Supporting Information for

Shape-Control of One-Dimensional PtNi Nanostructure as Efficient Electrocatalysts for Alcohol Electrooxidation

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1. Materials and methods

1.1 Materials and Reagents

Platinum (II) acetylacetonate ($Pt(acac)_2$, reagent grade, 98%), Nickel acetylacetone ($Ni(acac)_2$, reagent grade, 97%), and Tungsten carbonyl ($W(CO)_6$, reagent grade, 99%), were all purchased from Sigma-Aldrich. Oleylamine (OAm, 80-90%), 1-octadecene (ODE, reagent grade, 95%), citric acid (CA, reagent grade, 99.5%), N-Hexadecyltrimethylammonium Chloride (CTAC, reagent grade, >97.0%) and were purchased from Aladdin. Glucose (reagent grade, 97%), potassium hydroxide (KOH), ethylene glycol (EG, A.R. grade, >99.5%), glycerol (A.R. grade, >99.5%) and ascorbic

acid (AA, reagent grade, 99%) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All the chemicals were used without further purification.

1.2 Preparation of Pt_3Ni UNWs, Pt_3Ni SNWs, and Pt_3Ni UNRs

In a typical preparation of ultrathin Pt_3Ni SNWs, $Pt(acac)_2$ (10 mg), $Ni(acac)_2$ (2.2 mg), $W(CO)_6$ (5 mg), CA (40 mg), CTAC (32 mg), 4 mL OAm and 1 mL ODE were added into a glass vial (volume: 20 mL). After the vial had been capped, the mixture was ultrasonicated for 2 h. The resulting homogeneous mixture was then heated from room temperature to 180 °C and maintained at 180 °C for 5 h in an oil bath. The products were collected by centrifugation and washed three times with a cyclohexane/ethanol mixture. The synthesis of Pt_3Ni UNWs and Pt_3Ni UNRs was similar to that of Pt_3Ni SNWs, except that 40 mg CA was replaced by glucose and AA: 60 mg glucose for Pt_3Ni UNWs, 60 mg glucose and 10 mg AA for Pt_3Ni UNRs, while keeping the other reactions parameters same.

1.3 Physical Characterizations

The morphological and structural characterizations of these PtNi nanocrystals were conducted on TECNAI-G20 electron microscope (TEM) conducted at an accelerating voltage of 200 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. The scanning electron microscope energy-dispersive X-ray spectroscopy (SEM-EDS) were taken with a HITACHI S-4700 cold field emission scanning electron microscope operated at 15 kV. XRD pattern was collected on X'Pert-Pro MPD diffractometer (Netherlands PANalytical) with a Cu Kα X-ray

source (λ = 1.54 Å). X-ray photoelectron spectroscopy (XPS) was investigated using a Thermo Scientific ESCALAB 250 XI X-ray photoelectron spectrometer. Trademarks for all the instruments used in experiments could be seen in Table. S4.

1.4 Electrochemical Measurements

A three-electrode cell was used for the electrochemical measurements, which comprised a glassy-carbon electrode (GCE) (diameter: 3 mm, area: 0.07 cm^2), a saturated calomel electrode (SCE) and a Pt wire, behaving as working, reference and counter electrode, respectively. Notably, the GCE needed to be polished with alumina powder and then rinsed with ethanol. The products of Pt_3Ni SNWs, Pt_3Ni UNWs, Pt_3Ni UNRs were collected by centrifugation and washed three times with cyclohexane/ethanol mixture. Then, we loaded the catalysts on carbon black (Vulcan XC72R carbon, C) by sonication and washed with ethanol at room temperature twice. Finally, the sample is centrifuged and dried. To prepare a catalyst-coated working electrode, the catalyst was dispersed in a mixture of solvents containing isopropanol and Nafion (5%) to form a 0.40 mg_{Pt}/mL suspension. A 5 μL portion of isopropanol dispersion of PtNi nanocatalysts on carbon (0.40 mg_{Pt}/mL) was deposited on a glassy carbon electrode to obtain the working electrodes after the solvent was dried naturally. EGOR and GOR was conducted in 1.0 M KOH + 1.0 M EG and 1.0 M KOH + 1.0 M glycerol solution, respectively. The durability test was performed at room temperature by applying the chronoamperometric (CA) curves and successive CVs at sweep rate of 50 mV/s for 250 cycles.

2. Supplementary Figures

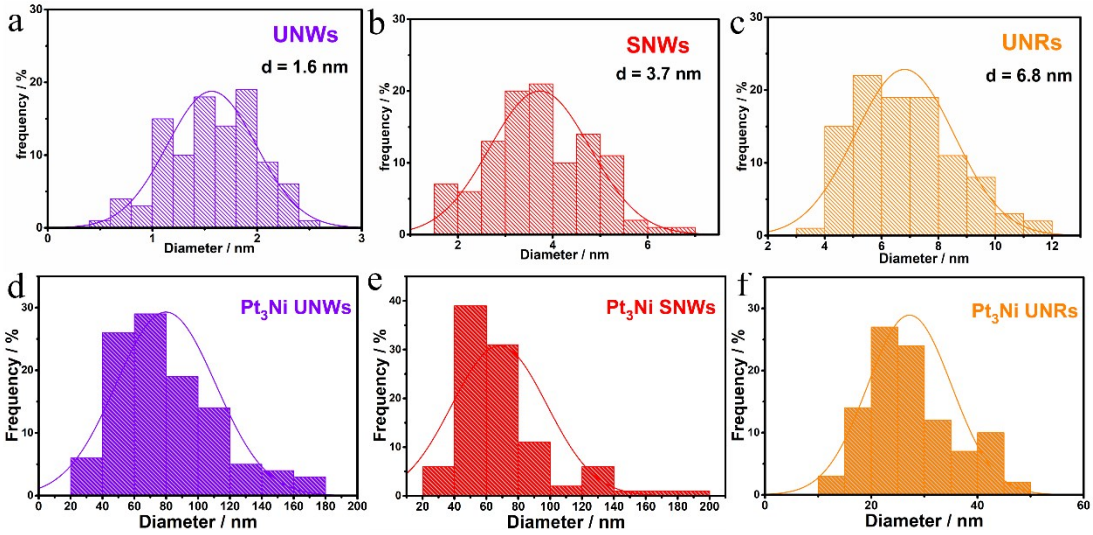

Fig. S1 Size distribution of (a) Pt_3Ni UNWs, (c) Pt_3Ni SNWs, and (e)Pt_3Ni UNRs in width, and size distribution of (d) Pt_3Ni UNWs, (e) Pt_3Ni SNWs, and (f)Pt_3Ni UNRs in length.

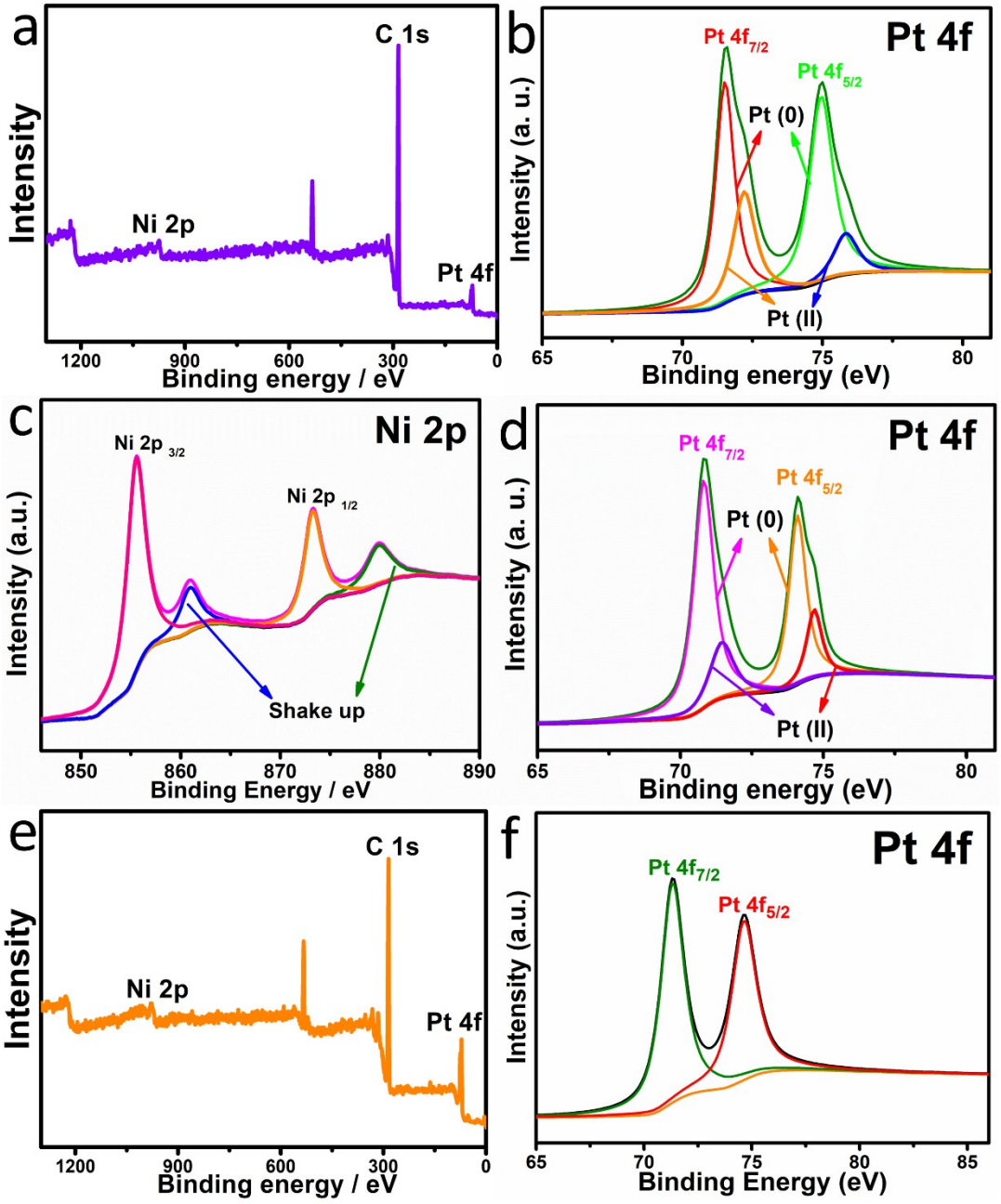

Fig. S2 XPS spectrum of (a) survey scan, (b) Pt 4f in Pt_3Ni UNWs, and (c) Ni 2p, (d) Pt 4f in Pt_3Ni SNWs, (e) survey scan, (f) Pt 4f in Pt_3Ni UNRs.

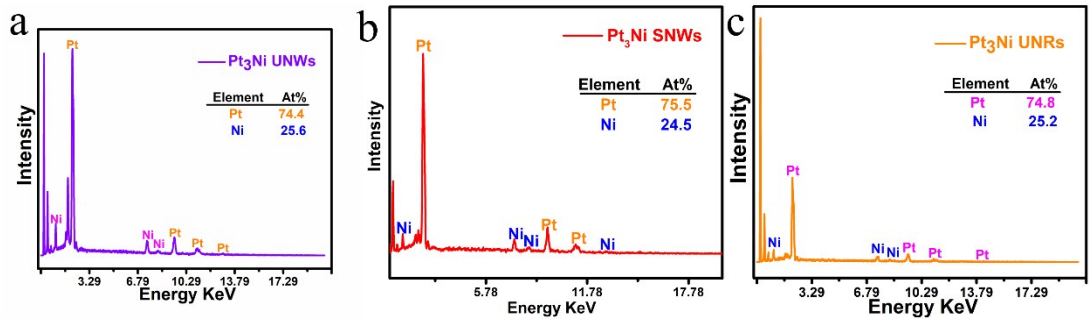

Fig. S3 SEM-EDX spectrum of (a) Pt_3Ni UNWs, (b) Pt_3Ni SNWs, and (c) Pt_3Ni UNRs.

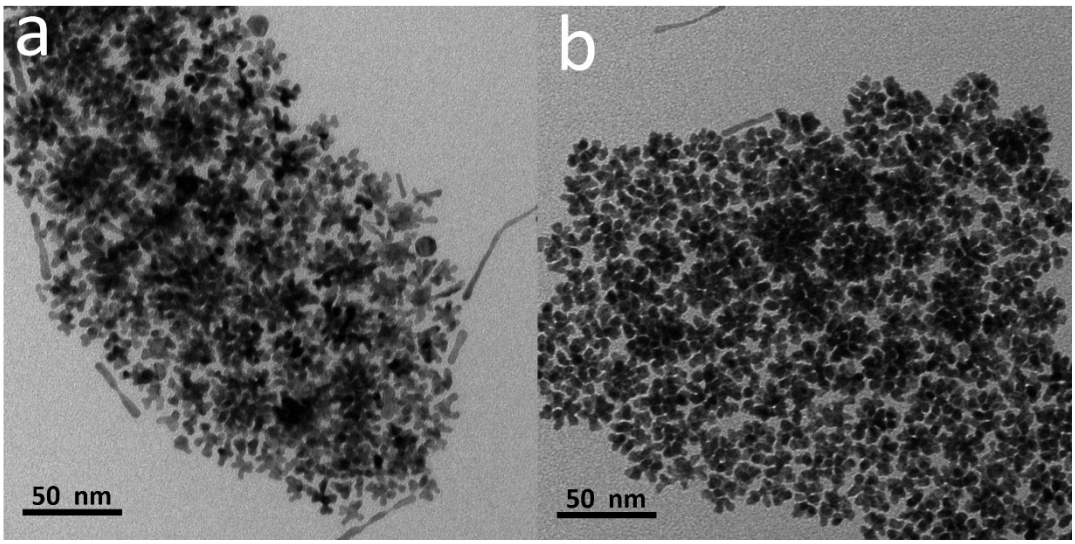

Fig. S4 TEM images of the products with the same reaction conditions as that of Pt_3Ni SNWs without the introduction of $W(CO)_6$.

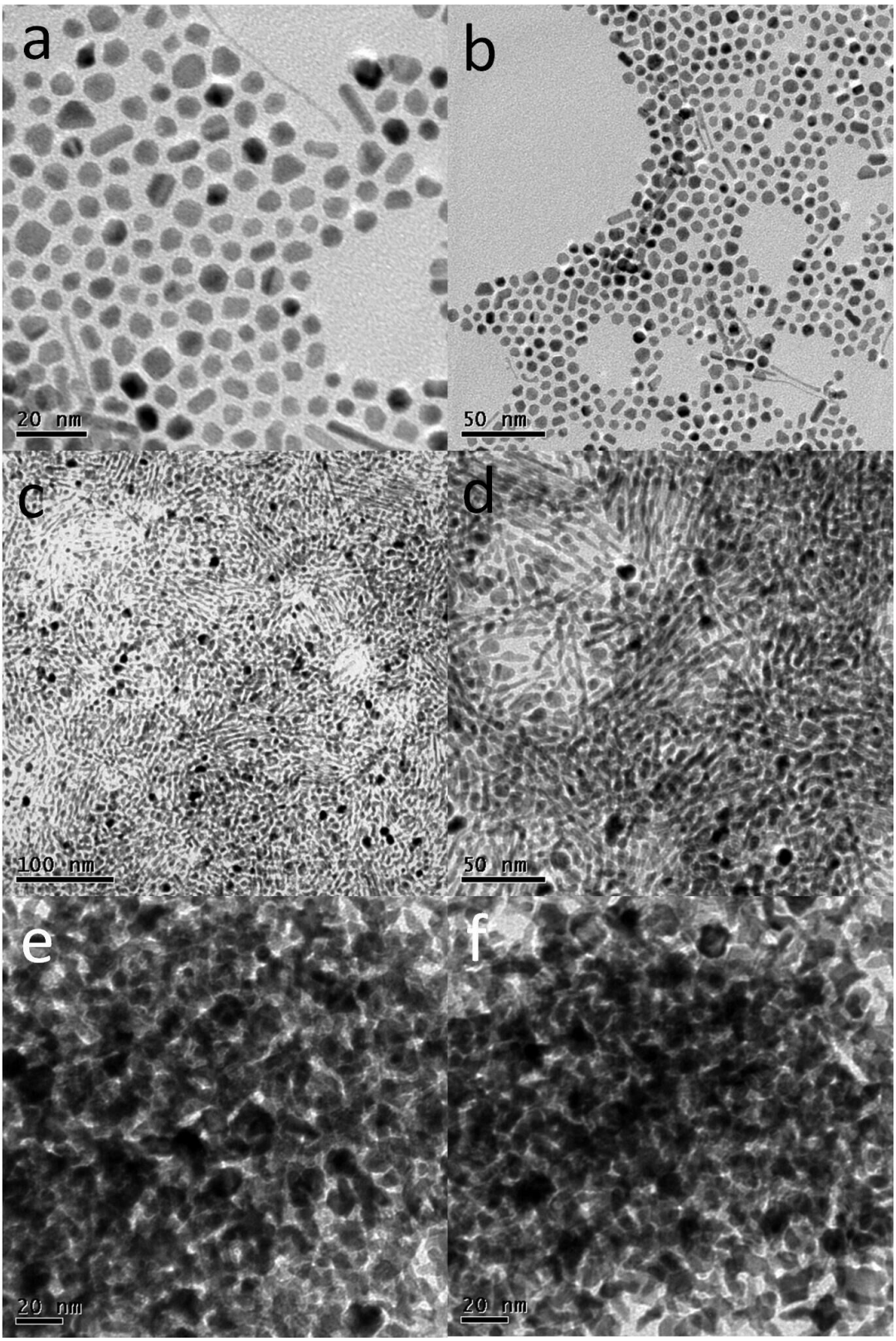

Fig. S5 TEM images of the products with the same reaction conditions as that of (a and b) Pt_3Ni UNRs, (c and d) Pt_3Ni UNWs, and (e and f) Pt_3Ni SNWs in the absence of CTAC.

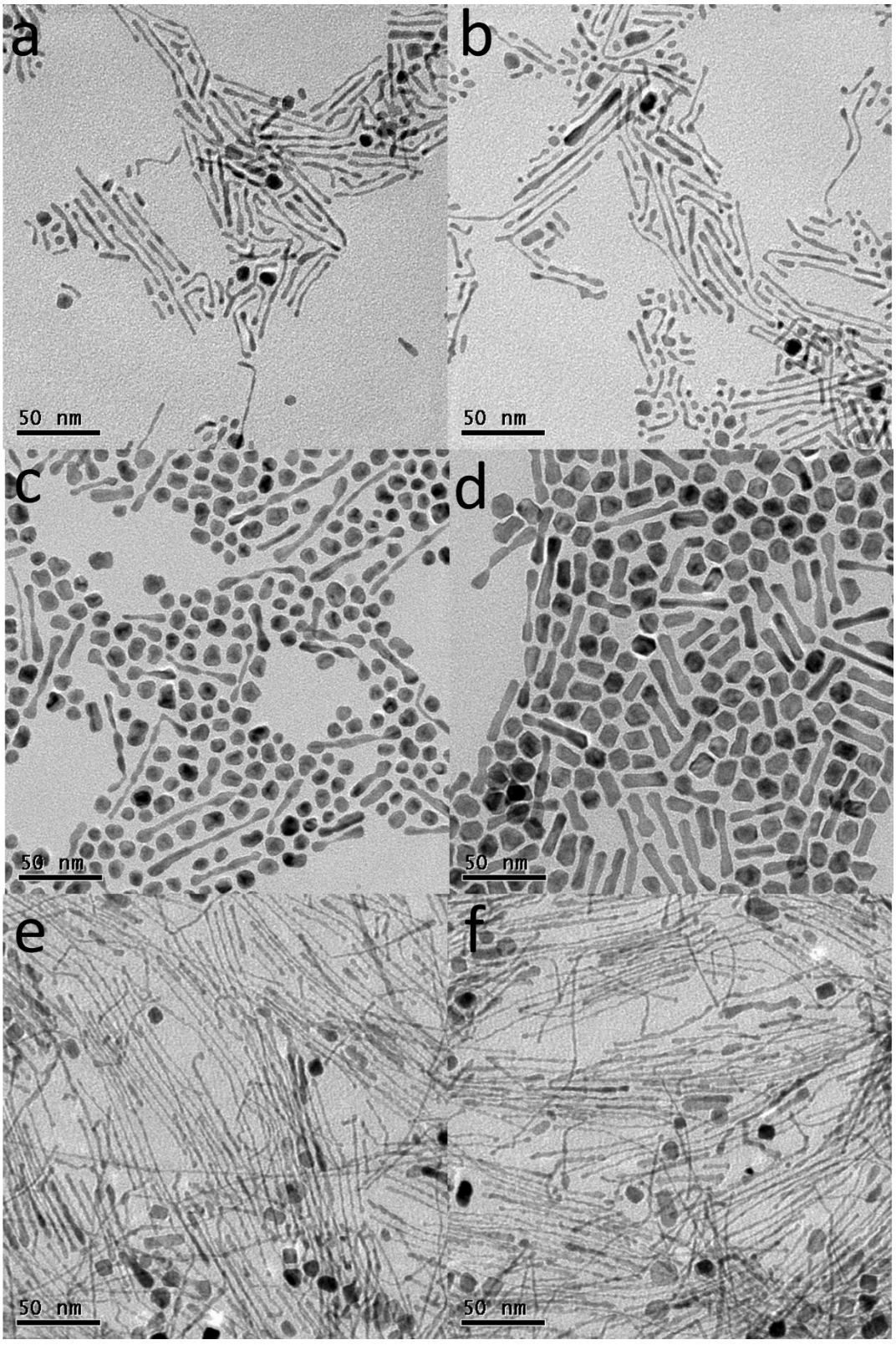

Fig. S6 TEM images of the products with the same reaction conditions as that of (a and b) Pt_3Ni SNWs, (c and d) Pt_3Ni UNRs, and (e and f) Pt_3Ni UNWs without the addition of ODE.

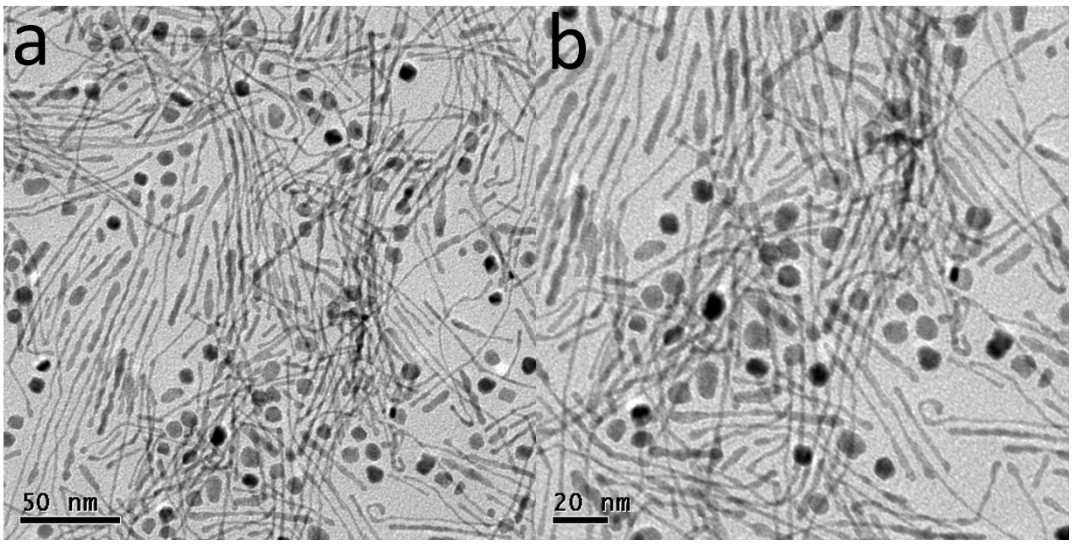

Fig. S7 TEM images of the products with the same reaction condition as that of Pt_3Ni UNRs without the addition of glucose.

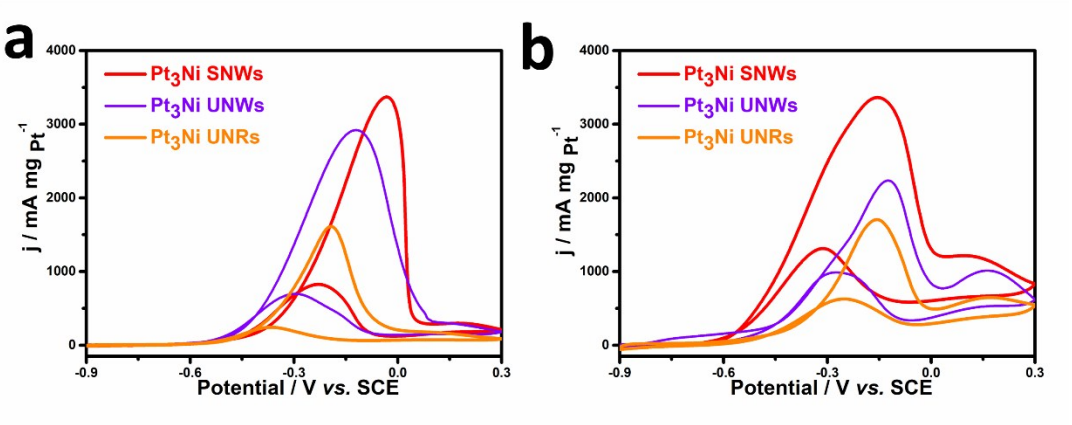

Fig. S8 CV curves Pt_3Ni SNWs, Pt_3Ni UNWs, Pt_3Ni UNRs catalysts (unloaded on C) operated in (a) 1 M KOH and 1 M EG and (b) 1 M KOH and 1 M glycerol solution.

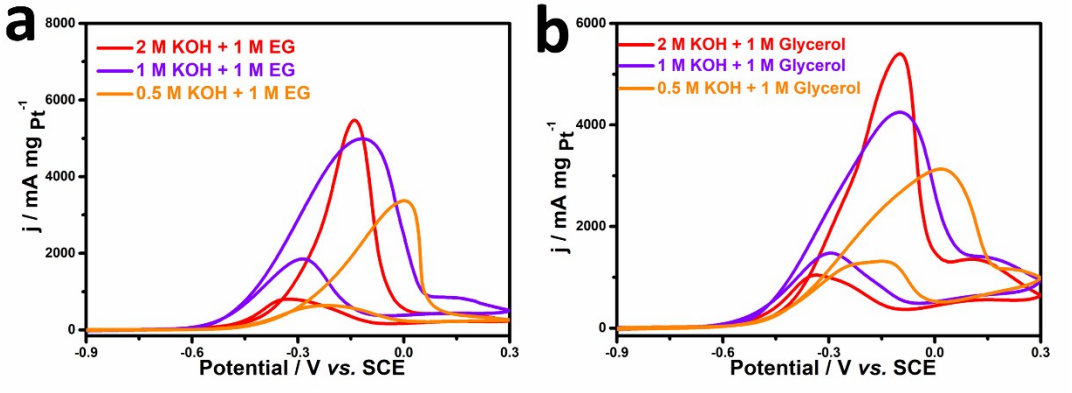

Fig. S9 CV curves of Pt_3Ni SNWs catalysts towards (a) EGOR and (b) GOR with

different KOH concentration.

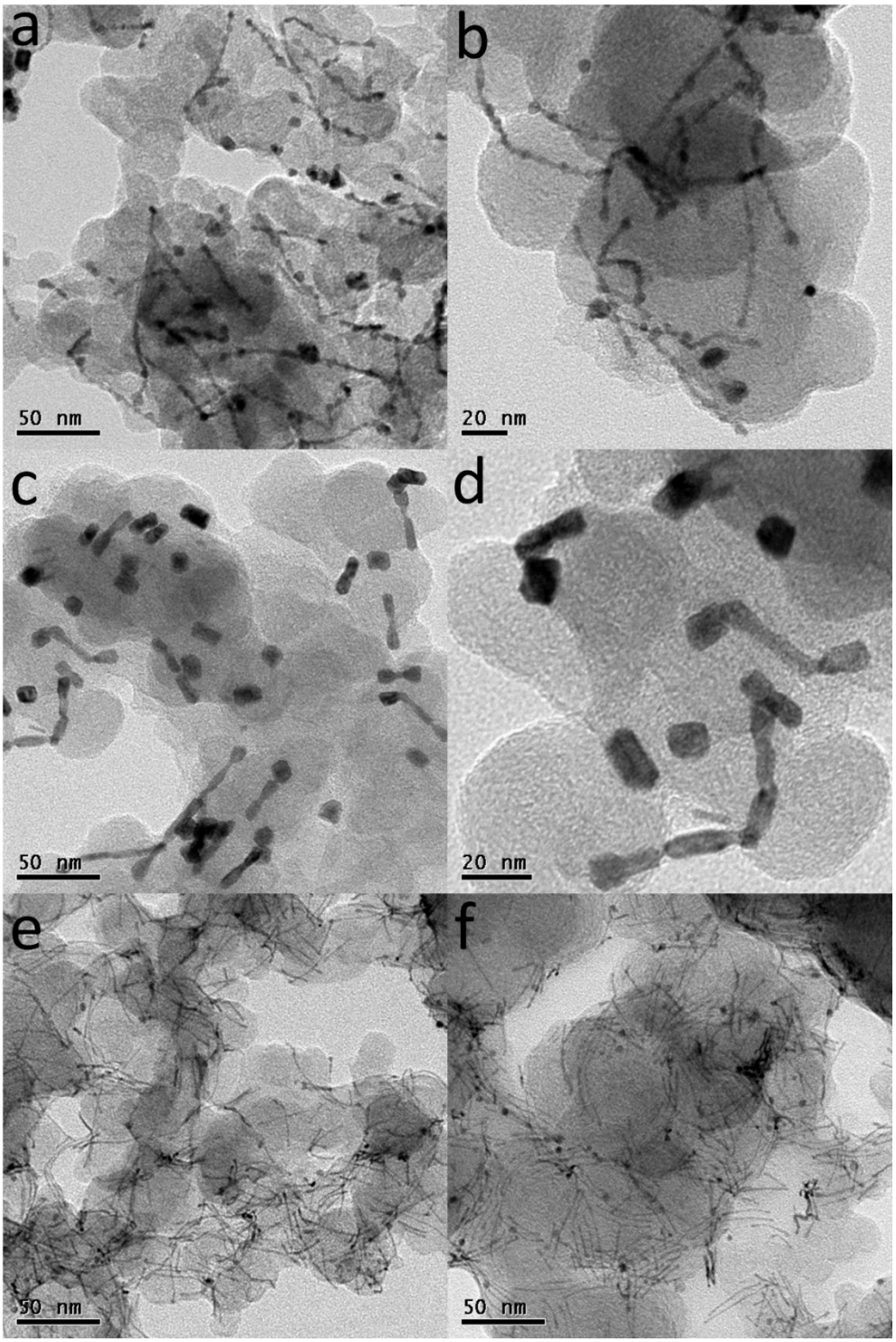

Fig. S10 Representative TEM images of (a and b) Pt_3Ni SNWs, (c and d) Pt_3Ni UNWs, and (e and f) Pt_3Ni UNRs catalysts before electrochemical measurements.

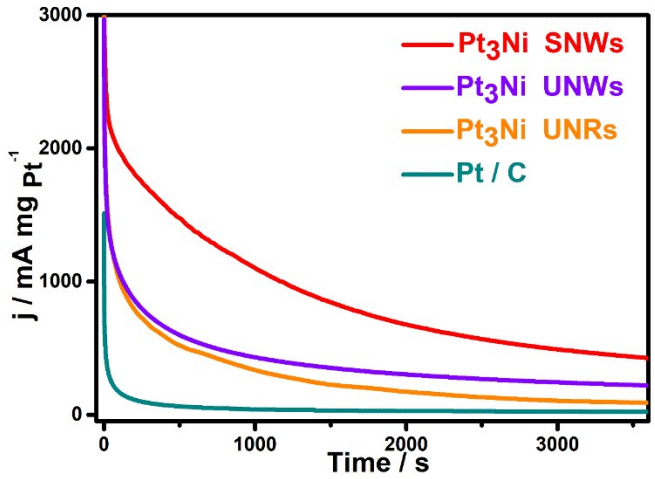

Fig. S11 CA curves of Pt_3Ni SNWs, Pt_3Ni UNWs, Pt_3Ni UNRs, and commercial Pt/C catalysts recorded in 1.0 M KOH +1.0 M glycerol solution.

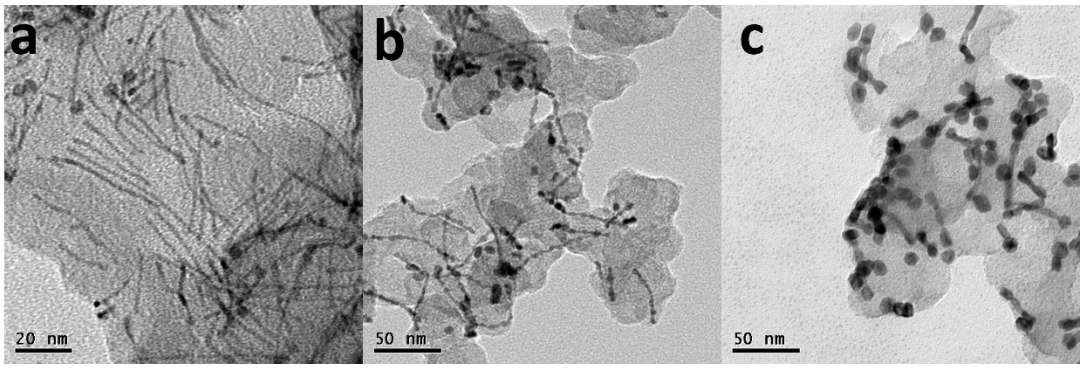

Fig. S12 Representative TEM images of (a) Pt_3Ni UNWs, (b) Pt_3Ni SNWs, and (C) Pt_3Ni UNRs catalysts after durability tests.

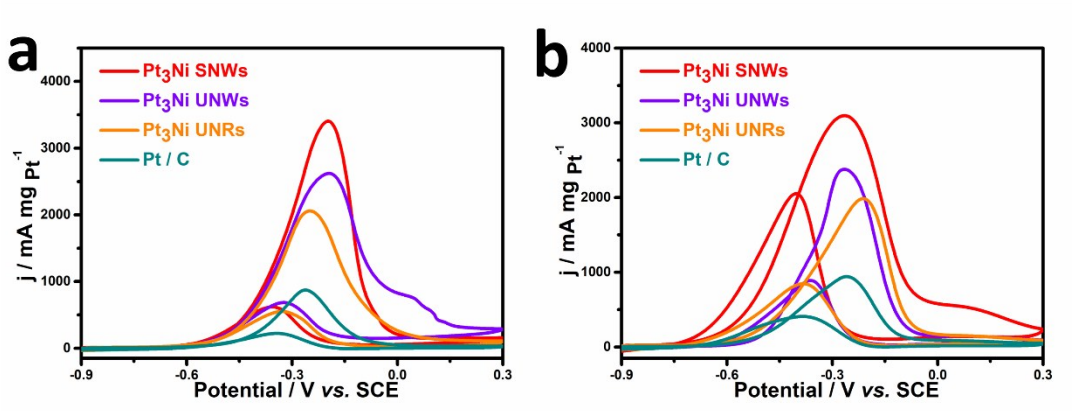

Fig. S13 CV curves of Pt_3Ni SNWs, Pt_3Ni UNWs, Pt_3Ni UNRs and commercial Pt/C catalysts operated in (a) 1 M KOH and 1 M methanol, (b) 1 M KOH and 1 M ethanol solution.

Table. S1 Electrocatalytic activity comparison of as-prepared catalysts (loaded on C or not)

		Pt_3Ni SNWs	Pt_3Ni UNWs	Pt_3Ni UNRs
GOR activity ($mA\ mg^{-1}$)	loaded on C	4250.0	3721.5	3022.5
	not loaded on C	3363.0	2236.0	1705.5
EGOR activity ($mA\ mg^{-1}$)	loaded on C	4889.5	4256.0	3429.5
	not loaded on C	3369.5	2920.0	1611.5

Table.S2 Other electrocatalysts for the glycerol electrochemical oxidation reaction.

Catalysts	Electrolyte	Mass activity ($mA\ mg^{-1}$)	Reference
Pt_3Ni SNWs	1 M KOH + 1 M glycerol	4250.0	This work
$Pd_{63}Ag_{37}$ nanocorals	1 M KOH + 1 M glycerol	1600	J. Mater. Chem. A **2015**, 3, 15920-15926
PtAg nanotubes	0.5 M KOH + 0.5 M glycerol	210	Electrochem.Commun.**2014**,46,36-39
$Pt_{52}Cu_{48}$ HTNCs	1 M $HClO_4$ + 1 M glycerol	3200	ACS Appl. Mater. Interfaces **2018**, 10, 12659−12665
$PdCu_2$	1 M KOH + 1 M glycerol	1600	ACS Appl. Mater. Interfaces **2016**, 8, 34497
PtAu ANFs	0.5 M KOH + 0.5 M glycerol	1210	Energy Environ. Sci., **2012**, 5, 8328-8334
PtRu NPs/XC	0.5 M H_2SO_4 + 0.5 M ethanol	189	Electrochim. Acta **2014**, 142, 223-

Table.S3 Other electrocatalysts for the ethylene glycol electrochemical oxidation reaction.

Catalysts	Electrolyte	Mass activity ($mA\ mg^{-1}$)	Reference
Pt_3Ni SNWs	1 M KOH + 1 M EG	4889.5	This work
PtRu alloy	1 M KOH + 1 M EG	3350	Appl. Surf. Sci. **2018**, 427, 83-89.
PtPd@Pt NCs/rGO	0.5 M KOH + 0.5 M EG	1167	Electrochim. Acta **2016**;187:576-83.
Pd_1Cu_1 nanosphere	1 M KOH + 1 M EG	3580	Electrochim. Acta **2018**, 261, 521-529.
PtAg-s NPs	1 M KOH +1 M EG	3200	Inorg. Chem. Front. **2018**, 5, 1174–1179
$PtNi_{0.67}Pb_{0.26}$ NWs/C	0.1 M $HClO_4$ + 0.2 M EG	420	J. Mater. Chem. A **2017**, *5*, 18977- 18983
Au@Pd	1 M KOH +1 M EG	4020	J. Alloys Compond. **2017**, 723, 36-42

Table. S4 Trademarks for all the instruments used in characterization section.

Instruments	Trademarks
Transmission electron microscope (TEM)	FEI TECNAI G20, Field Electron and Ion Company, America
X-ray powder diffractometer (XRD)	X'Pert-Pro MPD, PANalytical B.V., Holland
X-ray photoelectron spectroscopy (XPS)	ESCALAB 250 XI, Thermo Scientific
High-magnification TEM	FEI TECNAI G2 F20, Field Electron and Ion Company, America
Elements mappings (HAADF-STEM-EDS)	FEI TECNAI G2, F20 Field Electron and Ion Company, America

Energy dispersive X-ray spectrometer (EDX)	EVO 18, Carl Zeiss AG, German