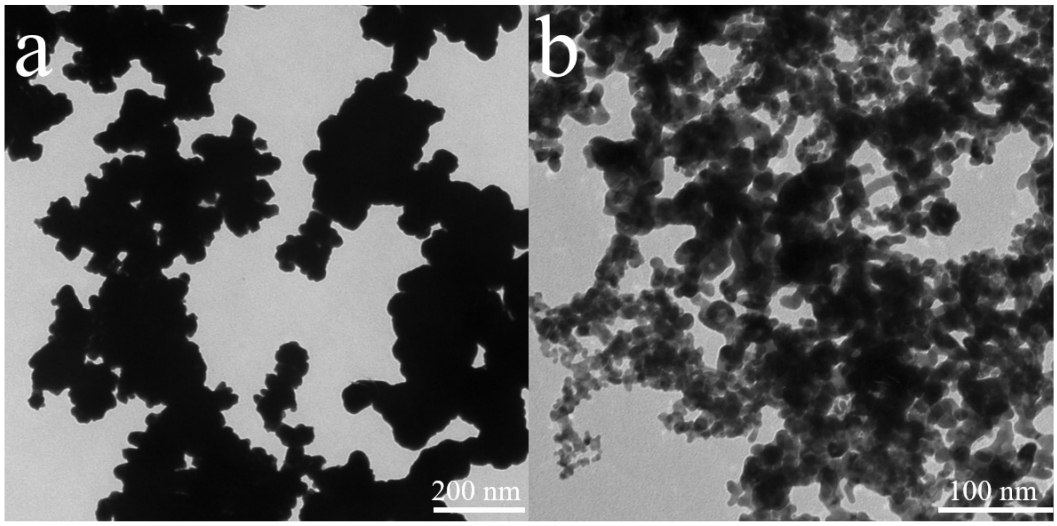

Fig S5 TEM images of the products with the same reaction conditions as that of PdSn NNWs-3 except that (a) without the addition of PVP, the amount of PVP change to (b) 50.0 mg and (c) 300.0 mg.

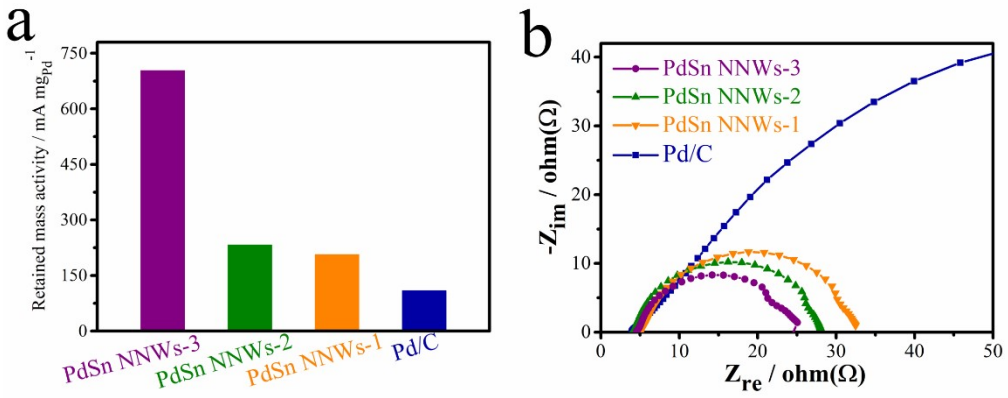

Fig S6 (a) The calculated retained specific activities after 3600 s current-time tests and (b) the EIS spectrum of catalysts in 1 M KOH and 1 M ethanol.

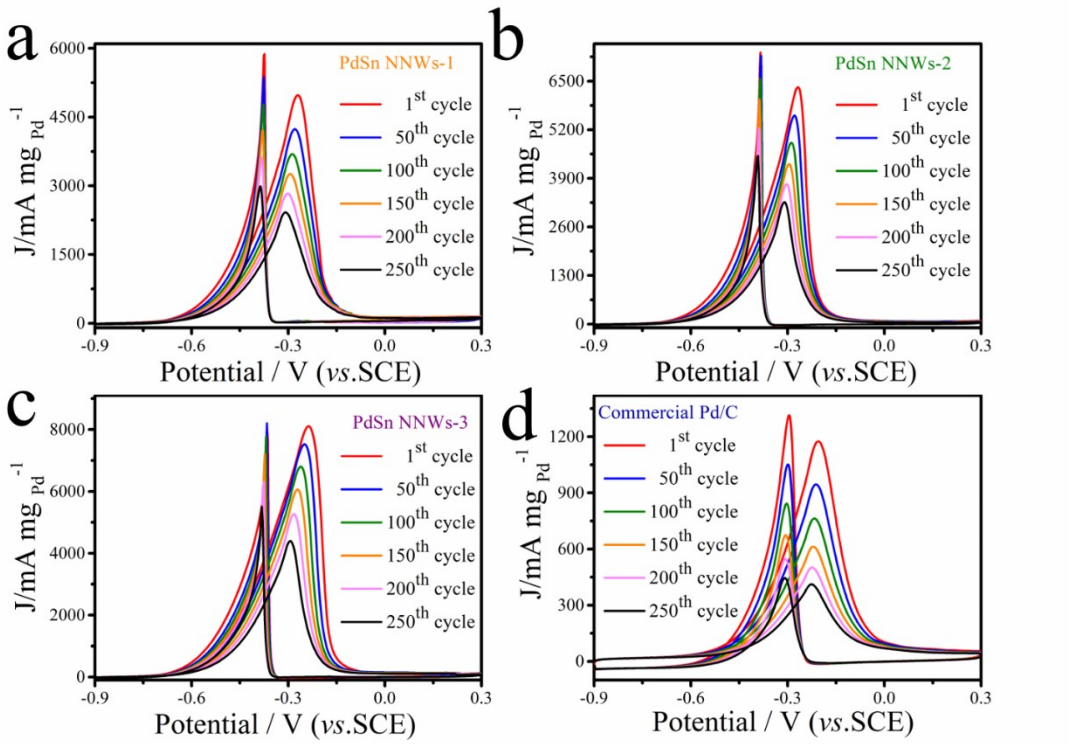

Fig S7 The CV curves of (a) PdSn NNWs-1, (b) PdSn NNWs-2, (c) PdSn NNWs-3, and (d) commercial Pd/C catalysts after CV sweeps for 250 cycles in the solution of 1 M KOH + 1 M ethanol.

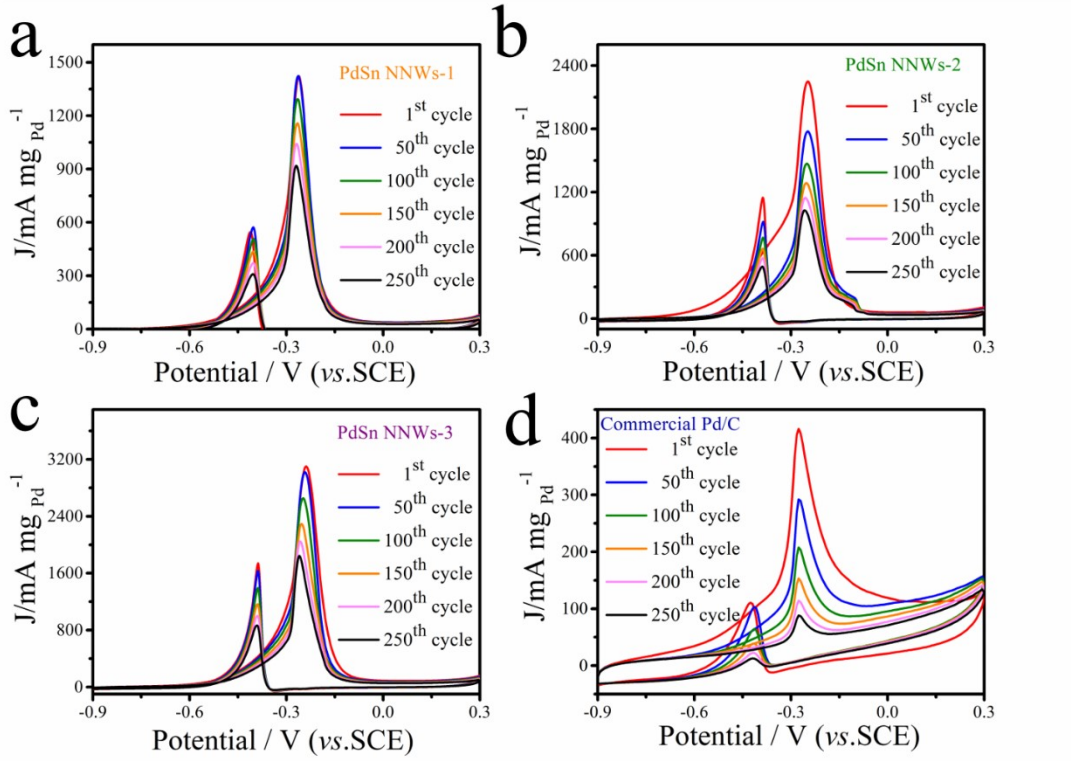

Fig S8 The CV curves of (a) PdSn NNWs-1, (b) PdSn NNWs-2, (c) PdSn NNWs-3,

and (d) commercial Pd/C catalysts after CV sweeps for 250 cycles in the solution of 1 M KOH + 1 M methanol.

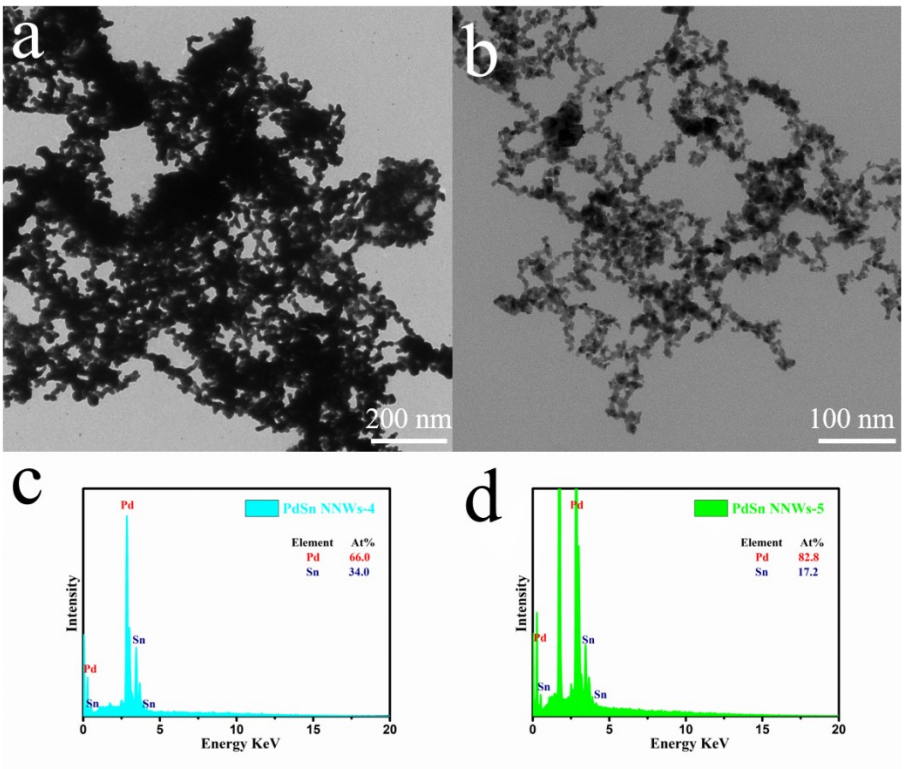

Fig S9 TEM images and SEM-EDS spectra of (a, c) PdSn NNWs-4 and (b, d) PdSn NNWs-5.

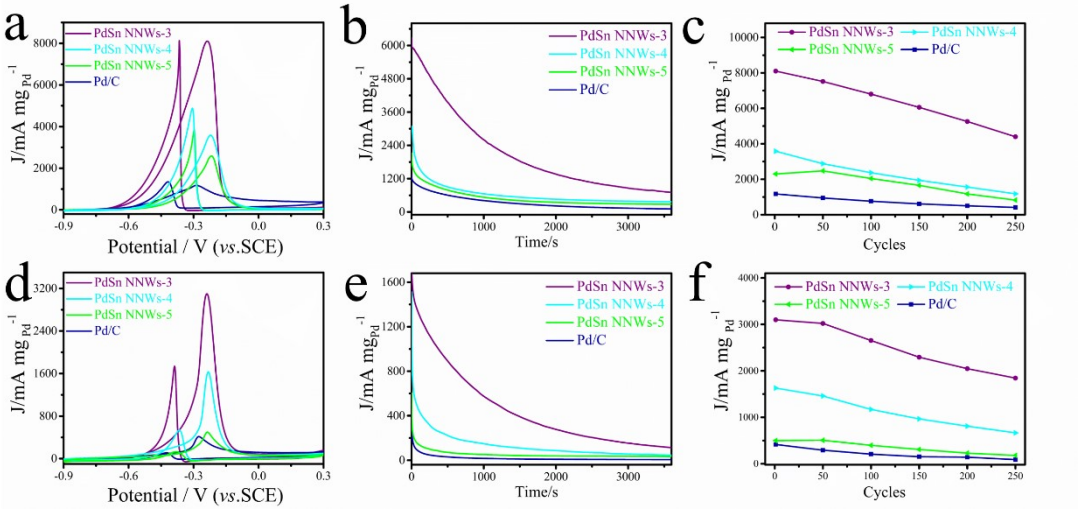

Fig S10 (a) CV curves, (b) Current-time curves, and (c) Durability comparison of PdSn NNWs-3/4/5 and commercial Pd/C conducted in 1 M KOH + 1 M ethanol solution. (d) CV curves, (e) Current-time curves, and (f) Durability comparison of PdSn NNWs-3/4/5 and commercial Pd/C conducted in 1 M KOH + 1 M methanol solution.

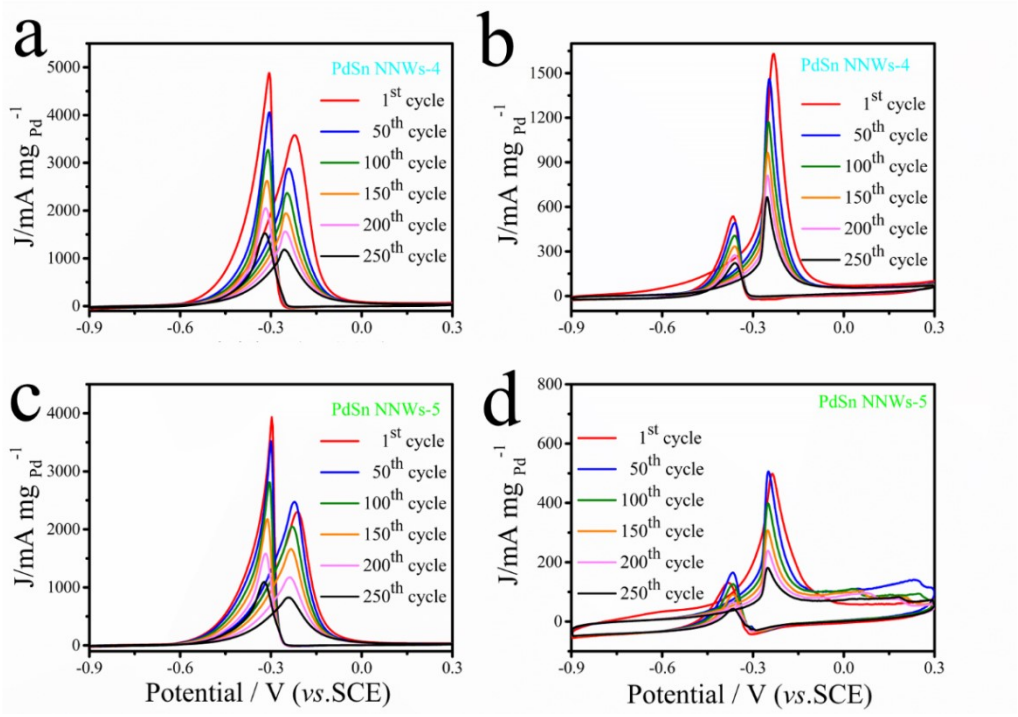

Fig S11 The CV curves of (a,b) PdSn NNWs-4 and (c,d) PdSn NNWs-5 after CV sweeps for 250 cycles in the solution of 1 M KOH + 1 M ethanol/1 M KOH + 1 M methanol.

Table S1 Electrochemical properties of catalysts.

Catalysts	Electrolyte	Mass activity ($mA\ mg^{-1}$)	Specific activity ($mA\ cm^{-2}$)	References
PdSn NNWs-1	1.0 M KOH + 1.0 M ethanol	4978.0	11.6	This work
PdSn NNWs-2	1.0 M KOH + 1.0 M ethanol	6340.0	13.2	This work
PdSn NNWs-3	1.0 M KOH + 1.0 M ethanol	8105.0	14.1	This work
PdSn NNWs-1	1.0 M KOH + 1.0 M methanol	1423.0	3.3	This work
PdSn NNWs-2	1.0 M KOH + 1.0 M methanol	2249.5	4.7	This work
PdSn NNWs-3	1.0 M KOH + 1.0 M methanol	3099.5	5.4	This work
C–PdSn/SnO_x	1 M KOH + 1 M ethanol	3200.0		[1]
Pd_3NiP/N-rGO	1 M KOH + 1	2223.0	3.9	[2]

	M ethanol			
Pd/a-$SrRuO_3$	1 M ethanol +1 M KOH	4000.0		[3]
Pd/NCB@NGS-2	1.0 M KOH + 1.0 M ethanol	2690.4	5.2	[4]
PdCuB@N-G	1.0 M KOH + 1.0 M ethanol	5830.0		[5]
Pd_3Sn-S	1 M KOH + 1 M CH_3CH_2OH	1405.5		[6]
$Pd_{1.5}Sn$/f-C	1 M NaOH + 1 M C_2H_5OH	3413.3		[7]
$Pd_1Sn_{0.40}/TiO_2$-GO	1 M KOH + 1 M ethanol	3005.0		[8]
PdNCs	1 M KOH solution + 1 M MeOH	2275.0		[9]
Pd_6Ru_4/TiO_2-1	0.5 M NaOH + 1.0 M CH_3OH	2803.3		[10]
Pd/BNG	1 M CH_3OH + 0.5 M NaOH	707.5		[11]
$Pd_{67}Au_{33}$	0.5 M NaOH + 2.0 M CH_3OH		5.3	[12]
$Pd_{1.2}Cu_{0.2}$	1 M CH_3OH and 1 M KOH	1101.6	0.8	[13]
Pd3Rh1 NAs	1.0 M methanol + 1.0 M KOH	869.0	3.0	[14]
Pd-PdO PNTs-260	1 M KOH + 1 M CH3OH	1111.3		[15]
Pd/C	1.0 M KOH + 1.0 M ethanol	1175.0	2.9	This work
Pd/C	1.0 M KOH + 1.0 M methanol	415.9	1.0	This work

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