

Supporting information for

Networked Pt-Sn Nanowires as Efficient Catalysts toward Alcohol Electrooxidation

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Experimental Section

Chemicals. Potassium tetrachloroplatinate (II) (K_2PtCl_4 , 98%) and polyvinylpyrrolidone (PVP, MW=58000) were purchased from Sigma-Aldrich. Tin (II) oxalate (SnC_2O_4 , reagent grade, 98.5%), phenol (C_6H_6O , reagent grade, 99%) and ethylene glycol (EG, reagent grade, 99%) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). The commercial Pt/C (20 wt%, 3 nm Pt nanoparticles) was purchased from Johnson Matthey Corporation. All the chemicals were used as received without further purification. The water (18 M Ω /cm) used in all experiments was prepared by passing through an ultra-pure purification system (Aqua Solutions).

Preparation of networked Pt₆Sn₃, Pt₆Sn₂, Pt₆Sn₁ NWs: In a typical preparation of networked Pt₆Sn₃ NWs, 10 mg K_2PtCl_4 , 2.4 mg SnC_2O_4 , 100 mg PVP, 50 mg phenol and 10 mL EG were added into a vial (volume: 30 mL). After the vial had been capped, the mixture was ultrasonicated for around 0.5 h. The resulting homogeneous mixture was heated at 160 °C for 5 h in an oil bath and further heated at 180 °C for 2 h before it was cooled to room temperature. The resulting colloidal products were collected by centrifugation and washed several times with an ethanol/acetone mixture. The preparation of networked Pt₆Sn₂ and Pt₆Sn₁ NWs was similar to that of networked Pt₆Sn₃ NWs except changing the amounts of SnC_2O_4 from 2.4 mg to 1.6 mg and 0.8 mg, respectively.

Characterizations. Transmission electron microscopy (TEM) was conducted on a HITACHIHT7700 transmission electron microscope at an acceleration voltage of 120 kV. Scanning transmission electron microscopy (STEM) was conducted on an FEITecni F20 transmission electron microscope at an acceleration voltage of 200 kV. Scanning electron microscope energy-dispersive X-ray spectroscopy

(SEM-EDX) was taken with a HITACHI S-4700 cold field emission scanning electron microscope. Powder X-ray diffraction (PXRD) patterns were collected on X'Pert-Pro MPD diffractometer (Netherlands PANalytical) with a Cu K α X-ray source ($\lambda = 1.540598 \text{ \AA}$). X-ray photoelectron spectroscopy spectra (XPS) was conducted on a Thermo Scientific ESCALAB 250 XI X-ray photoelectron spectrometer.

Alcohol fuels electrooxidation measurements: The electrochemical workstation was CHI660E fabricated by Chen Hua (Shanghai, China). A three-electrode cell was used to conduct the electrochemical measurements. The working electrode was a glassy-carbon electrode (GCE) (diameter: 5 mm, area: 0.196 cm²). A saturated calomel electrode (SCE) and a platinum wire were used as the reference electrode and counter electrode, respectively. 5 μ L isopropanol dispersion of catalyst (i.e. networked Pt₆Sn₃ NWs, networked Pt₆Sn₂ NWs and networked Pt₆Sn₁ NWs, and Pt/C, 0.4 mg_{Pt}/mL) was deposited on a glassy carbon electrode to obtain the working electrode after the solvent is dried naturally. The potential scan rate was 50 mV s⁻¹ for the cyclic voltammetry (CV) measurement. EOR was conducted in 0.1 M HClO₄ + 0.5 M CH₃CH₂OH solution. MOR was conducted in 0.1 M HClO₄ + 0.5 M CH₃OH solution. The scan rate for both EOR and MOR was 50 mV s⁻¹.

Supporting Figures and Tables.

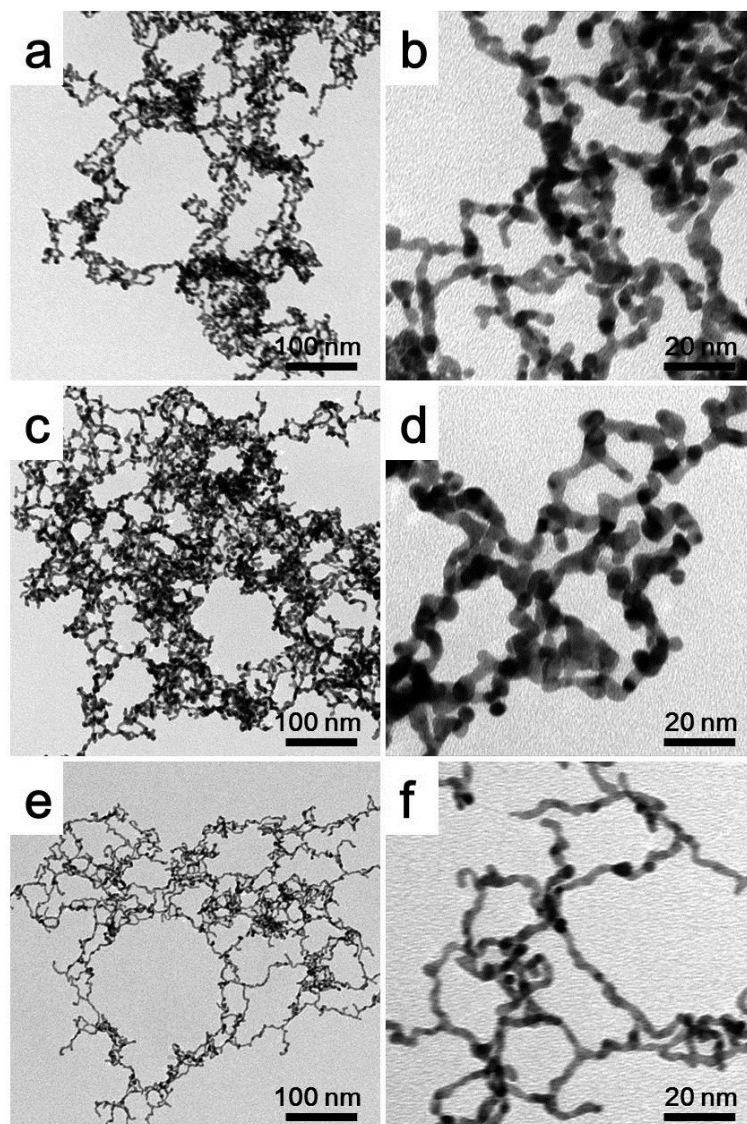


Fig. S1 TEM images of the networked NWs prepared under the same condition as that of networked Pt_6Sn_2 NWs but varying amounts of phenol: (a, b) 0 mg, (c, d) 25mg and (e, f) 100 mg.

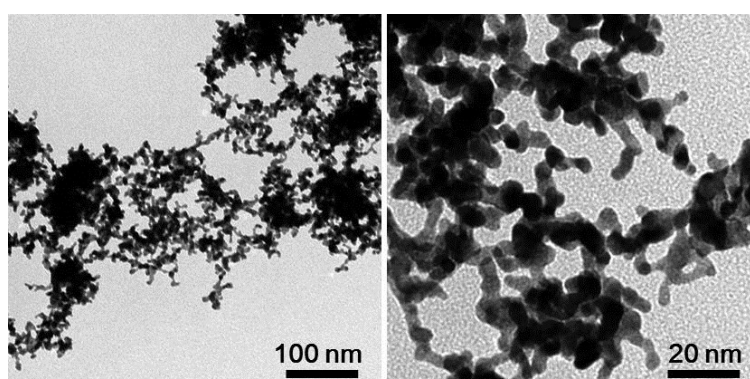


Fig. S2 TEM images of the products prepared under the same condition as that of networked Pt_6Sn_2 NWs but in absence of PVP.

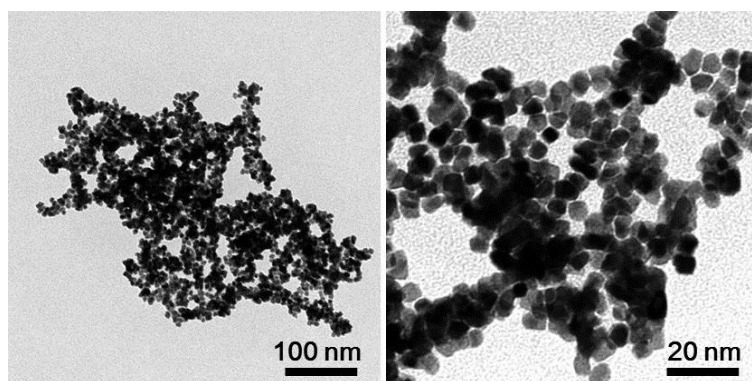


Fig. S3 TEM images of the products prepared under the same condition as that of networked Pt_6Sn_2 NWs but changing EG into NMP.

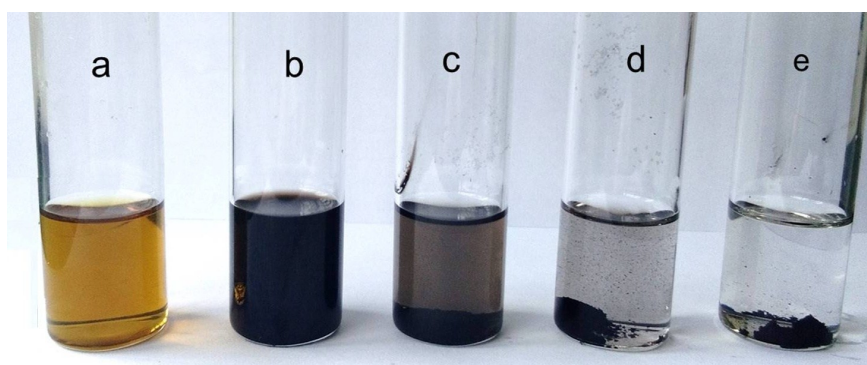


Fig. S4 Images of the formation of aerogel at different times as that of networked Pt_6Sn_3 NWs: the clarified orange solution was ultrasonicated for around 30 min (a) and then heated at $160\text{ }^\circ\text{C}$ in an oil bath. The formation of black solution was observed at the early stage (b). The black product slowly sank into the bottom of the bottle (c) and then aggregated (d) and the product was completely linked together to form the aerogel finally (e).

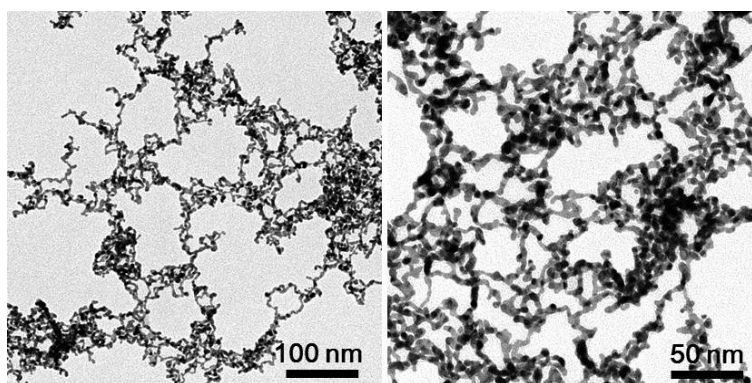


Fig. S5 Additional TEM images of the networked Pt_6Sn_3 NWs.

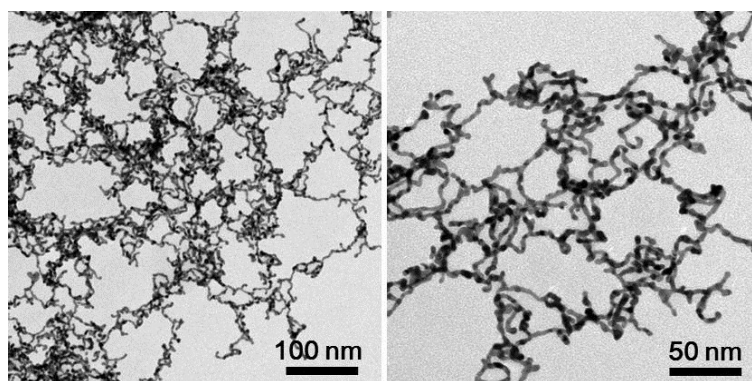


Fig. S6 Additional TEM images of the networked Pt₆Sn₂ NWs.

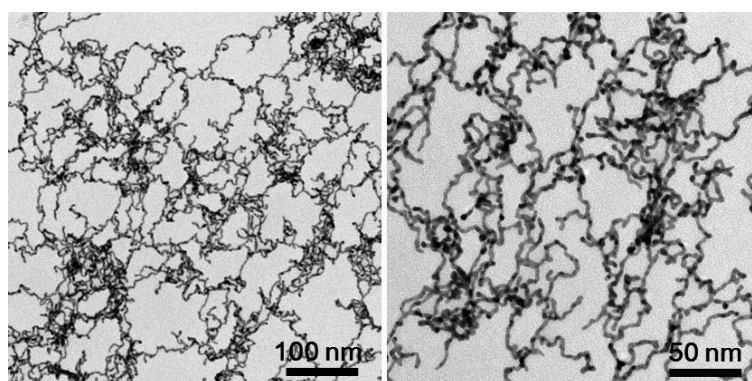


Fig. S7 Additional TEM images of the networked Pt₆Sn₁ NWs.

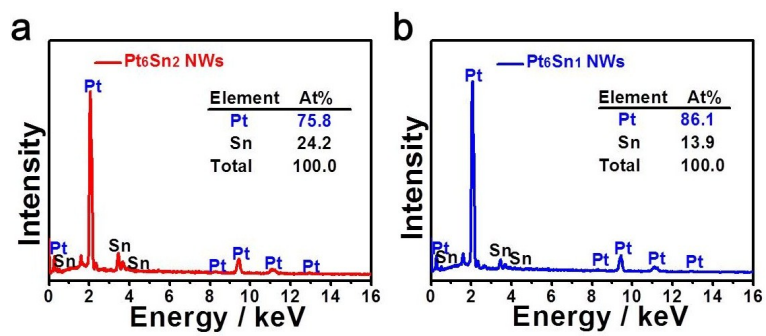


Fig. S8 SEM-EDX of (a) the networked Pt₆Sn₂ NWs and (b) the networked Pt₆Sn₁ NWs.

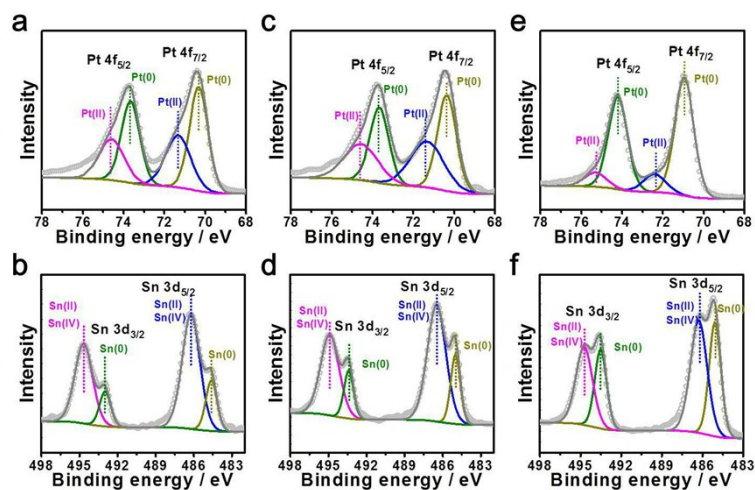


Fig. S9 (a, c, e) Pt 4f and (b, d, f) Sn 3d XPS spectra of (a, b) networked Pt₆Sn₃ NWs, (c, d) networked Pt₆Sn₂ NWs, and (e, f) networked Pt₆Sn₁ NWs.

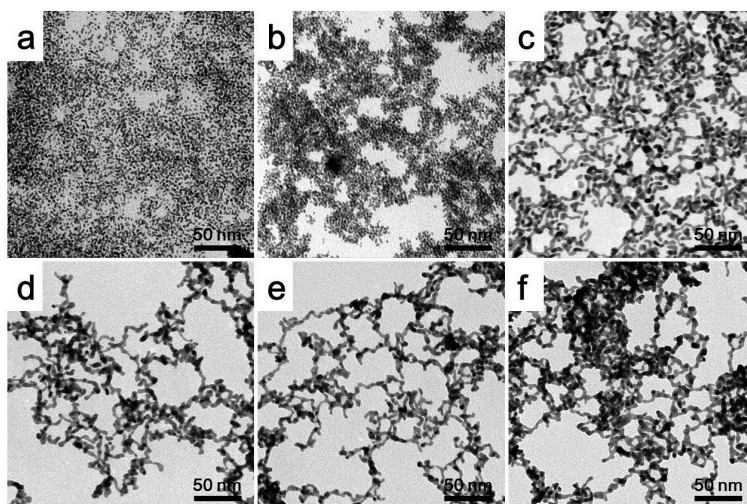


Fig. S10 TEM images of the networked Pt₆Sn₃ NWs intermediates obtained after the reaction have been processed for (a) 10 min, (b) 20 min, (c) 30 min, (d) 1 h, and (e) 5 h at 160 °C, and (f) 5 h at 160 °C + 2 h at 180 °C.

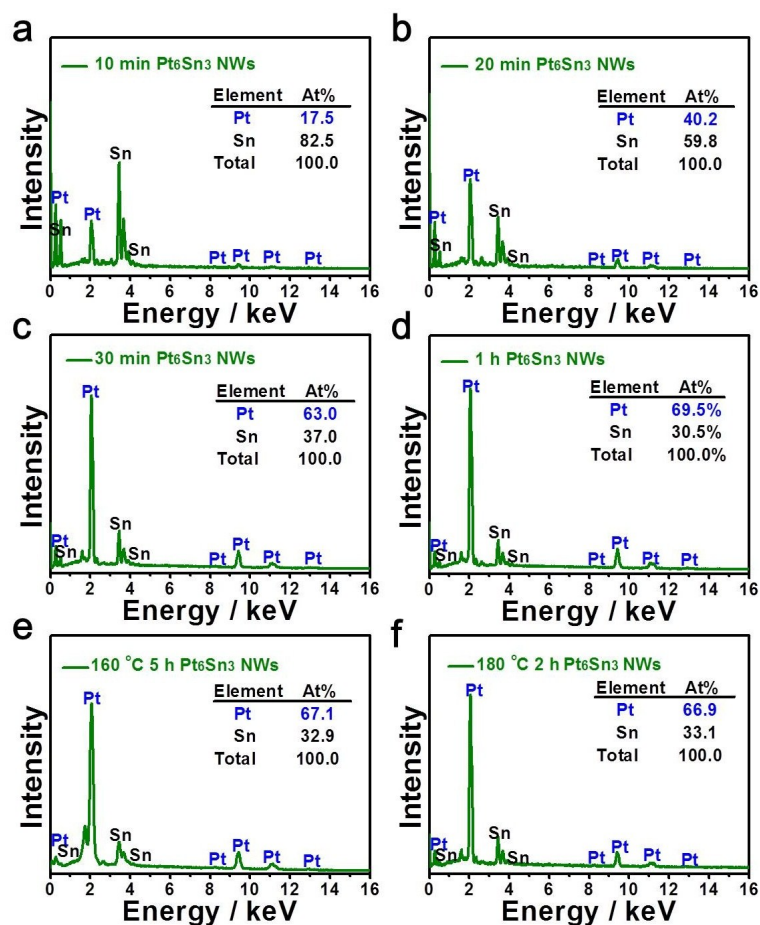


Fig. S11 SEM-EDX spectra of the networked Pt_6Sn_3 NWs intermediates obtained after the reaction have been processed for (a) 10 min, (b) 20 min, (c) 30 min, (d) 1 h, and (e) 5 h at 160 °C, and (f) 5 h at 160 °C + 2 h at 180 °C.

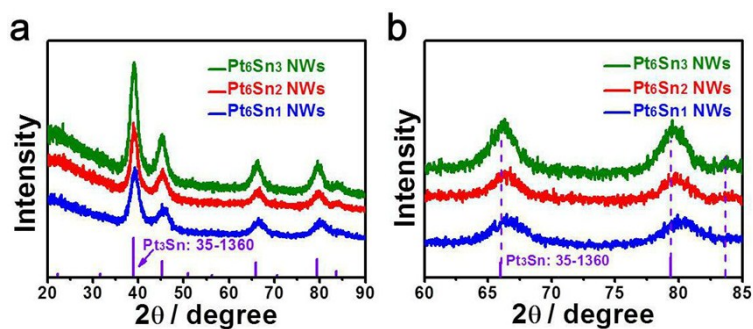


Fig. S12 (a) PXRD patterns and (b) enlarged PXRD patterns of networked Pt_6Sn_3 NWs, Pt_6Sn_2 NWs and Pt_6Sn_1 NWs.

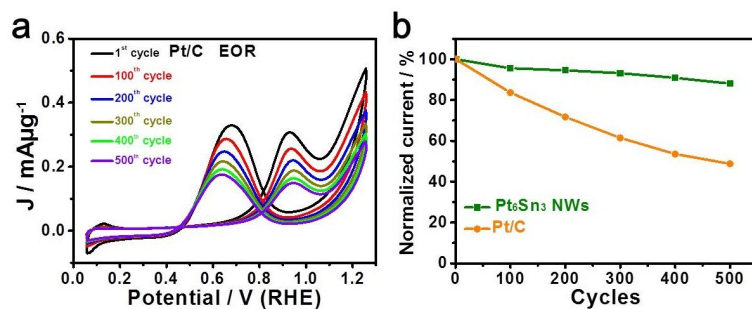


Fig. S13 (a) CV curves of Pt/C for EOR for 500 cycles, and (b) Changes of peak current densities of electro-oxidation during potential cycling of different catalysts. Potential was scanned for 500 cycles in 0.1 M HClO₄ and 0.5 M CH₃CH₂OH at 50 mV s⁻¹.

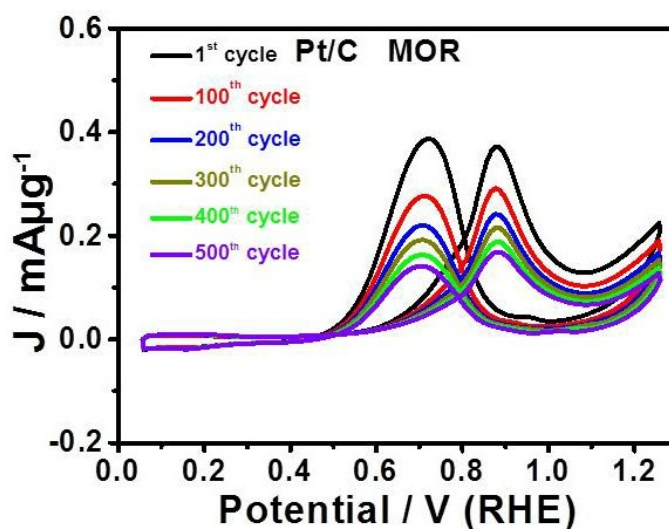


Fig. S14 CV curves of Pt/C for MOR for 500 cycles.

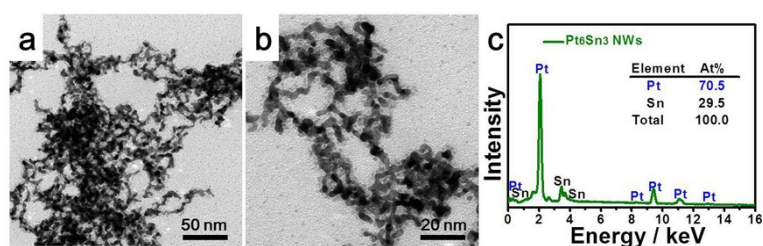


Fig. S15 TEM images of (a, b) networked Pt₆Sn₃ NWs, SEM-EDX of (c) networked Pt₆Sn₃ NWs after 500 cycles at 50 mV s⁻¹ in 0.1 M HClO₄ containing 0.5 M CH₃OH.

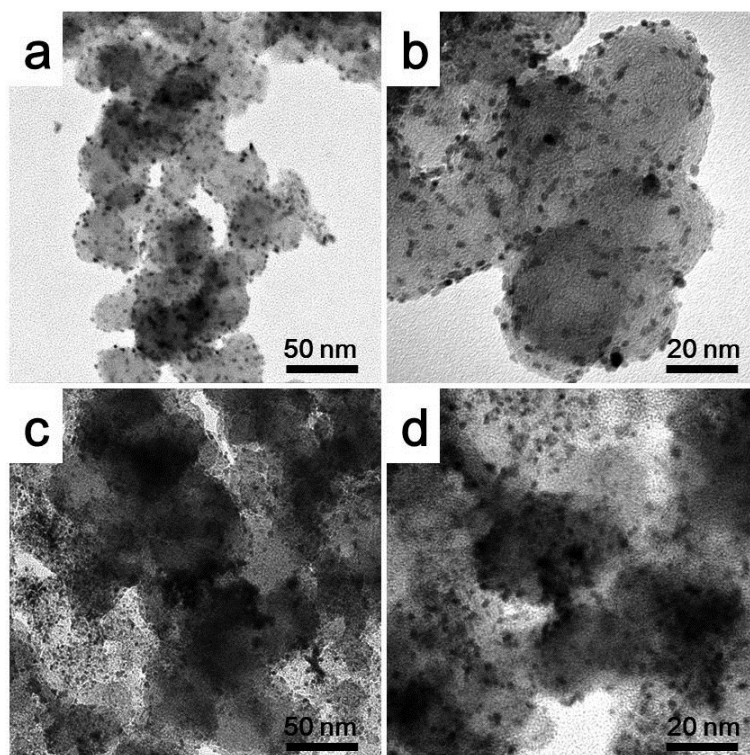


Fig. S16 TEM images of Pt/C (a, b) before and (c, d) after 500 cycles in 0.1 M HClO₄ containing 0.5 M CH₃OH at 50 mV s⁻¹.

Table S1 EOR performances of Pt-Sn NWs and various published Pt-based catalysts.

Catalysts	Peak currents from CV curves		Electrolytes	References
	J_m (A/mg _{Pt})	J_s (mA/cm ²)		
Pt₆Sn₃ NWs	1.08	1.40	0.1 M HClO₄ + 0.5 M Ethanol	This Work
PtSn Nanocrystals/CNT		~ 0.741	0.5 M H ₂ SO ₄ + 1 M Ethanol	S1
PtRh NW/GNS	1	2.8	1 M H ₂ SO ₄ + 1 M Ethanol	S2
PtPb _{0.27} NWs	~ 1.7	~ 0.9	0.1 M HClO ₄ + 0.15 M Ethanol	S3
Pt-Cu Nanocone	~ 0.4	2.97	0.5 M H ₂ SO ₄ + 0.1 M Ethanol	S4
Pt-Cu Nanosheet	~ 0.7	~ 1.8		
PtRhNi/C	0.378		0.1 M HClO ₄ + 0.5 M Ethanol	S5

S1 F.Wu, D. Zhang, M. Peng, Z. Yu, X. Wang, G. Guo, Y. Sun, *Angew. Chem. Int. Ed.* 2016, **55**, 4952-4956.

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S3 N. Zhang, S. Guo, X. Zhu, J. Guo, X. Huang, *Chem. Mater.* 2016, **28**, 4447-4452.

S4 F. Saleem, Z. Zhang, B. Xu, X. Xu, P. He, X. Wang, *J. Am. Chem. Soc.* 2013, **135**, 18304-18307.

S5 N. Erini, S. Rudi, V. Beermann, P. Krause, R. Yang, Y. Huang, P. Strasser, *ChemElectroChem* 2015, **2**, 903-908.

Table S2 MOR performances of Pt-Sn NWs and various published Pt-based catalysts.

Catalysts	Peak currents from CV curves		Electrolytes	References
	J_m (A/mg _{Pt})	J_s (mA/cm ²)		
Pt₆Sn₃ NWs	1.45	1.88	0.1 M HClO₄ + 0.5 M Methanol	This Work
Pt ₃ Co Nanocubes/C		~ 1.5	0.1 M HClO ₄ + 1 M Methanol	S6
PtNi Concave Nanooctahedra/C	0.44	1.55	0.1 M HClO ₄ + 1 M Methanol	S7
PtZn/MWNT-E	~ 0.6	~ 1	0.5 M H ₂ SO ₄ + 1 M Methanol	S8
PtPb CNCs	0.97	2.09	0.1 M HClO ₄ + 0.5 M Methanol	S9
PtBi NPL/XC-72	0.47		0.5 M HClO ₄ + 0.5 M Methanol	S10
PtCu Clusters/C	~1.2		0.5 M H ₂ SO ₄ + 1 M Methanol	S11

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