Supporting information

Surface sites assemble strategy on Pt-Ru nanowires for accelerated methanol oxidation

Mingxuan Li,[†] Yao Wang,[†] Jing Cai,[†] Yunrui Li,[†] Yujie Liu,[†] Yin Dong,[†] Shuna Li,[†] Xiaolin Yuan,[†] Xin Zhang [,†] and Xiaoping Dai[†]*

[†]State Key Laboratory of Heavy Oil Processing, College of Chemical Engineering and Environment, China University of Petroleum, Beijing 102249, China

Corresponding author: Xin Zhang*

Characterization Techniques.

Transmission electron microscopy (TEM) images were collected by JEM-2100 at 200 kV. The magnified images of the NWs were confirmed by a Tecnai G2 F20 S-Twin high resolutions transmission electron microscope (HRTEM) operating at 200 kV. The crystal structure of the NWs was evaluated by X-ray diffraction (XRD) patterns using a Brüker D8 Advance diffractometer at 40 kV and 40 mA for Cu Kα radiation ($\lambda K_{\alpha 1}$= 1.5406 Å; $\lambda K_{\alpha 2}$= 1.5443 Å), with a scan speed of 5 °/min and a step size of 0.02 in 2θ, instrument broadening: 0.12°. The valence states of Pt and Ru was carried out on X-ray photoelectron spectrum (XPS) test using PHI 5000 Versaprobe system with monochromatic Al Kα radiation (1486.6 eV), all the values of binding energy were calibrated by the C1s peak at 284.6 eV. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was performed on IRIS Intrepid II XSP (Thermo Fisher), working parameters: RF power, 1150 W; nebulizer flow, 26.0 PSI; auxiliary gas, 1.0 LPM.

Table S1. The compositions of RuPt NWs and Ru@Pt NWs catalysts determined by ICP-OES.

Catalysts	Mass ratio (Pt: Ru)
Ru/Pt NWs	100:0.45
Ru@Pt NWs	100:0.42
0.09%Ru/Pt NWs	100:0.09
1.9%Ru/Pt NWs	100:1.92
Ru/Pt NWs after stability test	100:0.40

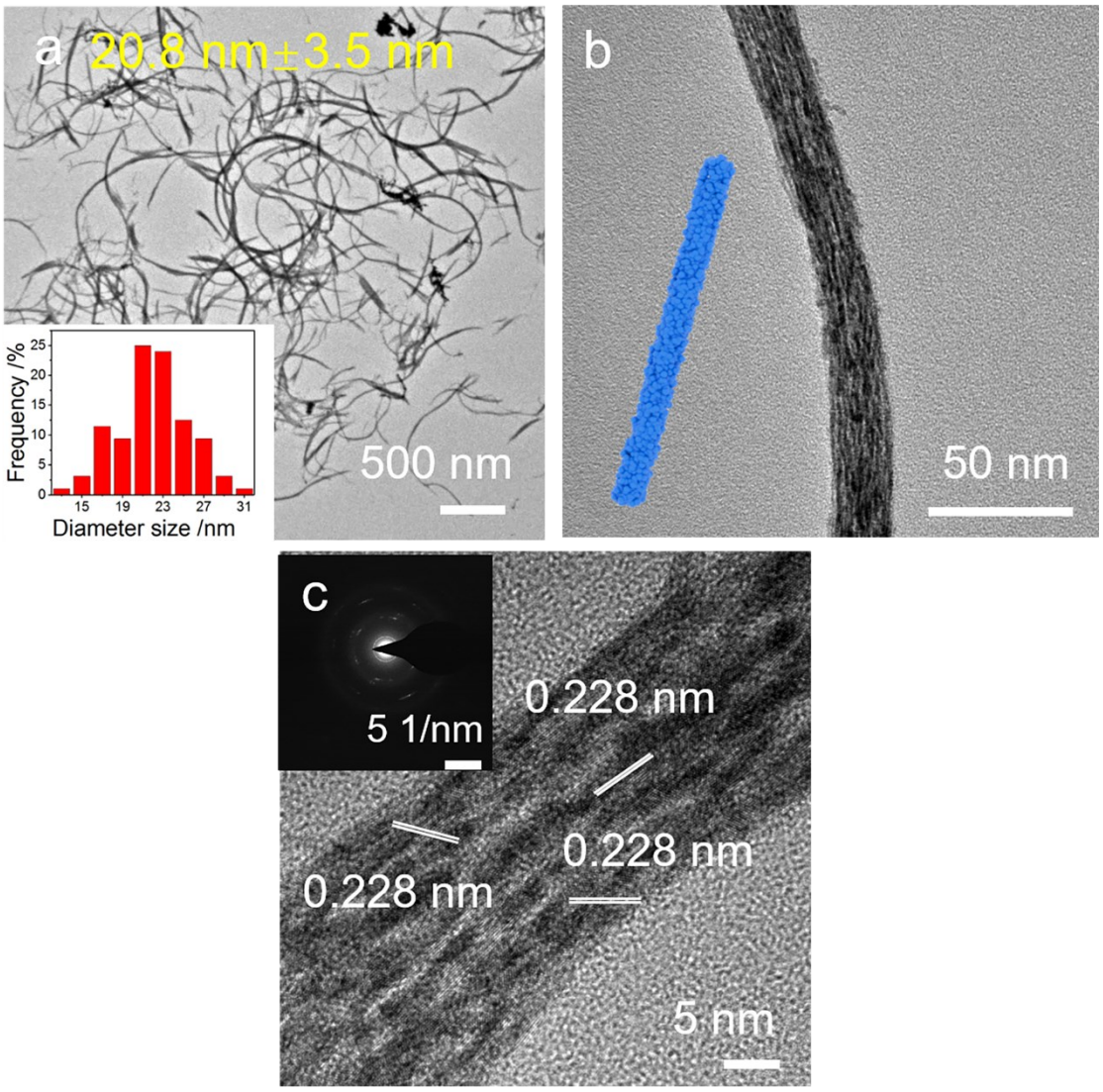

Fig. S1. (a) (b) TEM and (c) HRTEM images of pure Pt NWs.

Table S2 The XRD data of different materials.

materials	2θ /degree (111)	lattice parameter (Å)	strain (%)
Pt crystal (PDF#04-0802)	39.76	0.2538	-
Ru/Pt NWs	40.124	0.2519	0.75
Ru@Pt NWs	40.068	0.2522	0.63

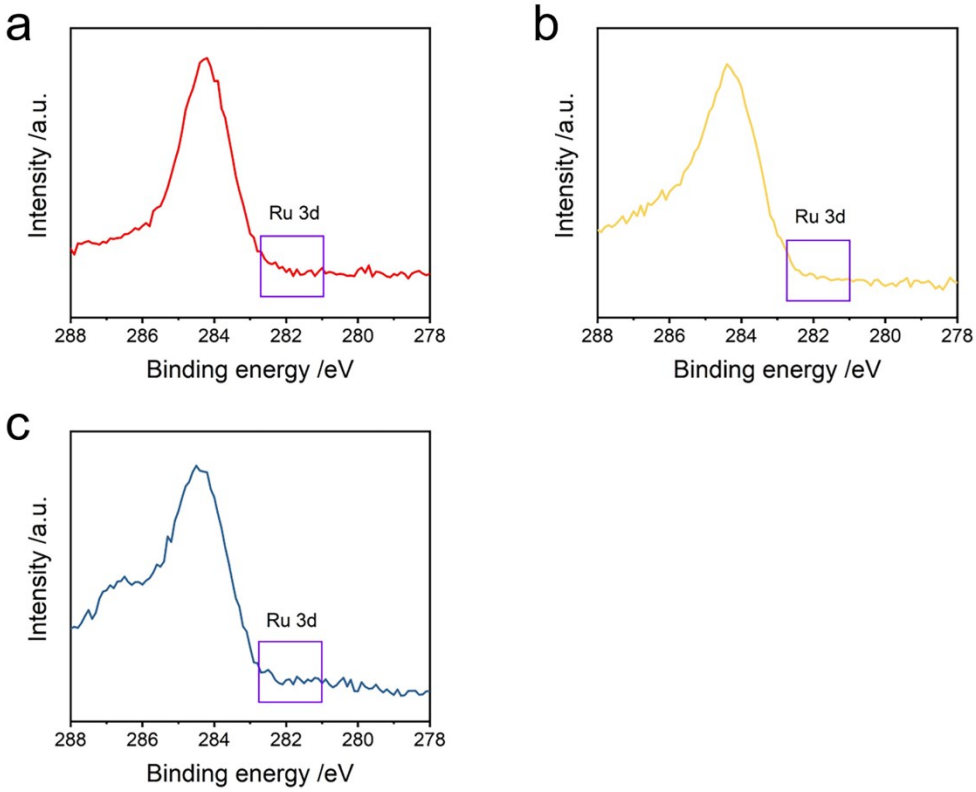

Fig. S2. XPS patterns of the Ru 3d of the as-prepared (a) Pt NWs (b) Ru/Pt NWs and (d) Ru@Pt NWs catalysts.

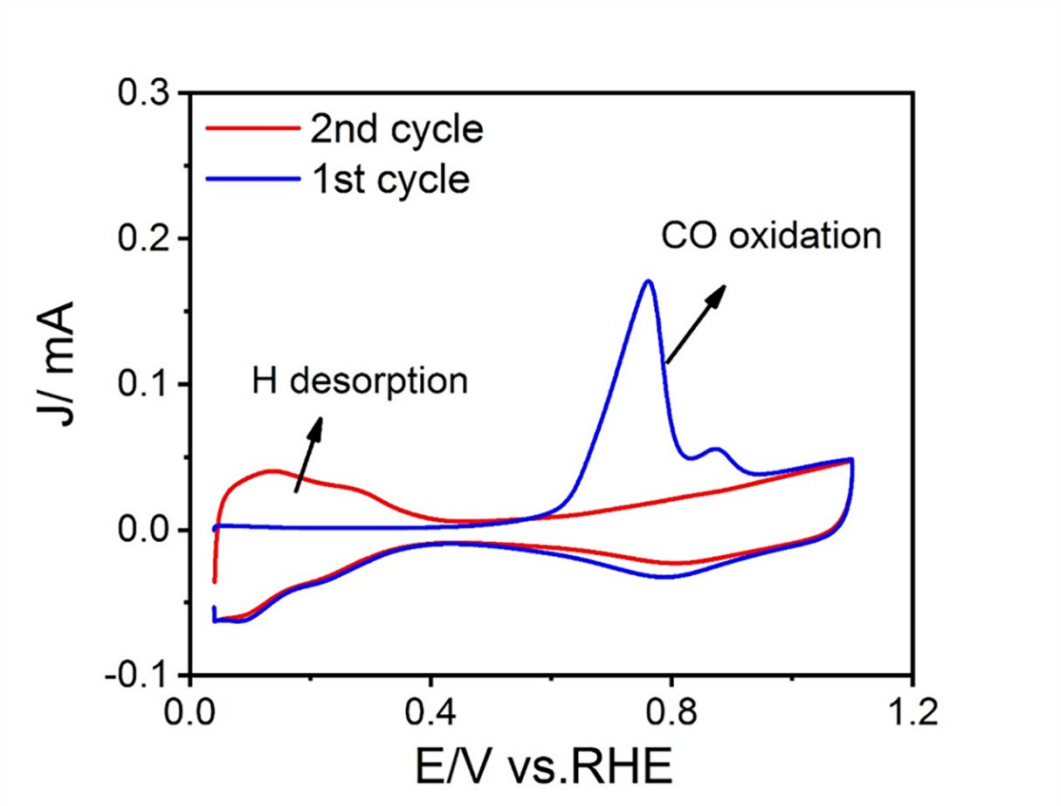

Fig. S3. Illustration of CO-stripping curves of Ru/Pt NWs.

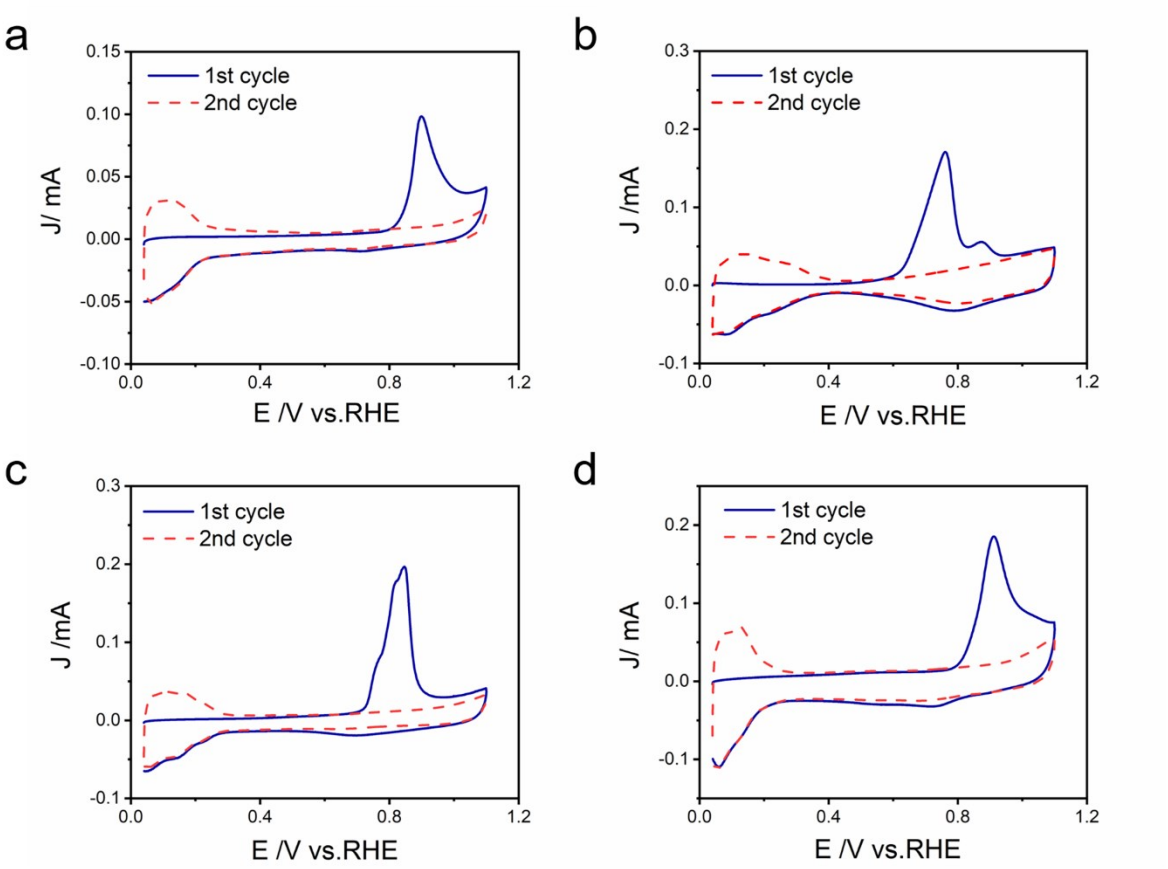

Fig S4. The whole CO stripping curves of (a) Pt NWs, (b) Ru/Pt NWs, (c) Ru@Pt NWs and (d) Pt/C modified electrodes.

Table S3. Summaries of $ECSA_H$,$ECSA_{CO}$ and their ratios; the two peak areas of CO oxidation and their ratios in 0.1 M $HClO_4$ solution at a sweep rate of 50 mV s^{-1}.

sanples	$ECSA_H$ (m^2 g^{-1}_{pt})	$ECSA_H$/ $ECSA_{CO}$	$ECSA_{CO}$ of first peak (m^2 g^{-1}_{pt})	$ECSA_{CO}$(m^2 g^{-1}_{pt})	First peak area/total peak area
Pt NWs	9.39	1.00: 1.08	-	10.14	-
Ru/Pt NWs	19.75	1.00: 0.99	18.64	19.55	95.37%
Ru@Pt NWs	13.54	1.00: 1.14	3.59	15.44	23.23%
Pt/C	23.93	1.00: 1.11	-	26.56	-
0.09%Ru/Pt NWs	17.47	1.00: 1.16	19.20	20.26	94.74%
1.9%Ru/Pt NWs	13.55	1.00: 1.09	14.24	14.76	96.49%

Table S4. Summaries of MOR activity of the prepare NWs and commercial Pt/C in 0.1 M $HClO_4$ +1 M CH_3OH solution at 30 °C.

Sample	Based on H_{upd}		Based on CO stripping
	Specific activity ($mA\ cm^{-2}$)	Mass activity ($mA\ mg^{-1}_{Pt}$)	Specific activity ($mA\ cm^{-22}$)
Pt NWs	1.94	219.51	1.80
Ru/Pt NWs	3.93	568.40	3.97
Ru@Pt NWs	2.58	292.89	0.77
Commercial Pt/C	1.68	280.00	1.51
0.09%Ru/Pt NWs	2.60	244.62	2.24
1.9%Ru/Pt NWs	3.25	337.44	2.98

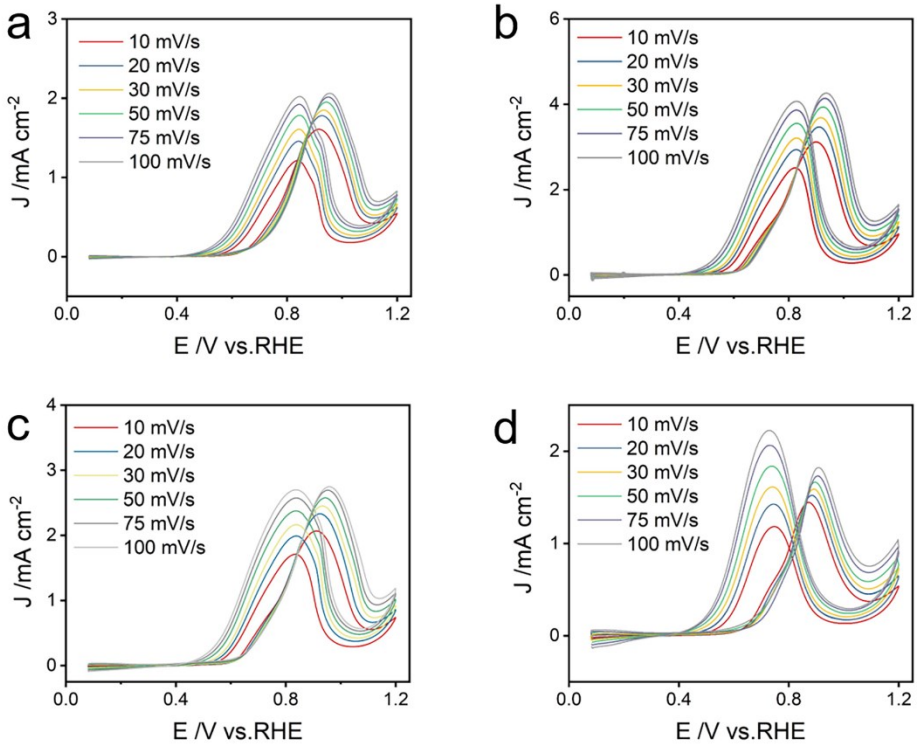

Fig. S5. CV plots of methanol electrooxidation on (a) Pt NWs, (b) Ru/Pt NWs, (c) Ru@Pt NWs and (d) Pt/C modified electrodes at different scan rates.

Table S5. The slope values of catalysts in this work

Sanples	Slope value	Pearson correlation coefficient
Pt NWs	0.063	0.96845
Ru/Pt NWs	0.1642	0.98223
Ru@Pt NWs	0.104	0.97599
Pt/C	0.054	0.99683
0.09%Ru/Pt NWs	0.1403	0.98153
1.9%Ru/Pt NWs	0.1144	0.99005

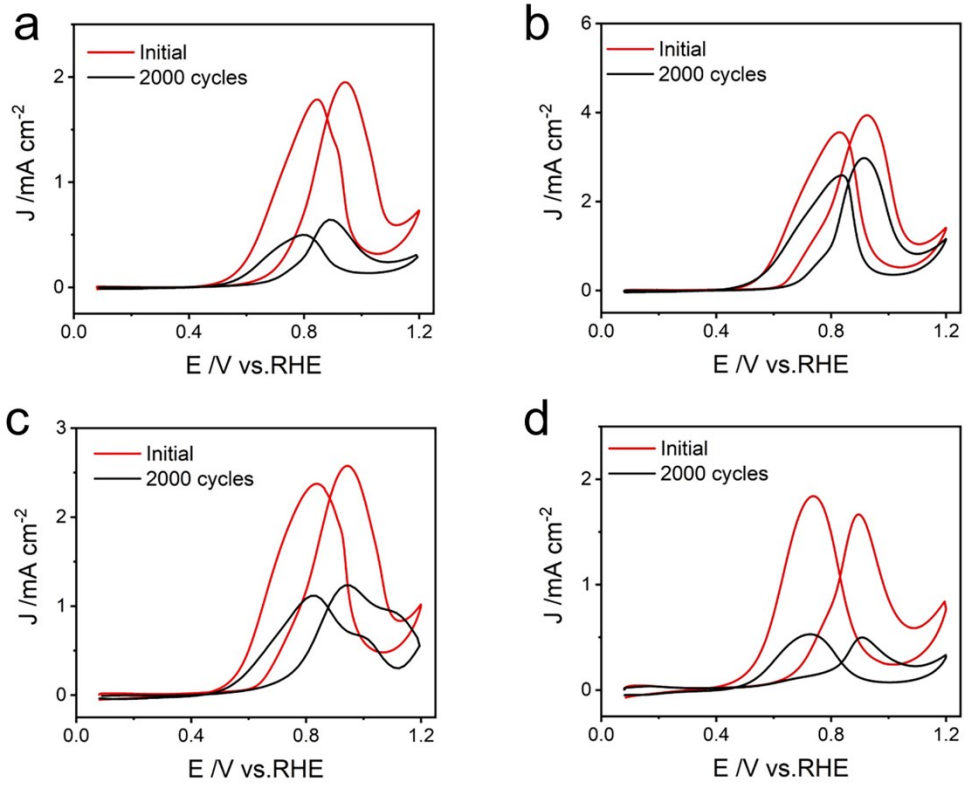

Fig. S6. The initial and after 2000 cycles of MOR for (a) Pt NWs, (b) Ru/Pt NWs, (c) Ru@Pt NWs and (d) Pt/C in 0.1M $HClO_4$ and 1 M methanol solution at a scan rate of 50 mV s^{-1}.

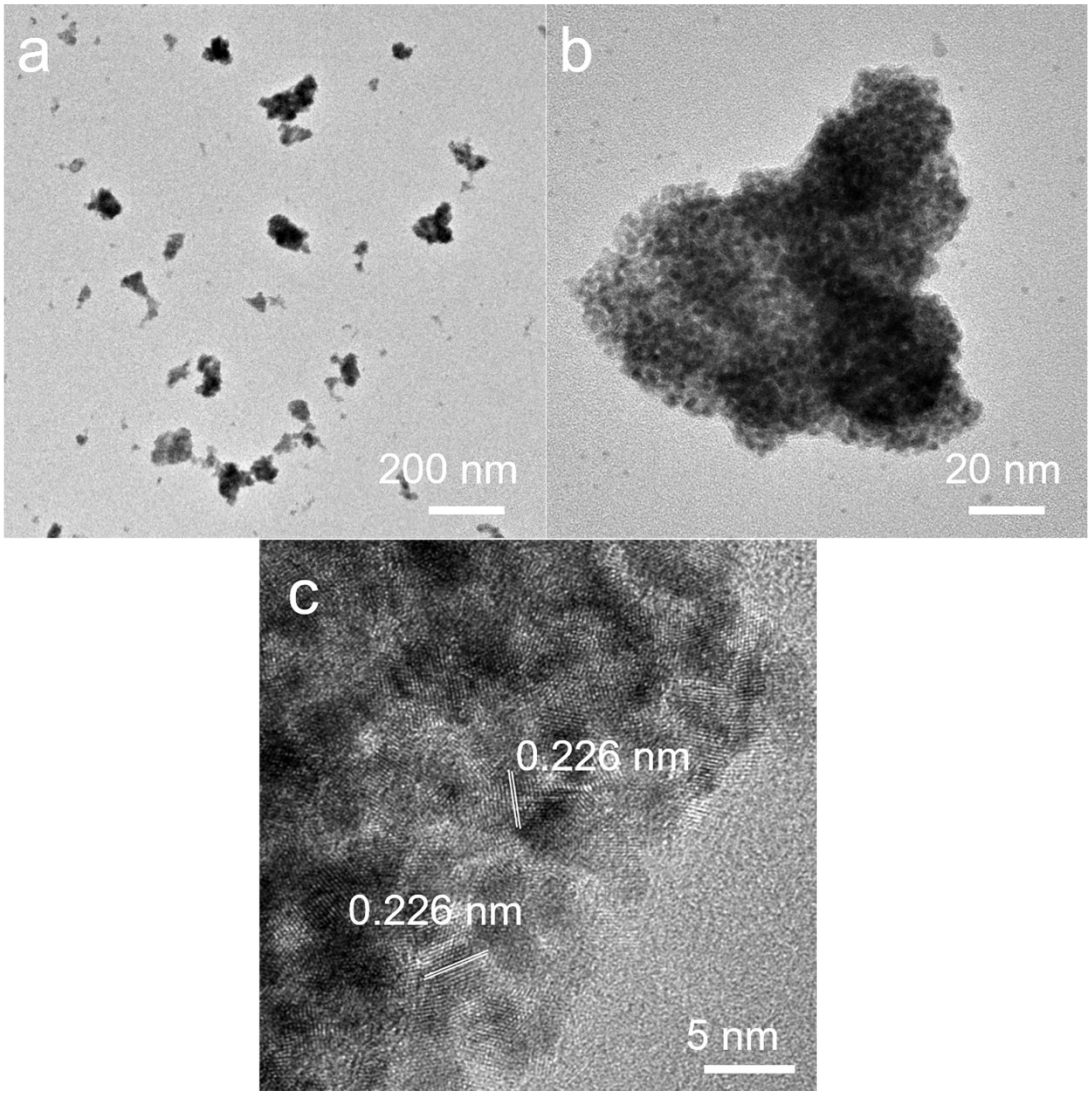

Fig. S7. TEM images of Pt_3Ru_1 clusters.

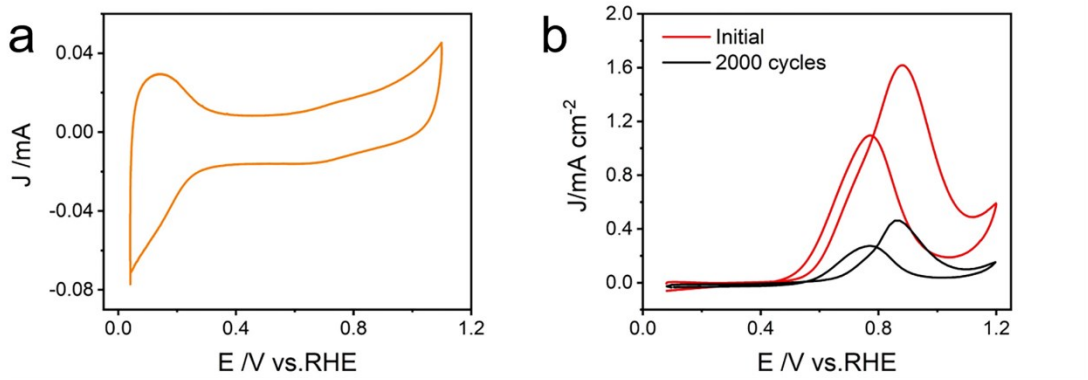

Fig. S8. A) CV curves, B) the initial and after 2000 cycles of MOR of Pt_3Ru_1 catalyst in 0.1 M $HClO_4$ and 1 M methanol solution at a sweep rate of 50 mV s^{-1}.

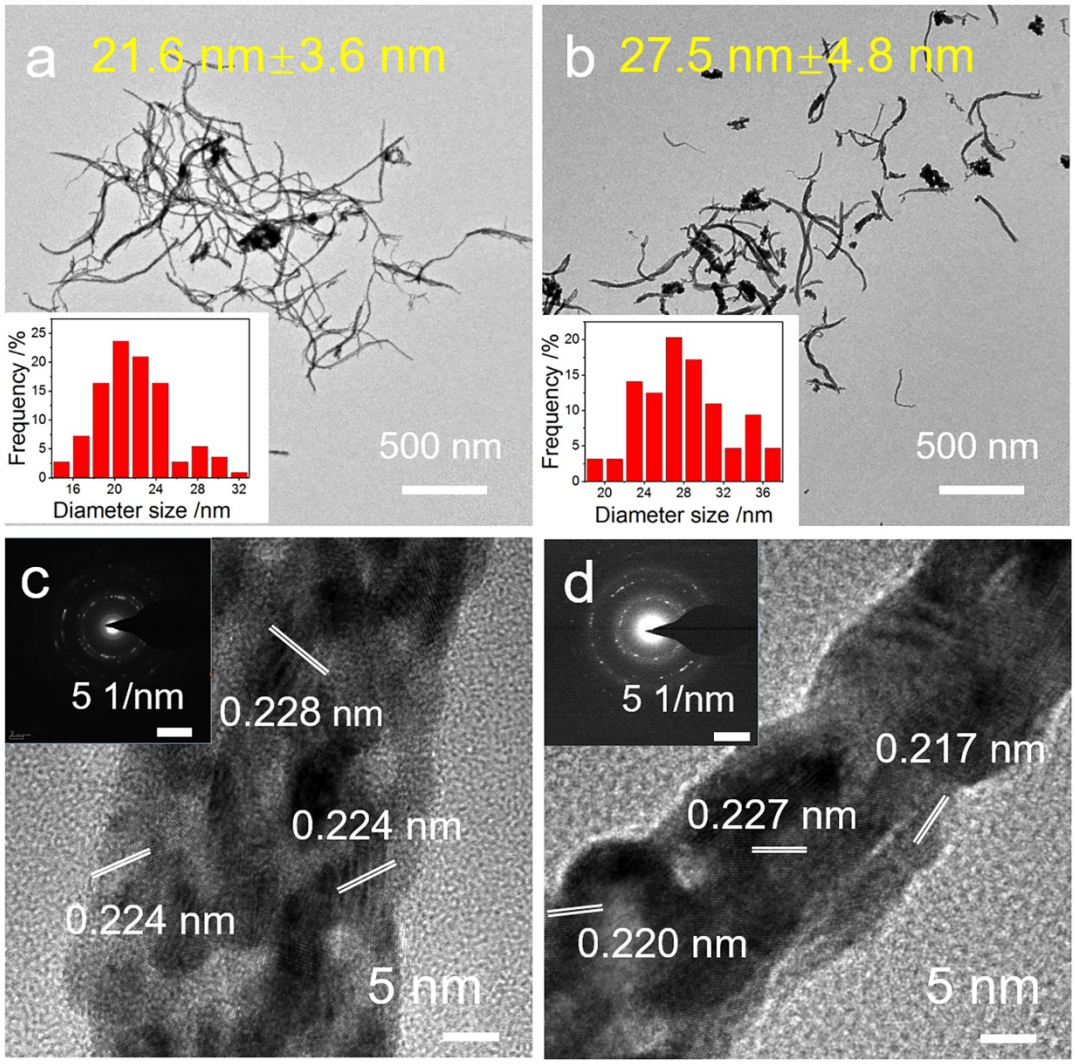

Fig. S9. (a) (b) TEM and (c) (d) HRTEM images of 0.09% Ru/Pt NWs and 1.9%Ru/Pt NWs.

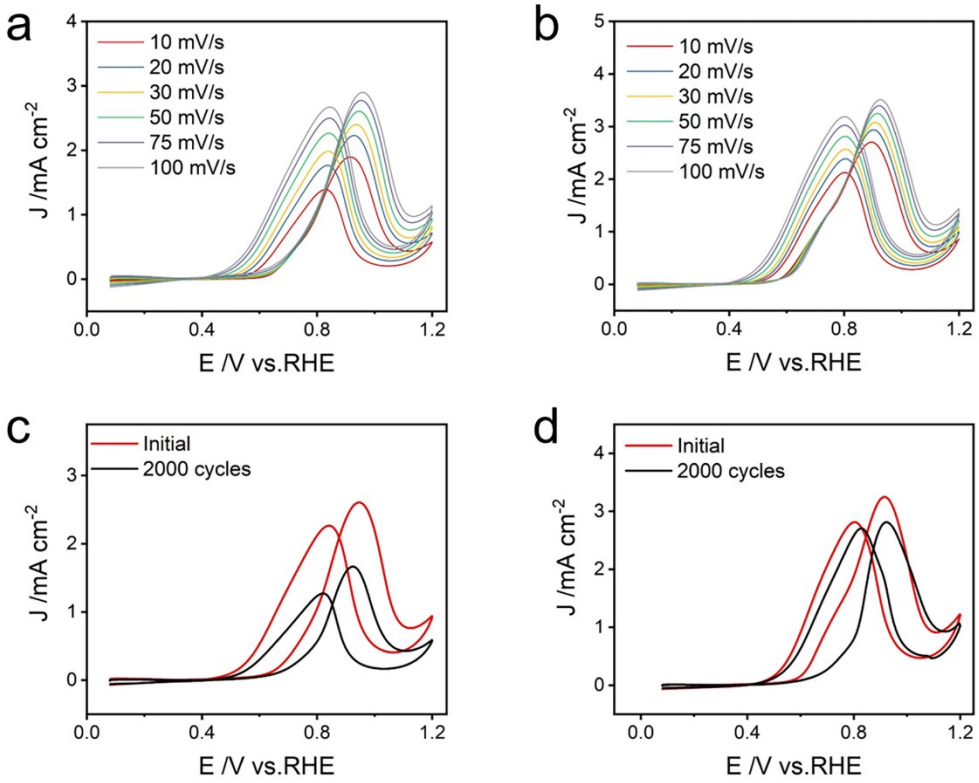

Fig. S10. (a-b) CV plots of methanol electrooxidation on (a) 0.09%Pt NWs and (b) 1.9%Ru/Pt NWs modified electrodes at different scan rates. (c-d) The initial and after 2000 cycles of MOR for (c) 0.09%Ru/Pt NWs and (d) 1.9%Ru/Pt NWs in 0.1M $HClO_4$ and 1 M methanol solution at a sweep rate of 50 mV s^{-1}.

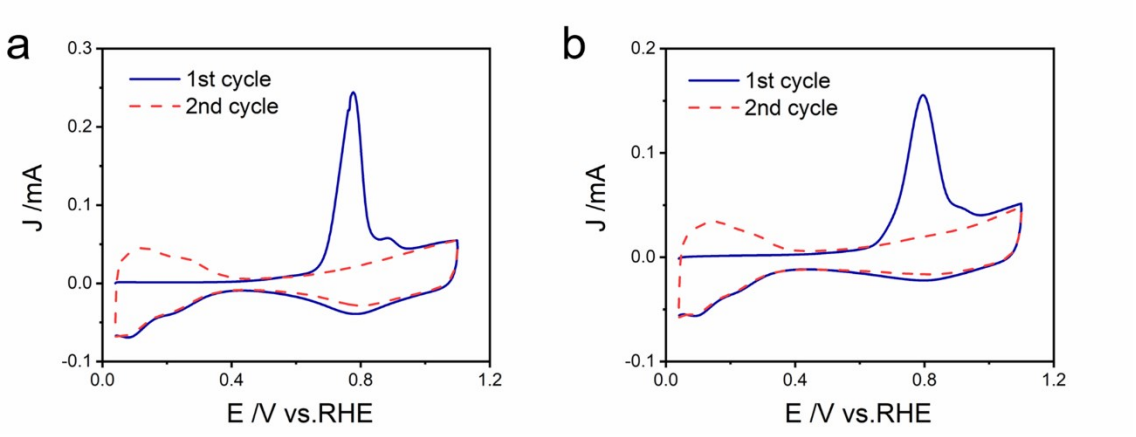

Fig S11. The whole CO stripping curves of (a) 0.09% Ru/Pt NWs and (b) 1.9% Ru/Pt NWs modified electrodes.