Electronic Supplementary Information for:

Ultrathin nanodendrites surrounded PtRuNi nanoframes as efficient catalyst for methanol electrooxidation

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Experimental

1.1 Reagents

Chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, AR), ruthenium acetylacetonate ($Ru(acac)_3$, 97%), nickel acetylacetonate ($Ni(acac)_2$, 95%) oleylamine (OAm, 80–90%) and perchloric acid ($HClO_4$, GR 70.0–72.0%) were bought from Aladdin. Nitric acid (HNO_3, AR), ethanol (AR), methanol (AR) and n–hexane (AR) were bought from Beijing Chemical Works. Commercial Pt/C (10 wt%) was purchased from Alfa Aesar. All the reagents were used as received.

1.2 Preparation of PtRuNi nanoframes with ultrathin nanodendrites (PtRuNi FDs).

PtRuNi nanoframes with untrathin nanodendrites were prepared by etching the corresponding solid PtRuNi nanomaterials with nitric acid. In a typical procedure for the synthesis of solid PtRuNi nanomaterials, $H_2PtCl_6 \cdot 6H_2O$ (26 mg), $Ru(acac)_3$ (20 mg), and $Ni(acac)_2$ (20 mg) were added into a three-necked flask. After 10 mL oleylamine was injected, the mixture was subjected to ultrasonication until a transparent solution was obtained. Subsequently, the reaction solution was heated in oil bath for 2 hours which had been preheated to 250°C. The whole reaction process was conducted under N_2 flow. At last, the reaction mixture was naturally cooled to room temperature. The products were collected by centrifugation and washed with the mixture solution of ethanol and n–hexane (V/V = 1/4) for several times. Finally, the products were dispersed in ethanol. In the etching step, 3 mL ethanol suspension of the solid nanomaterial was mixed with 1 mL concentrated HNO_3. 12 hours later, PtRuNi FDs was collected through centrifugation and washing with ethanol twice. At last, the PtRuNi FDs was dried at 60°C. The ultimate product obtained with above mentioned methods was denoted as PtRuNi FDs_1 and the elemental ratio of Pt:Ru:Ni in PtRuNi FDs_1 was 1:0.87:0.75 determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

The reaction conditions for PtRuNi FDs_2 and PtRuNi nanodendrites (NDs) were the same with PtRuNi FDs_1 except for changing the amounts of $Ni(acac)_2$ to 40 mg and 80 mg. PtNi FDs was prepared in the absence of $Ru(acac)_3$ and the reaction time was reduced to 30 min while other reaction conditions kept the same with PtRuNi FDs_1. The elemental ratios of Pt:Ru:Ni in PtRuNi FDs_2 and PtRuNi NDs were 1:0.83:0.59 and 1:0.96:0.32 while the elemental ratio of Pt:Ni in PtNi FDs was 1:0.21.

1.3 Structural and compositional characterizations

High-resolution transmission electron microscopy (HRTEM), energy dispersive X-ray spectroscopy (EDS), and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) measurements were performed with a Tecnai G2 high-resolution transmission electron microscope (200 kV). SEM-EDS results were obtained with an XL30 ESEM scanning electron microscope. X-ray diffraction (XRD) patterns were obtained with a Bruker D8 Advance diffraction system using a Ni filtered $Cu_{K\alpha}$ source (λ=0.154 nm). X-ray photoelectron spectroscopy (XPS) analysis were conducted with Thermo ESCALAB 250 spectrometer. The elemental compositions of the catalysts were measured with inductively coupled plasma-atomic emission spectroscopy (ICP-AES, ThermoScientific iCAP6300, USA).

1.4 Electrochemical tests

Before the electrochemical tests, the synthesized nanocrystals were loaded onto Vulcan XC-72 carbon. Typically, about 2 mg nanocrystals and 8 mg carbon were mixed and dispersed in ethanol under ultrasonication. After stirred for 12 hours, the catalysts were collected with centrifugation and then dried under 80°C. The samples were further heated to 220°C in air and maintained at 220°C for 1 hour to remove the adsorbed organic surfactants. The catalyst inks were prepared by dispersing the carbon supported nanocrystals into the mixture of ethanol and Nafion (5 wt%) (V/V=1:0.005) with sonication. The concentrations of different metal elements in the inks were determined with ICP-AES. Subsequent electrochemical tests were conducted with three-electrode system while glassy carbon electrode (GCE) with the diameter of 5 mm was used as working electrode and KCl saturated Ag/AgCl electrode was used as reference electrode. The loading amounts of Pt for prepared catalysts and commercial Pt/C were fixed to 7.32 μg cm^{-2}. The catalytic properties for methanol oxidation were evaluated in the aqueous solution containing 0.1 M $HClO_4$ and 0.5 M CH_3OH.

Table S1 Summary of the synthesis recipes and corresponding products.

Nanomaterials	$H_2PtCl_6 \cdot 6H_2O$ (mg)	$Ru(acac)_3$ (mg)	$Ni(acac)_2$ (mg)
PtRu NDs	26	20	0
PtRuNi FDs$_1$	26	20	20
PtRuNi FDs$_2$	26	20	40
PtRuNi NDs	26	20	80
PtRuNi FDs$_{1\text{-}10}$	26	10	20
PtRuNi FDs$_{1\text{-}5}$	26	5	20
PtNi FDs	26	0	20

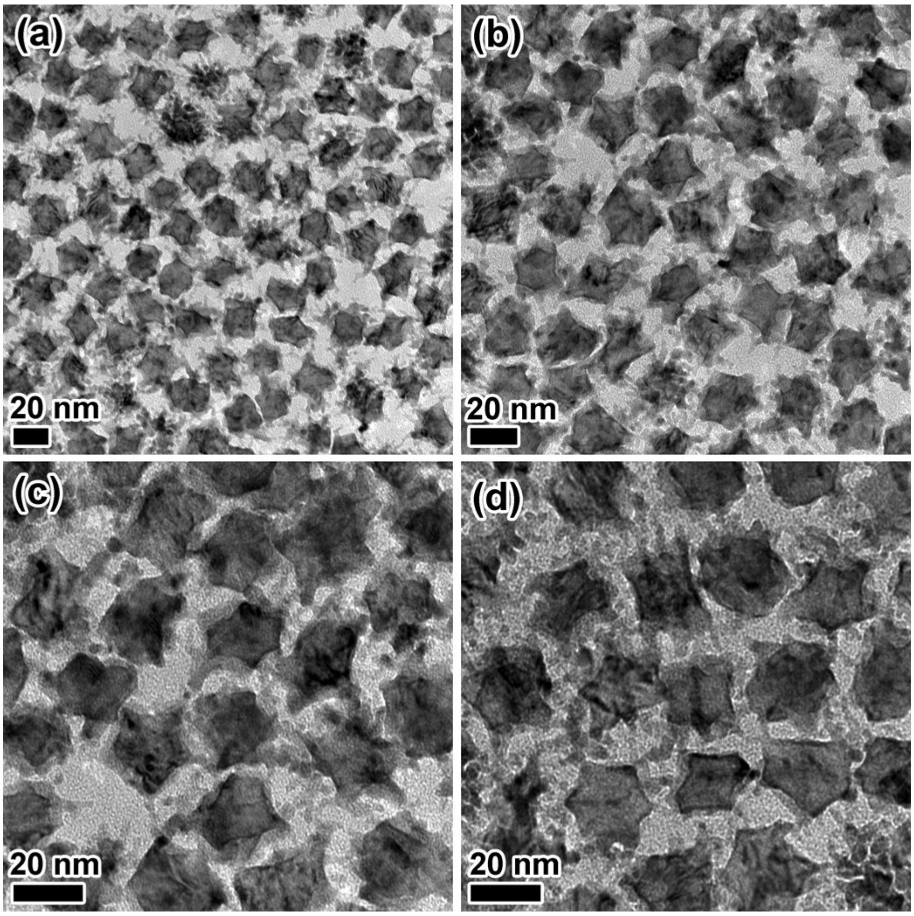

Fig. S1 TEM images of PtRuNi solid nanomaterials before etching with nitric acid. PtRuNi solid nanomaterials showed here can be used to prepare PtRuNi FDs_1 by etching with nitric acid. Apparently, the profile of PtRuNi solid nanomaterials is similar with PtRuNi FDs_1. Ultrathin nanodendrites can also be found in the vertexes of these solid nanocrystals.

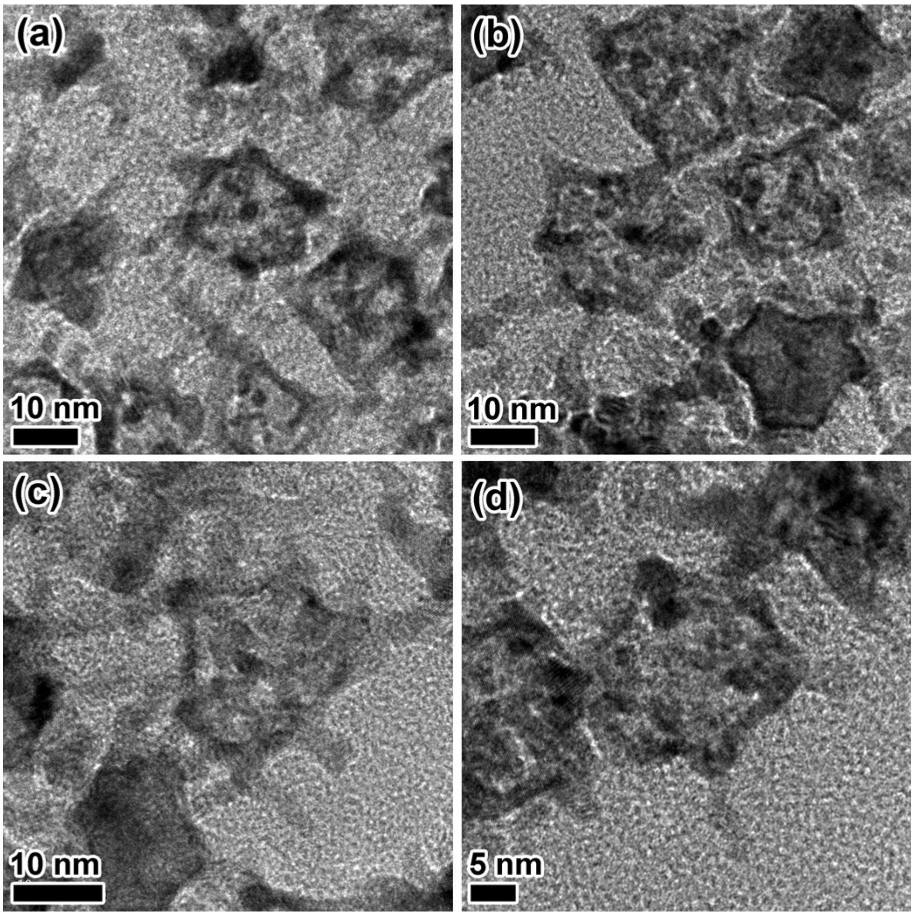

Fig. S2 Representative magnified TEM images of PtRuNi FDs_1.

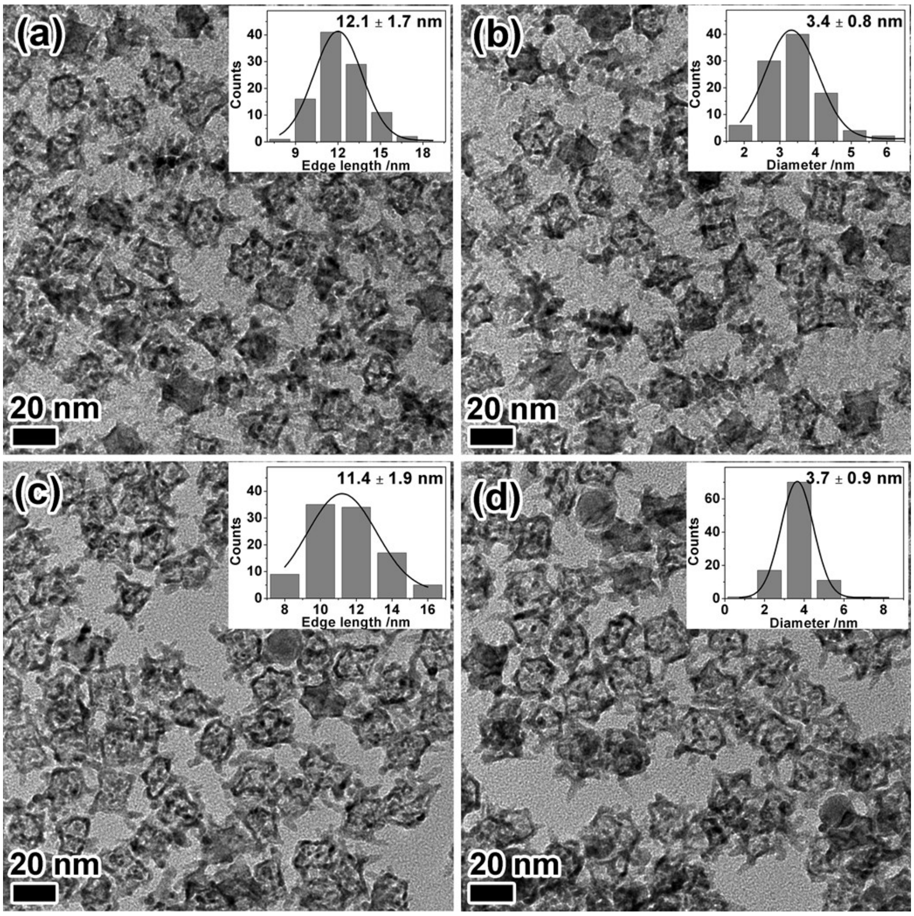

Fig. S3 Typical TEM images of (a, b) PtRuNi FDs_1 and (c, d) PtRuNi FDs_2. Insets in (a, c) and (b, d) show the corresponding average edge lengths of interior nanoframes and the diameters of nanodendrites, respectively.

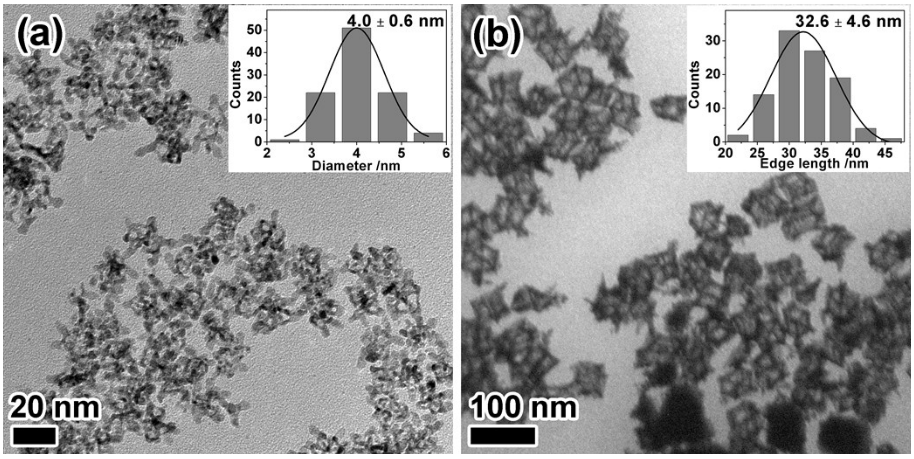

Fig. S4 Typical TEM images of (a) PtRuNi NDs and (b) PtNi FDs. Insets in (a) and (b) show the corresponding average diameters of nanodendrites and the edge lengths of interior nanoframes.

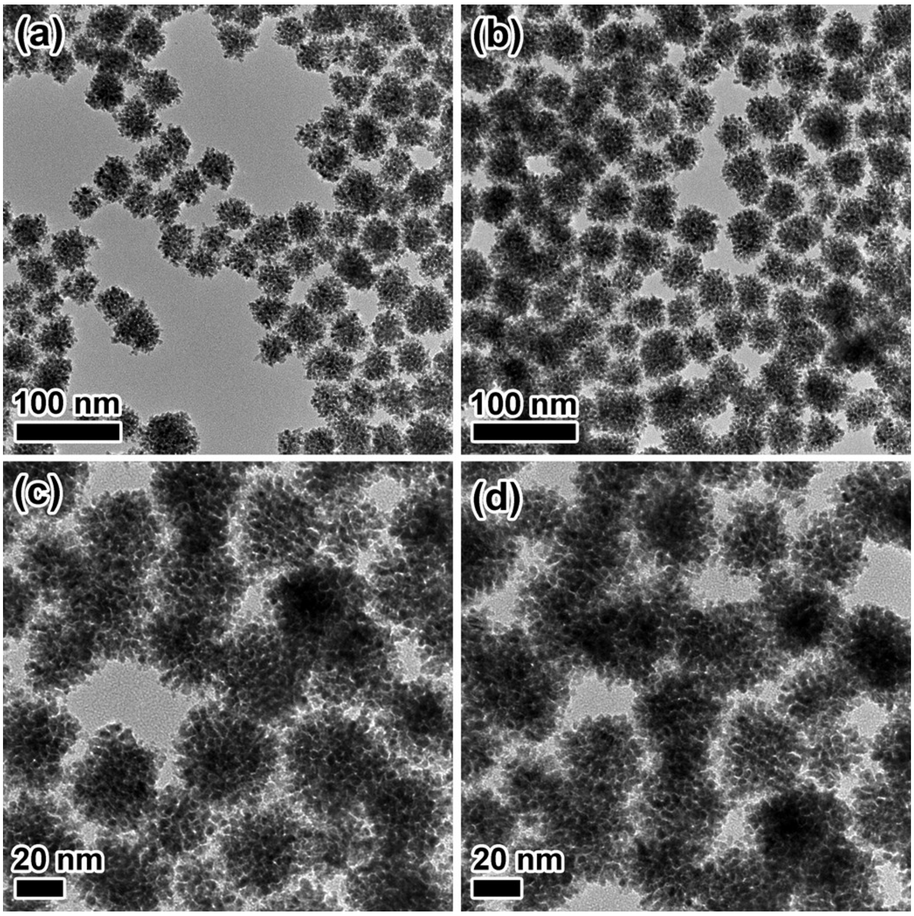

Fig. S5 TEM images of PtRu nanomaterials obtained in the absence of Ni(acac)$_2$ while other reaction parameters were identical with the synthesis of PtRuNi FDs$_1$.

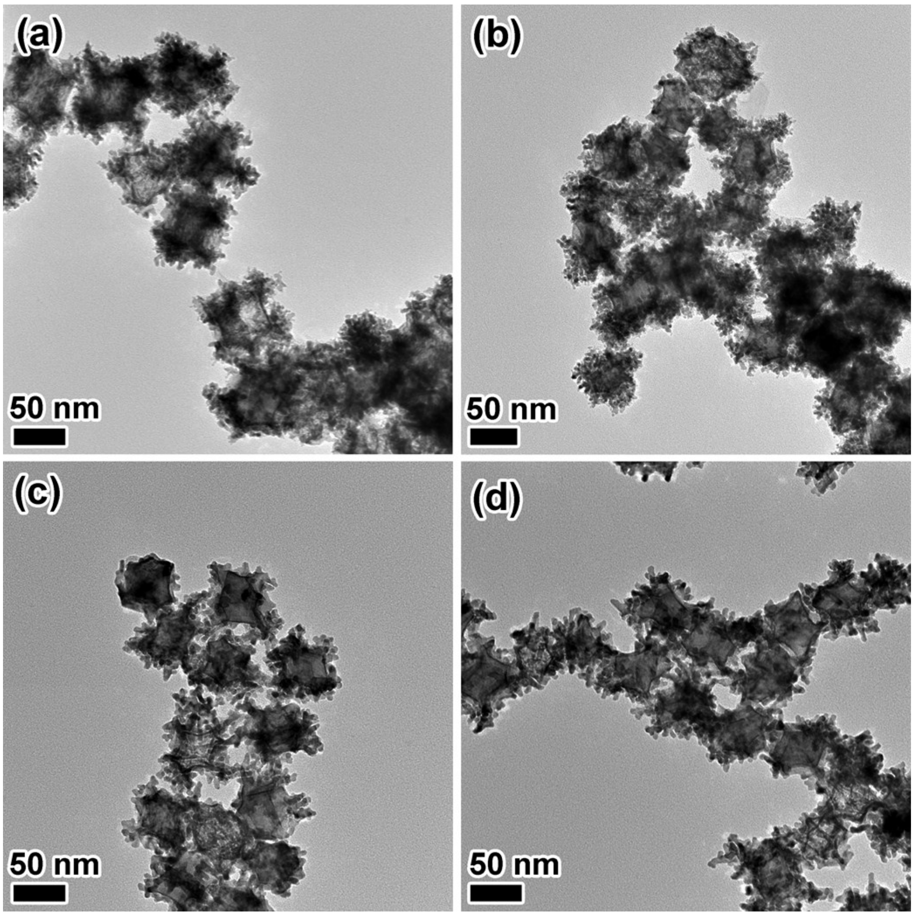

Fig. S6 TEM images of PtRuNi nanomaterials obtained when the amounts of Ru(acac)$_3$ were reduced to 10 mg (a, b, denoted as PtRuNi FDs$_{1\text{-}10}$) and 5 mg (c, d, denoted as PtRuNi FDs$_{1\text{-}5}$) while other reaction conditions were same with the preparation of PtRuNi FDs$_1$.

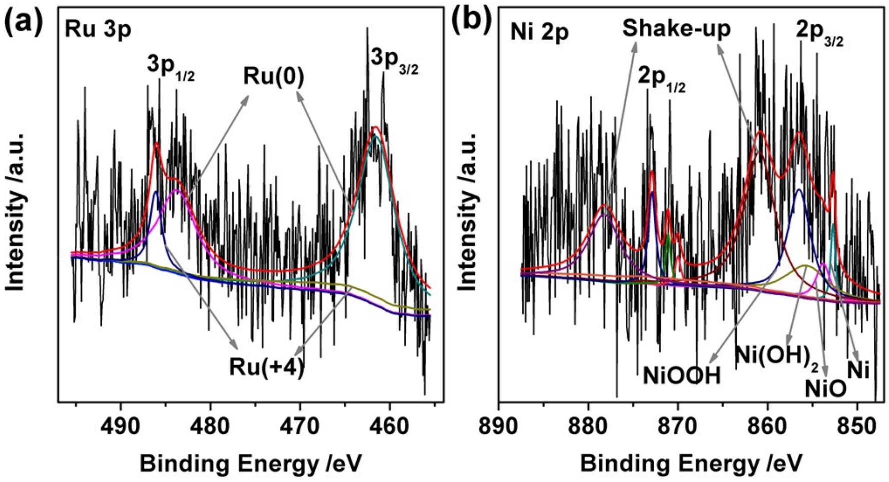

Fig. S7 (a) Ru 3p and (b) Ni 2p XPS spectra of as-prepared PtRuNi FDs_1.

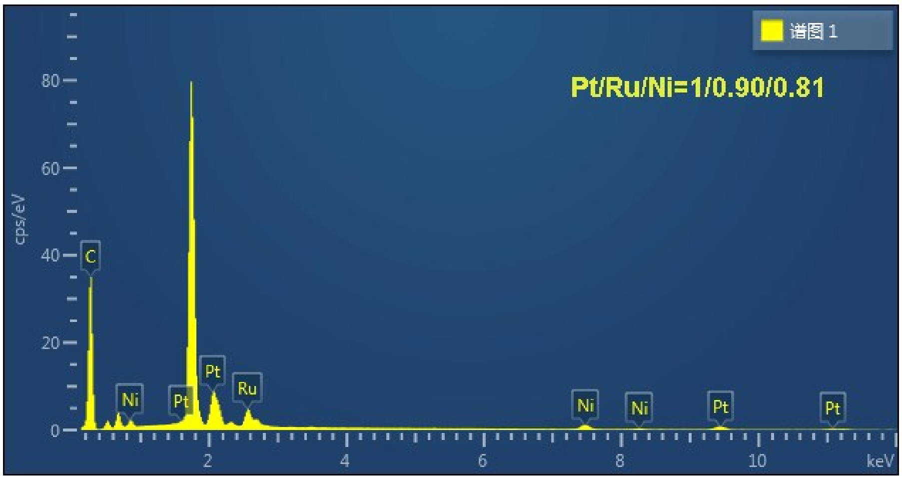

Fig. S8 SEM-EDS results of PtRuNi FDs$_1$/C. The atomic ratio of Pt:Ru:Ni is determined to be 1:0.90:0.81 which resembles the result of PtRuNi FDs$_1$ obtained through ICP-AES.

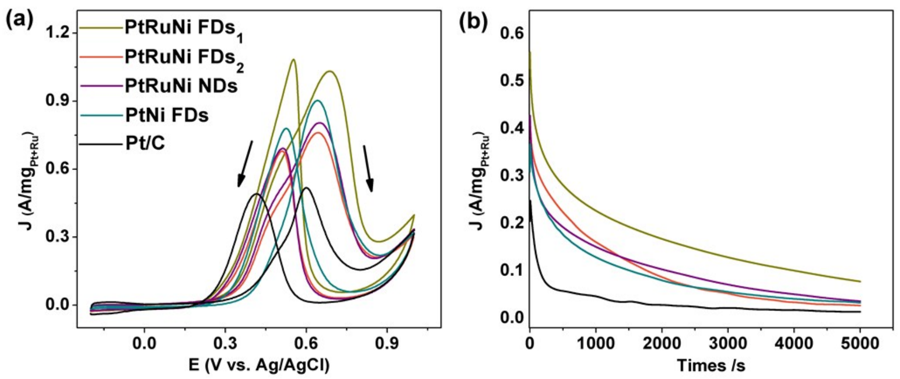

Fig. S9 (a) CV curves and (b) long term i-t curves of different catalysts in 0.1 M $HClO_4$ + 0.5 M methanol solution. The current values are normalized to the loading masses of Pt plus Ru.

Table S2 Comparison of catalytic properties for methanol oxidation reaction between PtRuNi FDs_1 and catalysts reported recently.

Catalysts	Electrolyte	Scan Rate （mV/s）	Mass Activity (A/mg_{Pt})	Reference
PtRuNi FDs_1	0.1 M $HClO_4$ + 0.5 M CH_3OH	50	1.49	This Work
PtRu nanodendrites	0.1 M $HClO_4$ + 1 M CH_3OH	50	1.08	Nanoscale, 2017, 9, 1033
Pt_1Ru_3 nano-sponge	0.5 M H_2SO_4 + 1 M CH_3OH	50	0.41	Nanoscale, 2015, 7, 9467
PtPdRuTe Nanotubes	0.5 M H_2SO_4 + 1 M CH_3OH	50	1.26	J. Am. Chem., Soc. 2017, 139 5890
PtCu nanoframes	0.1 M $HClO_4$ + 1 M CH_3OH	50	0.98	Chem. Commun., 2015, 51, 9722
PtRu icosahedra	0.5 M H_2SO_4 + 0.5 M CH_3OH	50	0.074	Nanoscale 2016, 8, 12812
Pt@RFC-8h	0.5 M H_2SO_4 + 1 M CH_3OH	50	0.66	J. Mater. Chem. A 2017, 5, 19857
Pt NW/N-LDG	1 M H_2SO_4 + 2 M CH_3OH	20	1.28	Small 2017, 13, 1603013
RDH Pt-Ni NFs/C	0.1 M $HClO_4$ + 0.2 M CH_3OH	50	1.04	Nano Lett. 2016, 16, 2762
Pt–Ni_2P/C	0.5 M $HClO_4$ + 1 M CH_3OH	50	1.43	Energy Environ. Sci. 2014, 7, 1628
PtCu/C nanoparticles	0.5 M H_2SO_4 + 1 M CH_3OH	50	1.34	J. Mater. Chem. A 2016, 4, 1579

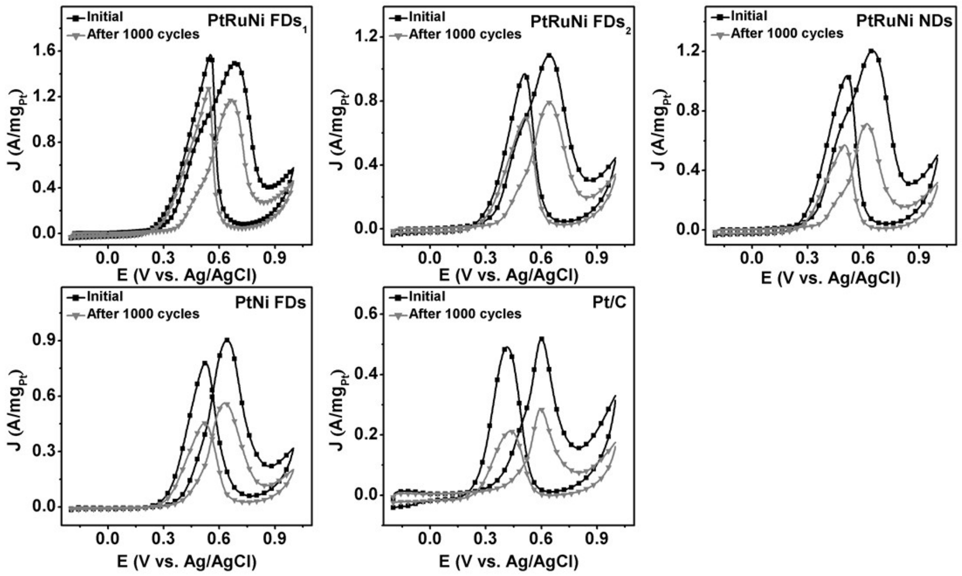

Fig. S10 Cyclic voltammetry curves of various catalysts obtained in 0.1 M $HClO_4$ + 0.5 M methanol at 50 mV s^{-1}. The current values were normalized to the loading masses of Pt and the durability tests were performed at 100 mV s^{-1} from −0.2 to 1.0 V.

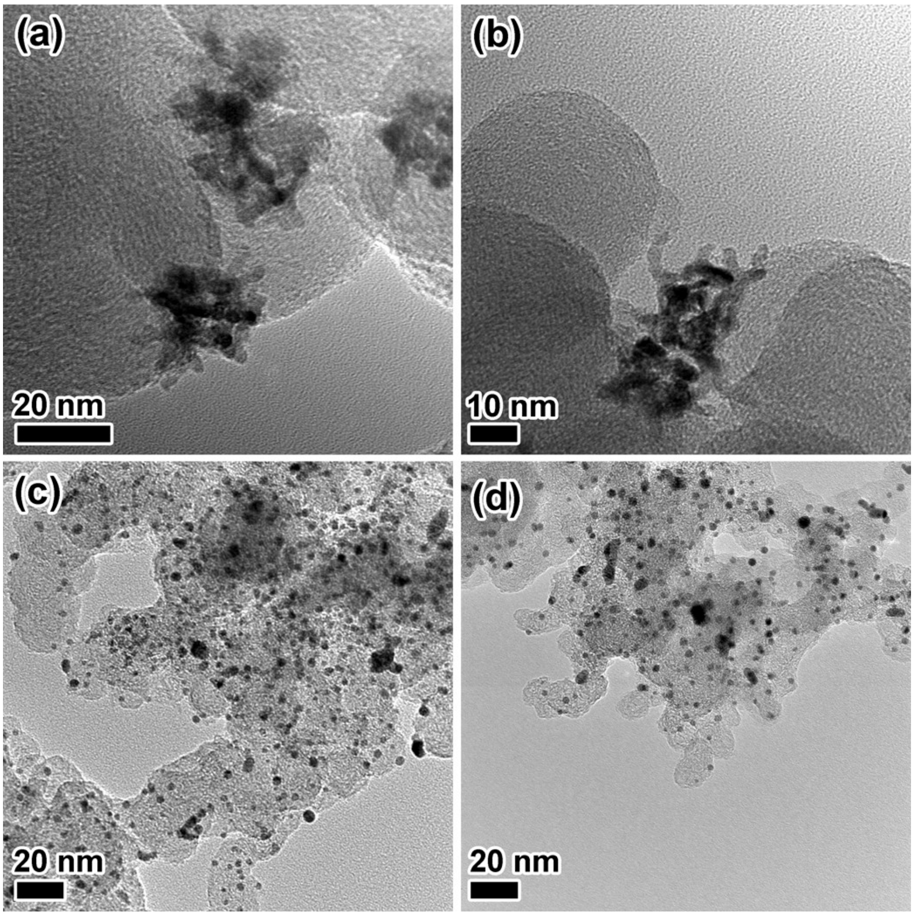

Fig. S11 TEM images of (a, b) PtRuNi FDs$_1$ and (c, d) commercial Pt/C after sweeping for 1000 cycles.

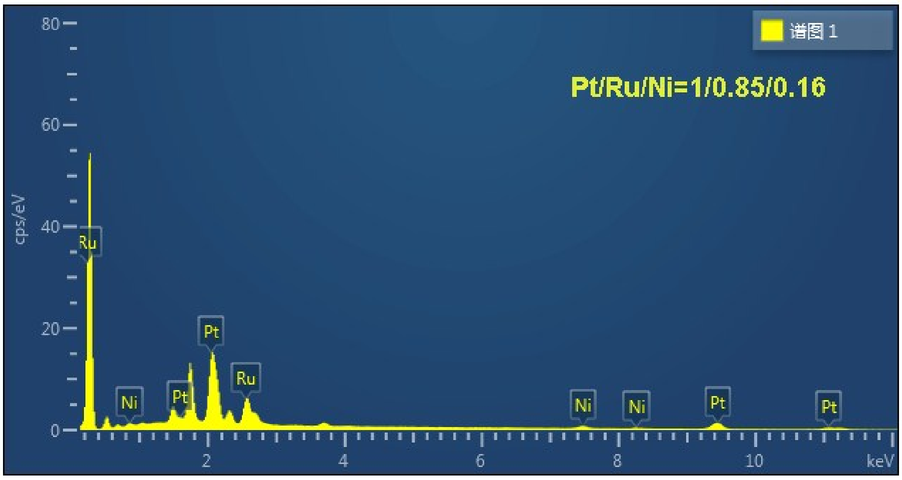

Fig. S12 SEM-EDS results of PtRuNi FDs$_1$/C after sweeping for 1000 cycles.