Supporting information for

Ternary PtNi/Pt_xPb/Pt core/multishell nanowires as efficient and stable electrocatalysts for fuel cell reactions

Nan Zhang,[a] Yiming Zhu,[a] Qi Shao,[a] Xing Zhu [b] and Xiaoqing Huang[a]*

[a]College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Jiangsu 215123, China
[b]Testing & Analysis Center, Soochow University, Jiangsu 215123, China.

Email: hxq006@suda.edu.cn

Experimental Section

Chemicals. Platinum(II) acetylacetonate ($Pt(acac)_2$, 97%), nickel(II) acetylacetonate ($Ni(acac)_2{\cdot}2H_2O$, 97%), lead(II) acetylacetonate ($Pb(acac)_2$, 97%) and oleylamine ($CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_2NH_2$, 68-70%) were all purchased from Sigma-Aldrich. Hexadecyltrimethylammonium bromide ($CH_3(CH_2)_{15}N(Br)(CH_3)_3$, CTAB, >97.0%) and glucose ($C_6H_{12}O_6$, reagent grade) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All the chemicals were used as received without further purification. The water (18 MΩ/cm) used in all experiments was prepared by passing through an ultra-pure purification system (Aqua Solutions).

Preparation of PtNiPb nanowires (NWs). In a typical preparation of $PtNi_{0.67}Pb_{0.26}$ NWs, $Pt(acac)_2$ (10.0 mg), $Ni(acac)_2{\cdot}2H_2O$ (7.8 mg), CTAB (36.5 mg), glucose (60.0 mg) and 5 mL oleylamine were added into a glass vial (volume: 30 mL). After the vial had been capped, the mixture was ultrasonicated for 1.0 h. The resulting homogeneous mixture was then heated from room temperature to 160 °C and maintained at 160 °C for 0.5 h in an oil bath under magnetic stirring. After cooling to 80 °C, $Pb(acac)_2$ (2.0 mg) dissolved in 2 mL oleylamine was then added dropwise to the above mixture under magnetic stirring. The reaction was then increased to 160 °C and kept at this temperature for 4.0 h. The products were collected by centrifugation and washed three times with an ethanol/cyclohexane mixture. The preparations of $PtNi_{0.73}Pb_{0.15}$ NWs and $PtNi_{0.78}Pb_{0.68}$ NWs were achieved by changing the amounts of $Pb(acac)_2$ to 1.5 mg and 3.0 mg, respectively, while keeping the other parameters the same.

Characterizations. The samples were prepared by dropping cyclohexane dispersion of samples onto

carbon-coated copper transmission electron microscopy (TEM) grids using pipettes and dried under ambient condition. Low-magnification TEM was conducted on a HITACHI HT7700 TEM at an acceleration voltage of 120 kV. High-magnification TEM and scanning transmission electron microscopy (STEM) were conducted on an FEI Tecnai F20 TEM at an acceleration voltage of 200 kV. Scanning electron microscopy (SEM) images were taken with a HITACHI S-4700 cold field emission scanning electron microscope operated at 15 kV. PXRD pattern was collected on X'Pert-Pro MPD diffractometer (Netherlands PANalytical) with a Cu Kα X-ray source (λ = 1.540598 Å). The concentration of catalyst was determined by the inductively coupled plasma atomic emission spectroscopy (710-ES, Varian, ICP-AES).

Methanol oxidation reaction (MOR), ethanol oxidation reaction (EOR), ethylene glycol oxidation reaction (EGOR), glycerol oxidation reaction (GOR) and oxygen reduction reaction (ORR) measurements. A three-electrode cell was used for the electrochemical measurements. A glassy-carbon electrode (GCE) (diameter: 5 mm, area: 0.196 cm^2) from Pine Instruments was used as the working electrode, a saturated calomel electrode (SCE) was used as the reference electrode and a Pt wire was used as the counter electrode, respectively. To prepare the catalyst-coated working electrode, the catalyst was dispersed in a mixture containing isopropanol and Nafion (5%) to form a 0.20 mg_{Pt}/mL dispersion. 10 μL isopropanol dispersion of $PtNi_{0.73}Pb_{0.15}$ NWs, $PtNi_{0.67}Pb_{0.26}$ NWs or $PtNi_{0.78}Pb_{0.68}$ NWs on C (0.20 mg_{Pt}/mL) was deposited on a glassy carbon electrode to obtain the working electrode after the solvent was dried naturally. The electrochemical active surface area (ECSA) measurement was determined by integrating the hydrogen adsorption charge on the cyclic voltammetry (CV) at room temperature in 0.1 M $HClO_4$ solution. The scanning rate was 50 mV/s. MOR was conducted in 0.1 M $HClO_4$ + 0.2 M methanol solution. EOR was conducted in 0.1 M $HClO_4$ + 0.2 M ethanol solution. EGOR was conducted in 0.1 M $HClO_4$ + 0.2 M EG solution. GOR was conducted in 0.1 M $HClO_4$ + 0.2 M glycerol solution. The scan rates for MOR, EOR, EGOR and GOR were 50 mV/s. ORR measurement was conducted in a 0.1 M $HClO_4$ solution with purging O_2 during the measurement. The scan and rotation rate for ORR measurement were 10 mV/s and 1600 rpm, respectively. The durability test was performed at room

temperature in O_2-saturated 0.1 M $HClO_4$ solution by applying the cyclic potential sweep at sweep rate of 100 mV/s for 10000 cycles. All electrochemical experiments were performed at room temperature. For comparison, the commercial Pt/C was used as the baseline catalyst, and the same procedure as described above was applied to conduct the electrochemical measurements.

Supporting Figures and Tables.

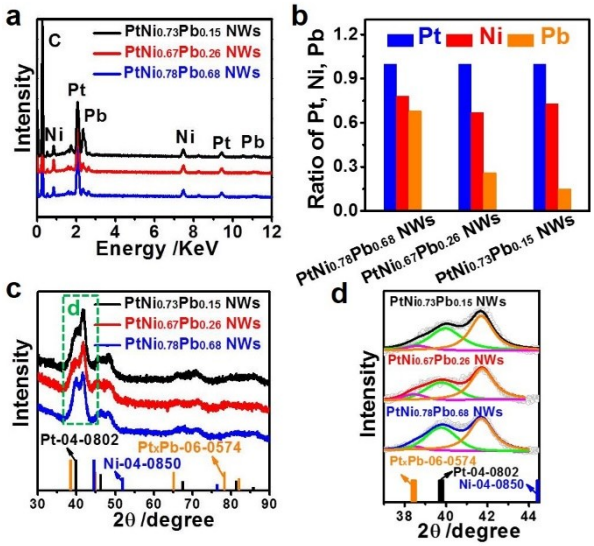

Fig. S1 (a) SEM-EDS spectra, (b) the changes of the ratios of Pt, Ni and Pb. (c) PXRD patterns of different NWs and (d) the fitted peak curves form the marked region in (c).

Table S1 ICP-AES data of PtNi/Pt_xPb/Pt core/multishell NWs with different compositions.

Number	*n*Pt:*n*Ni:*n*Pb*	Pt/Ni/Pb atomic ratio	Composition
1	1/1/0.15	1/0.75/0.14	$PtNi_{0.75}Pb_{0.14}$
2	1/1/0.20	1/0.73/0.20	$PtNi_{0.73}Pb_{0.20}$
3	1/1/0.30	1/0.83/0.52	$PtNi_{0.83}Pb_{0.52}$

*Molar ratio between the Pt, Ni and Pb salt precursors

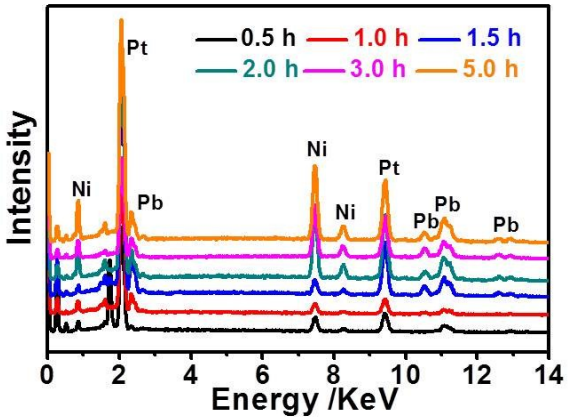

Fig. S2 SEM-EDS spectra of the $PtNi_{0.67}Pb_{0.26}$ NWs intermediates obtained after different reaction time.

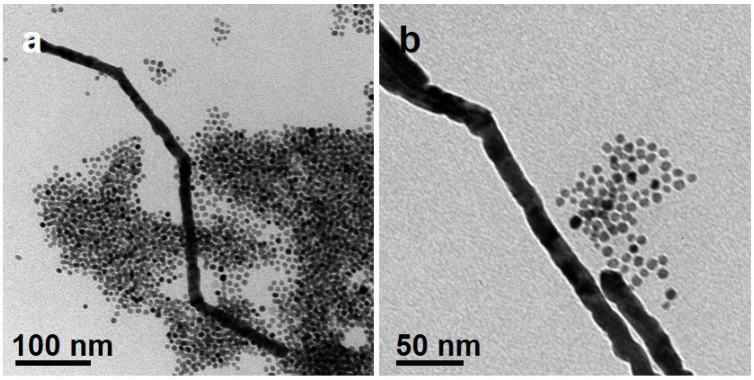

Fig. S3 TEM images of the products obtained if the reaction temperature was not cooled to 80 °C.

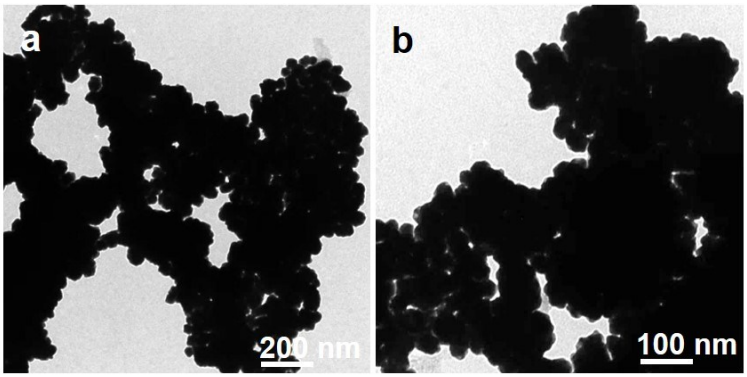

Fig. S4 TEM images of the products obtained when three different precursors were added in the reaction solution at the same time.

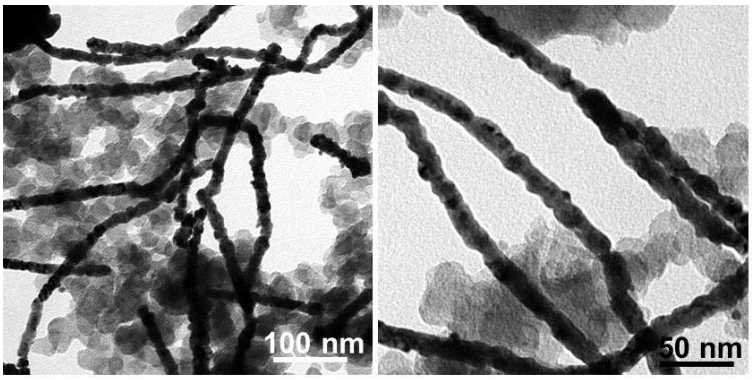

Fig. S5 TEM images of $PtNi_{0.67}Pb_{0.26}$ NWs/C.

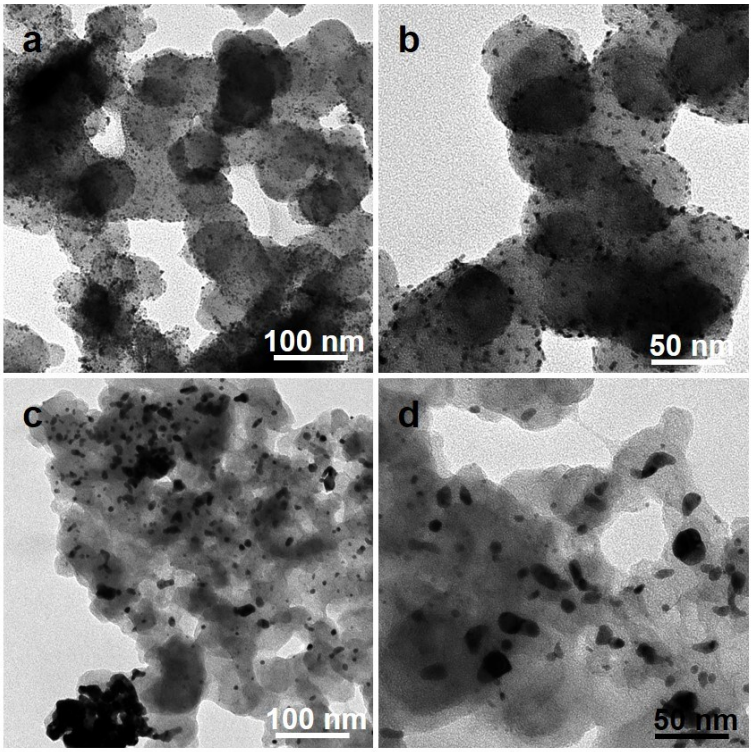

Fig. S6 TEM images of the commercial Pt/C (a, b) before and (c, d) after the electrochemical durability test.

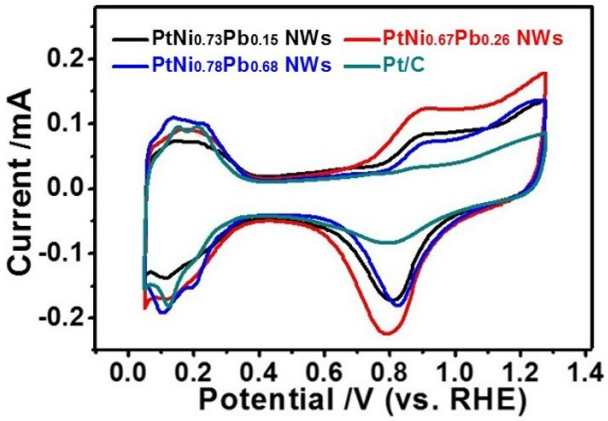

Fig. S7 CVs of the $PtNi_{0.73}Pb_{0.15}$ NWs, $PtNi_{0.67}Pb_{0.26}$ NWs, $PtNi_{0.78}Pb_{0.68}$ NWs and the commercial Pt/C in 0.1 M $HClO_4$ aqueous solution at scan rate of 50 mV/s.

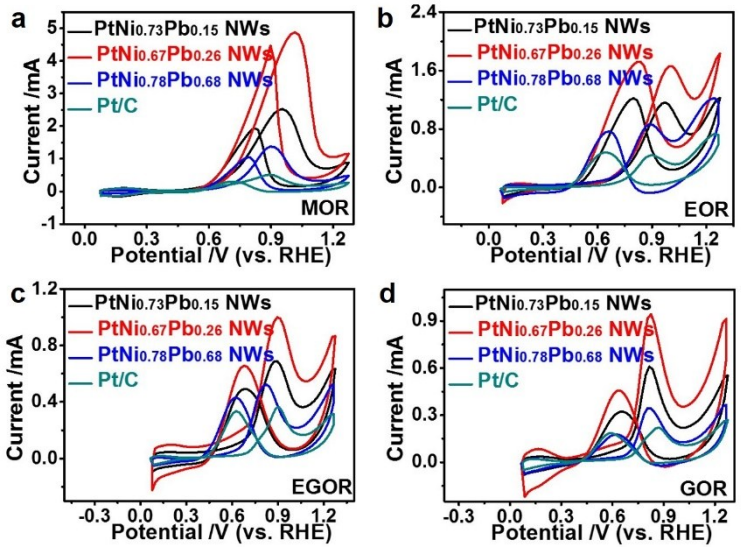

Fig. S8 CVs of the $PtNi_{0.73}Pb_{0.15}$ NWs, $PtNi_{0.67}Pb_{0.26}$ NWs, $PtNi_{0.78}Pb_{0.68}$ NWs and the commercial Pt/C for (a) MOR, (b) EOR, (c) EGOR and (d) GOR, respectively. The potential was scanned in 0.1 M $HClO_4$ aqueous solution containing 0.2 M methanol, 0.2 M ethanol, 0.2 M ethylene glycol or 0.2 M glycerol at scan rate of 50 mV/s.

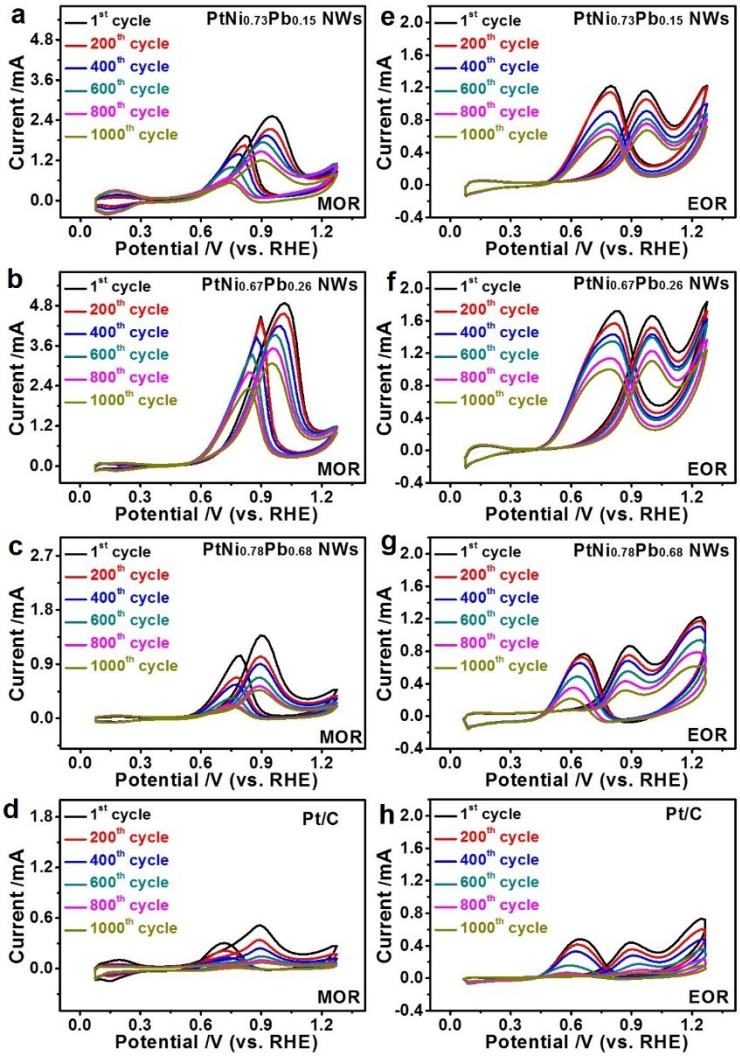

Fig. S9 CVs (1st, 200th, 400th, 600th, 800th and 1000th cycle) of (a, e) $PtNi_{0.73}Pb_{0.15}$ NWs, (b, f) $PtNi_{0.67}Pb_{0.26}$ NWs, (c, g) $PtNi_{0.78}Pb_{0.68}$ NWs and (d, h) the commercial Pt/C for MOR (left column) and EOR (right column). The potentials were continuously scanned for 1000 cycles in 0.1 M $HClO_4$ aqueous solution containing 0.2 M methanol or in 0.1 M $HClO_4$ aqueous solution containing 0.2 M ethanol at scan rate of 50 mV/s.

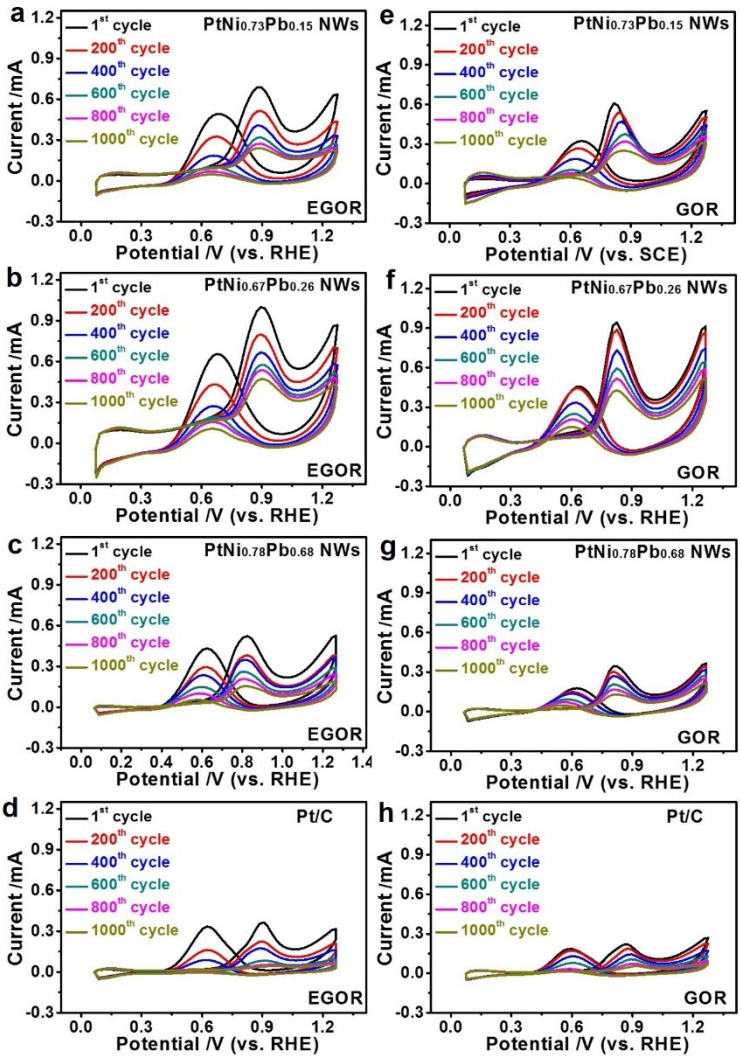

Fig. S10 CVs (1st, 200th, 400th, 600th, 800th and 1000th cycle) of (a, e) $PtNi_{0.73}Pb_{0.15}$ NWs, (b, f) $PtNi_{0.67}Pb_{0.26}$ NWs, (c, g) $PtNi_{0.78}Pb_{0.68}$ NWs and (d, h) the commercial Pt/C for EGOR (left column) and GOR (right column). The potentials were continuously scanned for 1000 cycles in 0.1 M $HClO_4$ aqueous solution containing 0.2 M ethylene glycol or in 0.1 M $HClO_4$ aqueous solution containing 0.2 M glycerol at scan rate of 50 mV/s.

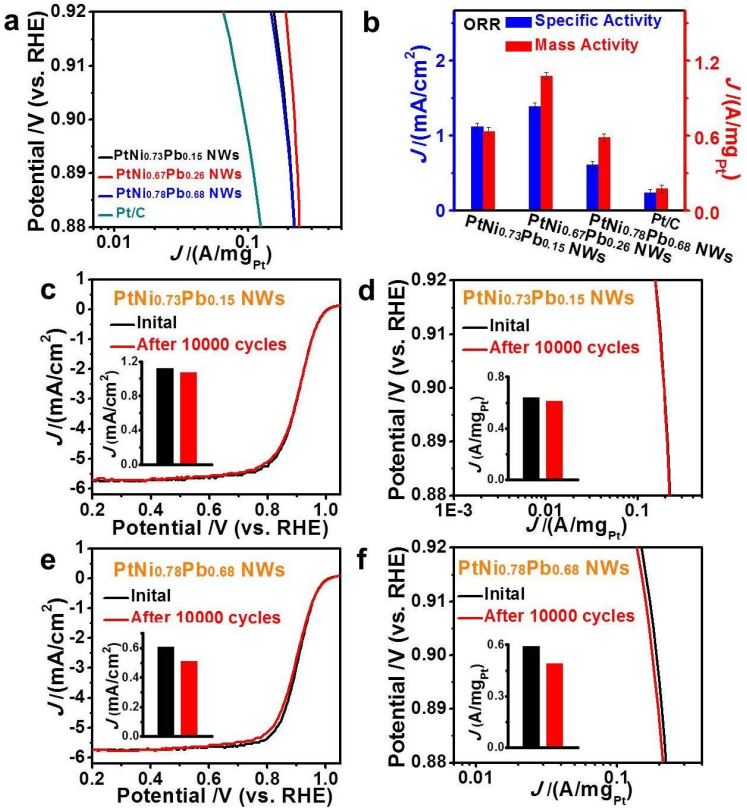

Fig. S11 (a) The Tafel plots and (b) specific and mass activities at 0.9 V versus RHE for the $PtNi_{0.73}Pb_{0.15}$ NWs, $PtNi_{0.67}Pb_{0.26}$ NWs, $PtNi_{0.78}Pb_{0.68}$ NWs and the commercial Pt/C. ORR polarization curves and specific activities of (c) $PtNi_{0.73}Pb_{0.15}$ NWs and (e) $PtNi_{0.78}Pb_{0.68}$ NWs before and after durability test. Tafel plots and mass activities of (d) $PtNi_{0.73}Pb_{0.15}$ NWs and (f) $PtNi_{0.78}Pb_{0.68}$ NWs before and after durability tests. The mass activities were depicted as kinetic-current densities normalized to the Pt mass. The specific activities were depicted as kinetic-current densities normalized to the ECSAs.

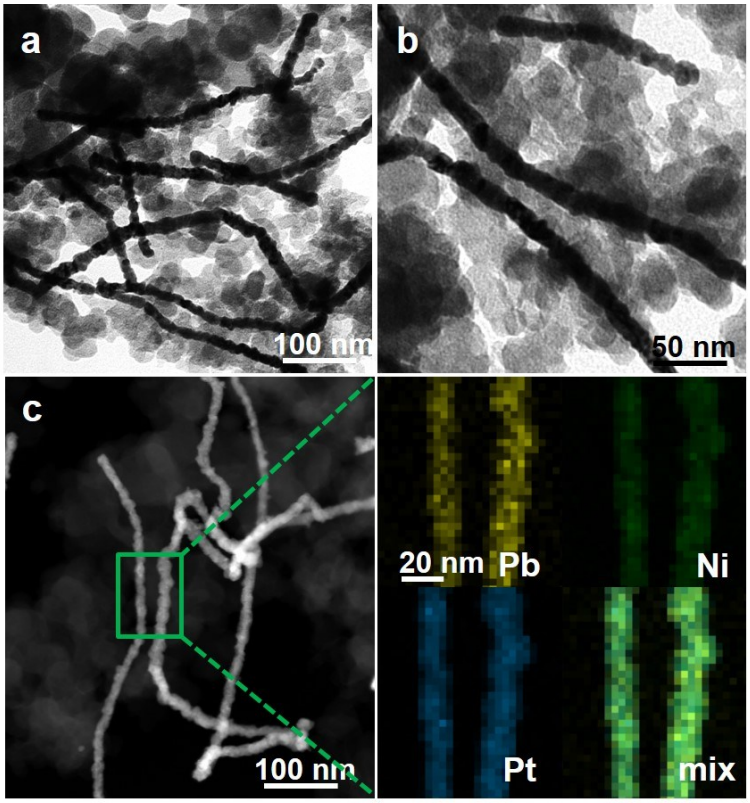

Fig. S12 (a, b) TEM images, (c) HAADF-STEM image and EDS mapping images of $PtNi_{0.67}Pb_{0.26}$ NWs/C after electrochemical durability test.

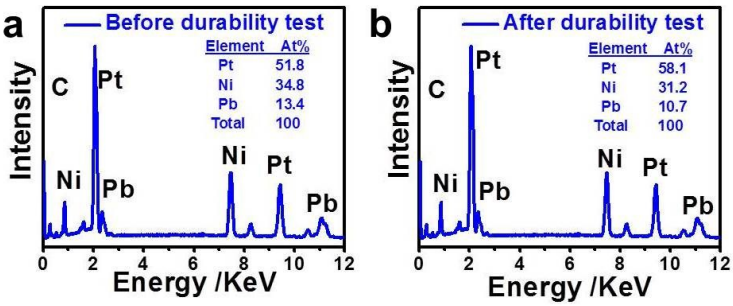

Fig. S13 SEM-EDS spectra of $PtNi_{0.67}Pb_{0.26}$ NWs/C (a) before and (b) after the electrochemical durability test.

Table S2 MOR performances of PtNiPb/C and various Pt-based catalysts from published works.

Catalysts	Peak currents from CV curves		Electrolytes	References
	Jm (A/mg_{Pt})	*Js* (mA/cm^2)		
$PtNi_{0.67}Pb_{0.26}$ NWs/C	**2.4**	**3.1**	**0.1 M $HClO_4$ + 0.2 M Methanol**	**This Work**
$PtPb_{0.27}$ NWs/C	1.21	2.41	0.1 M $HClO_4$ + 0.15 M Methanol	*Chem. Mater.* **2016**, 28, 4447-4452.
PtPb Nanorods/C	0.70		0.1 M H_2SO_4 + 0.5 M Methanol	*J. Am. Chem. Soc.* **2007**, 129, 8684-8685.
Pt-Ni Hexoctahedra	~ 0.14	1.71	0.5 M H_2SO_4 + 2 M Methanol	*Angew. Chem. Int. Ed.* **2014**, 53, 12522-12527.
Pt-Ni Concave-Nanocubes	~ 0.17	1.86		
Pt-Ni Nanocubes	~ 0.11	1.40		
Pt_3Co Nanocubes/C		~ 1.5	0.1 M $HClO_4$ + 1 M Methanol	*Angew. Chem. Int. Ed.* **2010**, 49, 6848-6851.
PtPb Nanoparticles/C	~ 0.78		0.5 M H_2SO_4 + 0.5 M Methanol	*J. Power Sources* **2008**, 184, 16-22.
PtCu Nanocubes/C		4.7	0.1 M $HClO_4$ + 1 M Methanol	*Angew. Chem. Int. Ed.* **2009**, 48, 4217-4221.
$Pt_{38}Fe_{28}Pd_{34}$ NWs/C	0.489		0.1 M $HClO_4$ + 0.2 M Methanol	*J. Am. Chem. Soc.* **2011**, 133, 15354-15357.
PtPd Nanocubes/C		2	0.1 M $HClO_4$	*J. Am. Chem. Soc.* **2011**,

PtPd Nanotetrahedrons/C		1.49	+ 1 M Methanol	133, 3816-3819.
PtNi Concave Nanoctahedra/C	0.44	1.55	0.1 M $HClO_4$ + 1 M Methanol	*Angew. Chem. Int. Ed.* **2012**, 51, 12524-12528.
PtZn Nanoparticles/C		~ 0.92	0.1 M H_2SO_4 + 0.5 M Methanol	*ACS Nano* **2012**, 6, 5642-5647.
PtPb Nanoparticles/C	1.53	7.95	0.5 M H_2SO_4 + 1 M Methanol	*Electrochim. Acta* **2012**, 63, 346-353.
PtRu Nanoparticles/C	1.43	~ 3		
PtAu Nanoparticls/C		3.4	0.1 M $HClO_4$ + 1 M Methanol	*J. Am. Chem. Soc.* **2013**, 135, 7985-7991.
Pt_3Cu Nanoicosahedra/C	0.736	2.14	0.1 M $HClO_4$ + 0.2 M Methanol	*ACS Nano* **2015**, 9, 7634-7640.
Pt_3Cu Nanoctahedra/C	0.518	1.63		

Table S3 EOR performances of PtNiPb/C and various Pt-based catalysts from published works.

Catalysts	Peak currents from CV curves		Electrolytes	References
	Jm (A/mg_{Pt})	*Js* (mA/cm^2)		
$PtNi_{0.67}Pb_{0.26}$ NWs/C	**0.83**	**1.07**	**0.1 M $HClO_4$ + 0.2 M Ethanol**	**This Work**
Pt-Cu Nanocone	~ 0.4	2.97	0.5 M H_2SO_4 + 0.1 M Ethanol	*J. Am. Chem. Soc.* **2013**, 135, 18304-18307.
Pt-Cu Nanosheet	~ 0.7	~ 1.8		
$PtPb_{0.27}$ NWs/C	0.89	1.78	0.1 M $HClO_4$ + 0.15 M Ethanol	*Chem. Mater.* **2016**, 28, 4447-4452.
PtRu Nanoparticles/XC	0.189		0.5 M H_2SO_4 + 1 M Ethanol	*Electrochim. Acta* **2014**, 142, 223-227.
Ni@PbPt Nanoparticles/XC	0.193			
Ni@PbPt Nanoparticles/G	0.281			
PdPt@Pt/rGO	0.074		0.5 M H_2SO_4 + 0.5 M Ethanol	*ACS Appl. Mater. Inter.* **2014**, 6, 10549-10555.
$Pt_{53}Cu_{47}$ Alloy	0.171		0.5 M H_2SO_4 + 1 M Ethanol	*J. Power Sources* **2015**, 296, 282-289.
PtSn Nanocrystals/CNT		~ 0.741	0.5 M H_2SO_4 + 1 M Ethanol	*Angew. Chem. Int. Ed.* **2016**, 55, 4952-4956.
Tetrahexahedral PtNi Nanoframes/C	0.77	1.99	0.1 M $HClO_4$ + 0.2 M Ethanol	*Nano Lett.* **2016**, 16, 2762-2767.
Rhombic Dodecahedral	0.98	1.79		

PtNi Nanoframes/C				

Table S4 EGOR performances of PtNiPb/C and various Pt-based catalysts from published works.

Catalysts	Peak currents from CV curves		Electrolytes	References
	Jm (A/mg_{Pt})	*Js* (mA/cm^2)		
$PtNi_{0.67}Pb_{0.26}$ NWs/C	**0.42**	**0.65**	**0.1 M $HClO_4$ + 0.2 M Ethylene glycol**	**This Work**
$Pt_{4.5}Pb$ NWs	0.73	0.30	0.1 M $HClO_4$ + 0.5 M Ethylene glycol	*Small* **2016**, 12, 4464-4470.
$Pt_{5.7}Pb$ NWs	0.63	0.22		
Pt/Ru/XC72 Catalyst	0.24		0.5 M H_2SO_4 + 0.4M Ethylene glycol	*J. Power Sources* **2011**, 196, 1078-1083.
PtPd@Pt Nanocrystals/rGO	0.23		0.5 M H_2SO_4 + 0.5 M Ethylene glycol	*Electrochim. Acta* **2016**, 18, 576-583.
Pt-Ru Nanocrystals/CNT	0.175		0.5 M H_2SO_4 + 1 M Ethylene glycol	*Int. J. Hydrogen Energy* **2012**, 37, 9941-9947.
Pt-Sn Nanocrystals/CNT	0.22		0.5 M H_2SO_4 + 1 M Ethylene glycol	*Int. J. Hydrogen Energy* **2011**, 36, 5, 3313-3321.
AuPt@Pt Nanocrystals/rGO	0.6		0.5 M H_2SO_4 + 0.5 M Ethylene glycol	*Electrochim. Acta* **2016**, 219, 321-329.

Table S5 GOR performances of PtNiPb/C and various Pt-based catalysts from published works.

Catalysts	Peak currents from CV curves		Electrolytes	References
	Jm (A/mg_{Pt})	*Js* (mA/cm^2)		
$PtNi_{0.67}Pb_{0.26}$ NWs/C	**0.36**	**0.61**	**0.1 M $HClO_4$ + 0.2 M Glycerol**	**This Work**
Pt/MWCNT		0.16	0.1 M $HClO_4$ + 1 M Glycerol	*Electrochim. Acta* **2012**, 66, 180-187.
Clean Pt Nanoparticles		~ 0.23	0.1 M H_2SO_4 + 0.255 M Glycerol	*Electrochim. Acta* **2013**, 98, 25-31.
Pt Nanoparticles		~ 0.35	0.1 M H_2SO_4 + 0.1 M Glycerol	*Electrocatal.* **2011**, 2, 96-105.