Electronic Supplementary Information

Ultra-low loading Pt atomic cluster electrode with Pt-O bond as an active site with the high hydrogen evolution reaction performance

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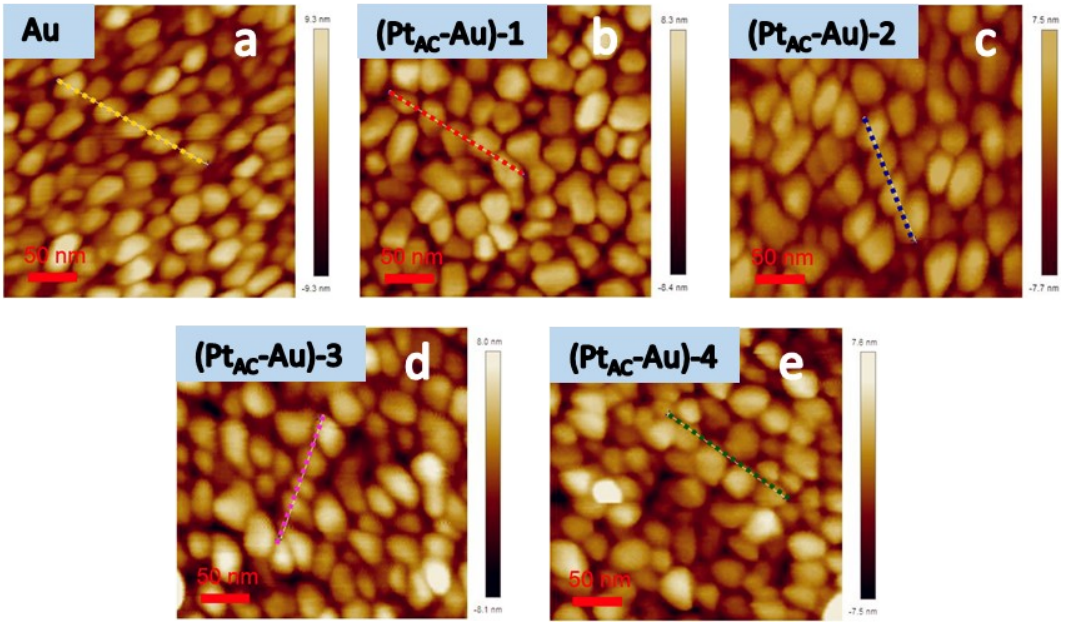

Figure S1 AFM images of Au and (Pt_{AC}-Au)-x (x=1, 2, 3, 4) with different Pt loading (Au (a), (Pt_{AC}-Au)-1 (b), (Pt_{AC}-Au)-2 (c), (Pt_{AC}-Au)-3 (d) and (Pt_{AC}-Au)-4 (e)).

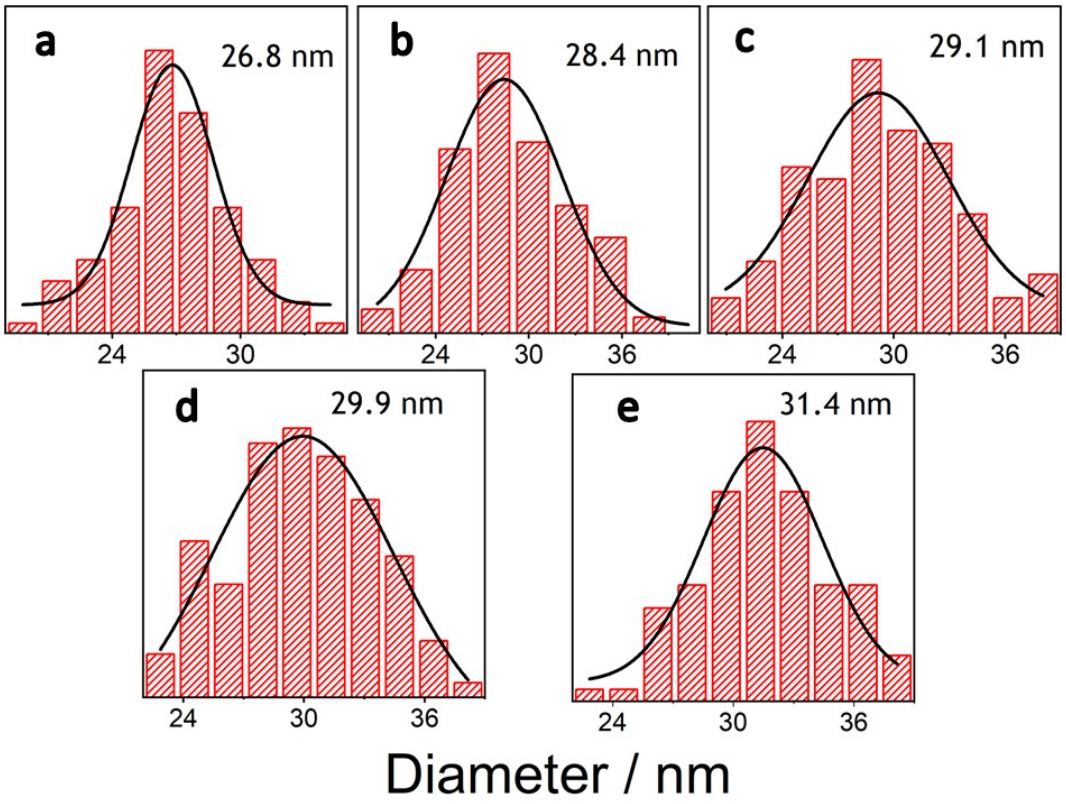

Figure S2 The particle sizes of Au and (Pt_{AC}-Au)-x (x=1, 2, 3, 4) with different Pt loading according to AFM image (Au (a), (Pt_{AC}-Au)-1 (b), (Pt_{AC}-Au)-2 (c), (Pt_{AC}-Au)-3 (d) and (Pt_{AC}-Au)-4 (e)).

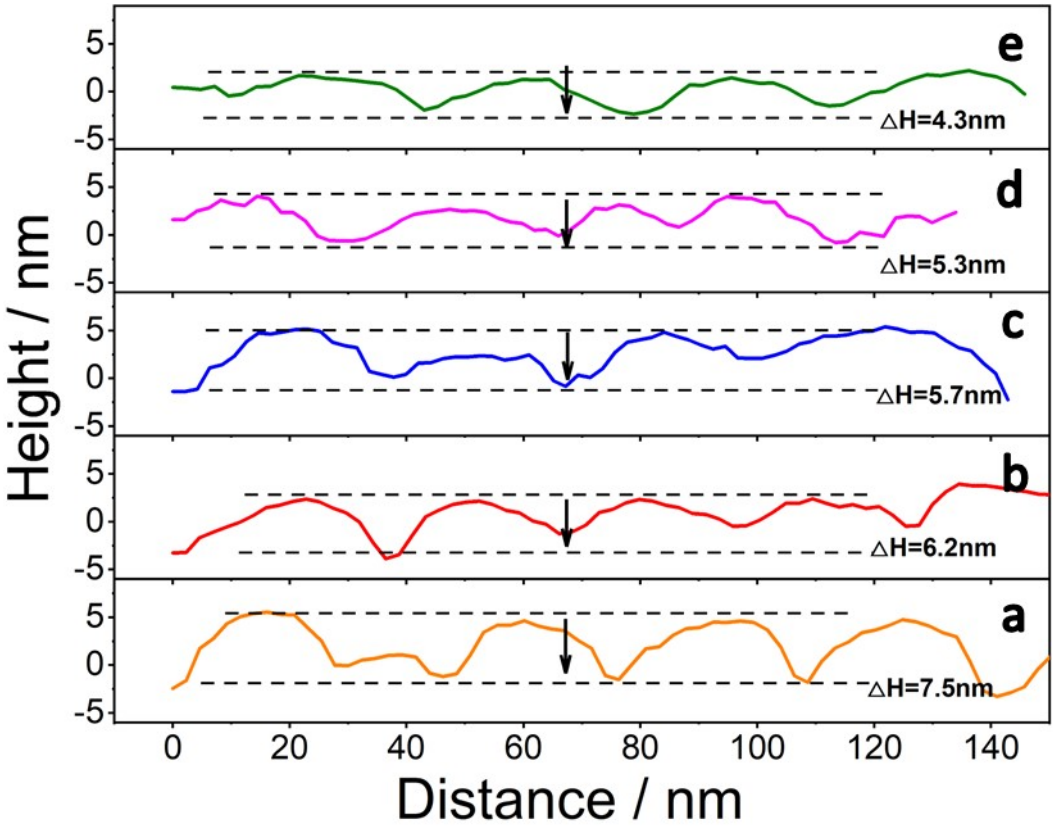

Figure S3 The height differences of Au and (Pt_{AC}-Au)-x (x=1, 2, 3, 4) with different Pt loading according to AFM image (Au (a), (Pt_{AC}-Au)-1 (b), (Pt_{AC}-Au)-2 (c), (Pt_{AC}-Au)-3 (d) and (Pt_{AC}-Au)-4 (e)).

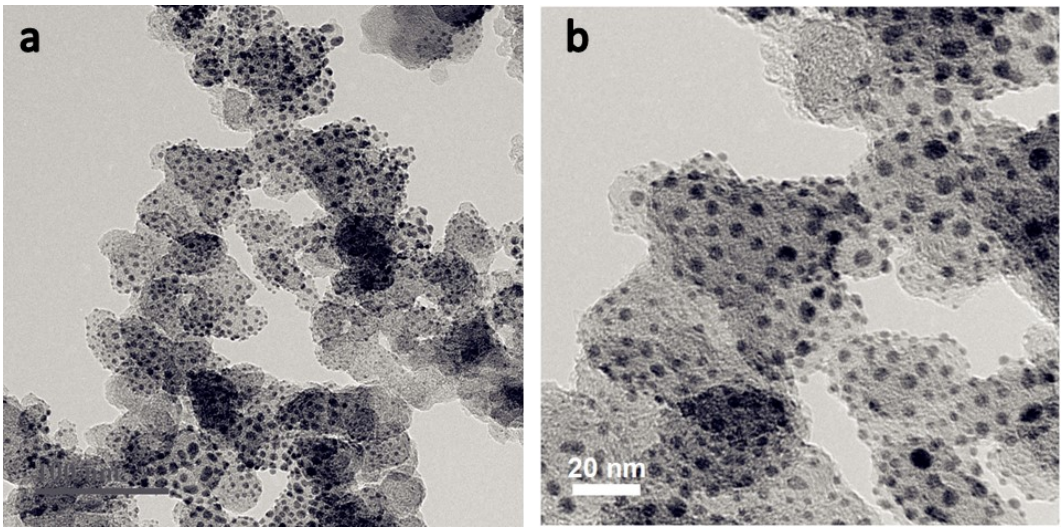

Figure S4 The TEM images of the (Pt_{AC}-Au)-1 electrode.

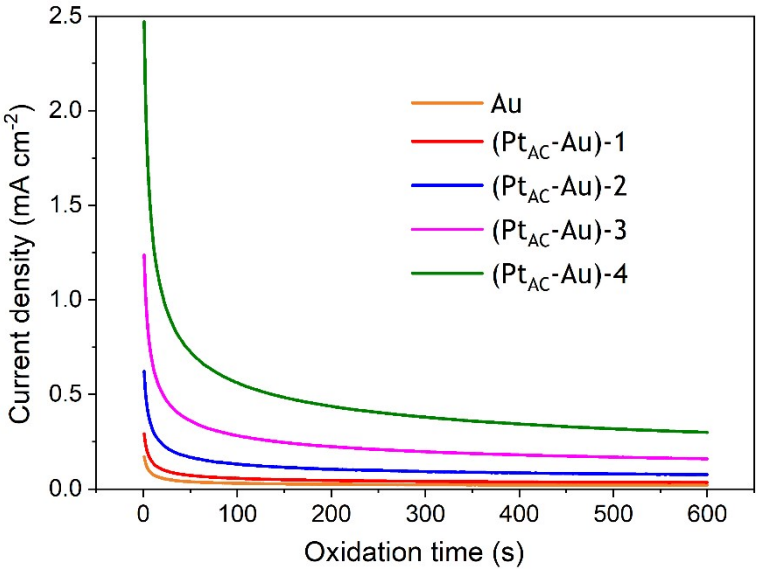

Figure S5 The anode oxidation curves of Au and (Pt_{AC}-Au)-x (x=1, 2, 3, 4) electrodes with different Pt loading at 1.7 V.

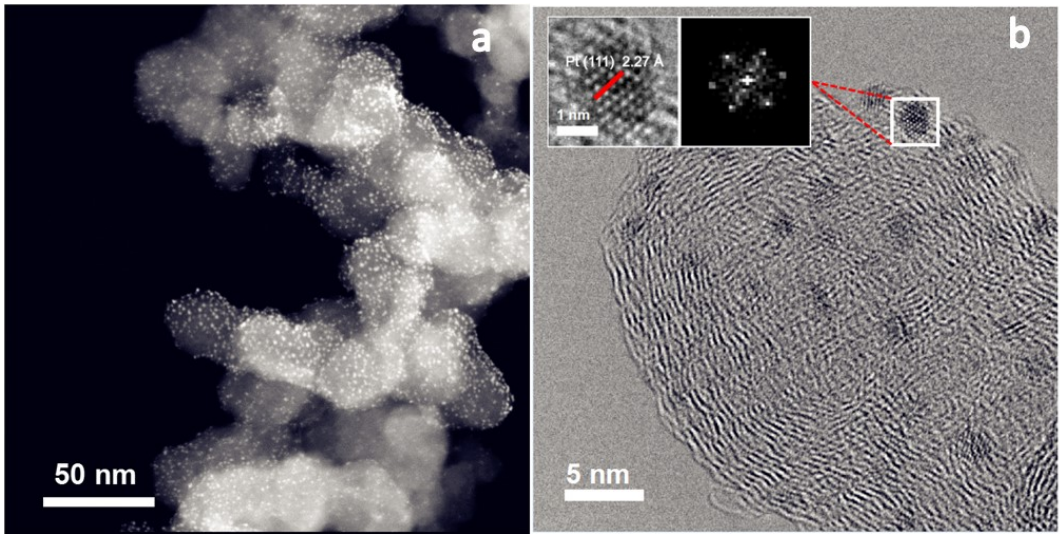

Figure S6 The HAADF-STEM (a) and HRTEM (b) of the Pt-1 electrode.

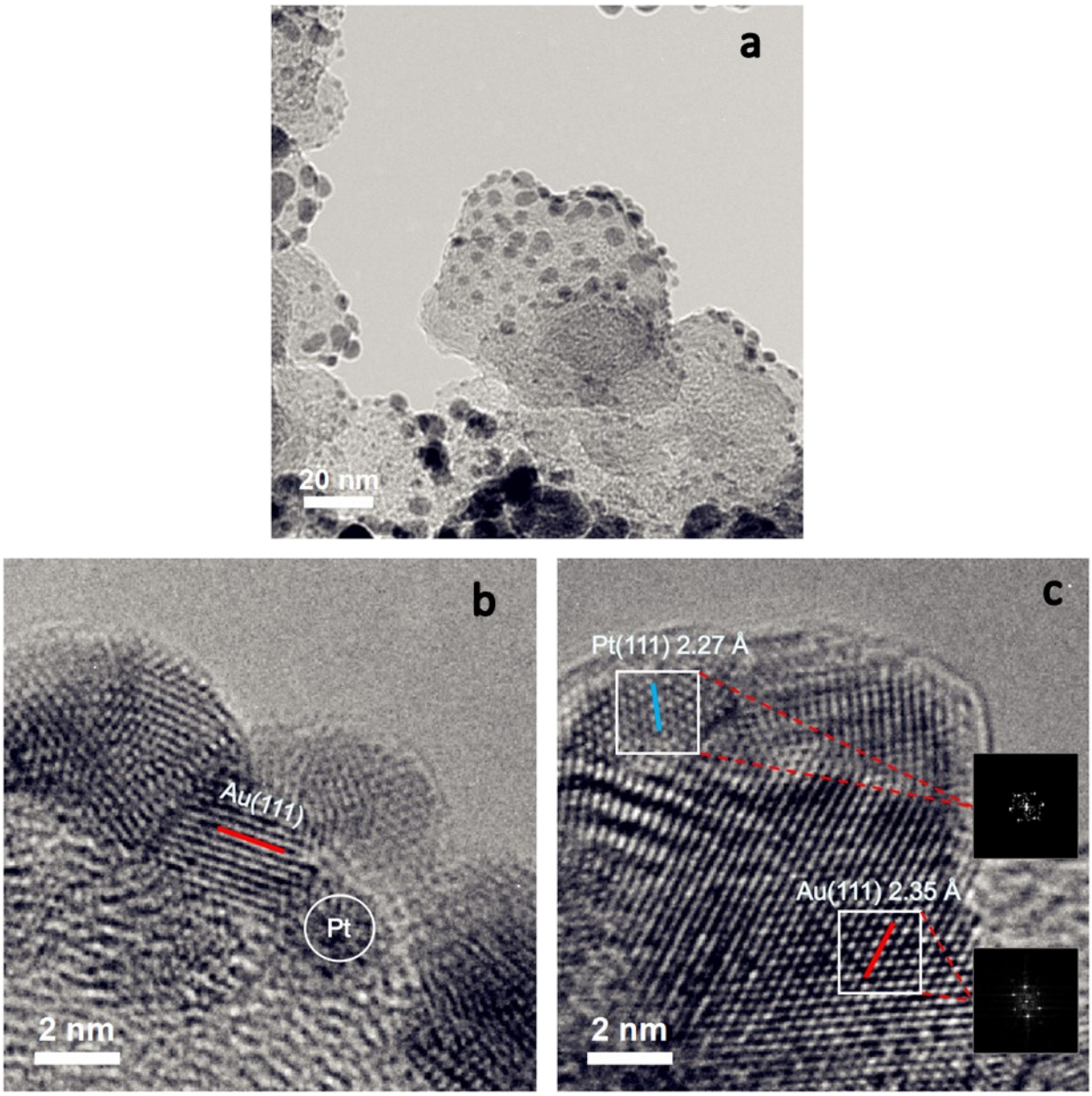

Figure S7 The TEM (a) and HRTEM (b, c) images of the (Pt_{AC}-Au)-4 electrode.

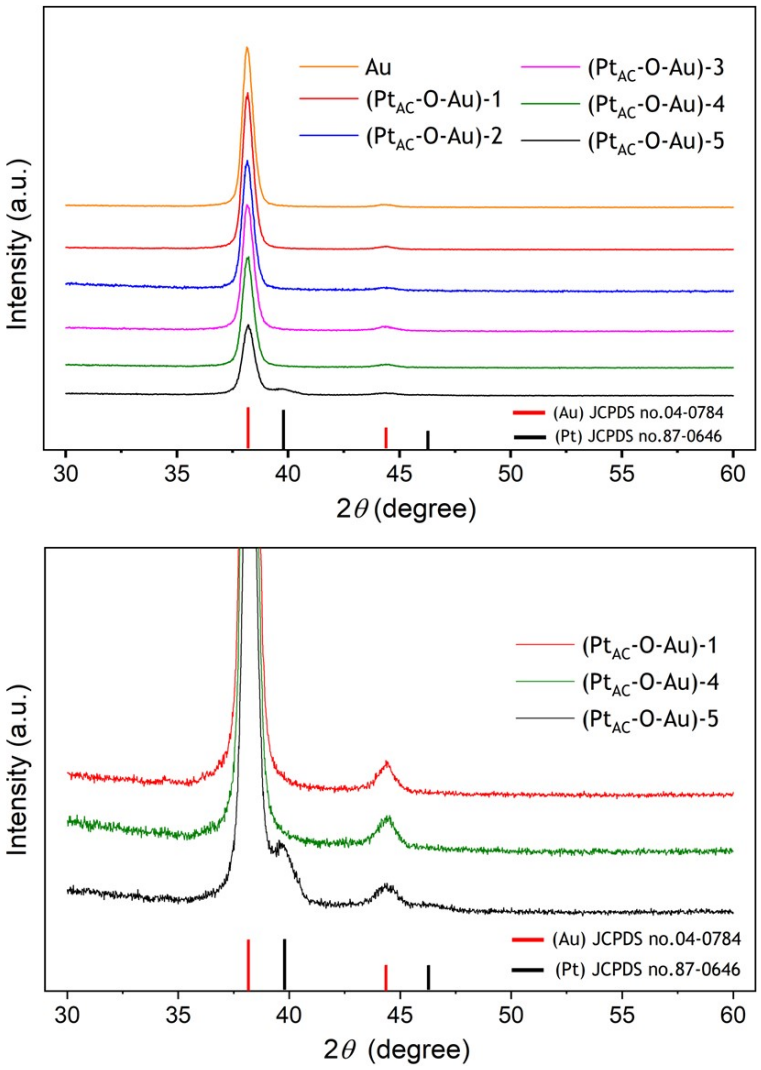

Figure S8 XRD diagrams of Au and (Pt_{AC}-O-Au)-x (x=1, 2, 3, 4, 5) with different Pt loading.

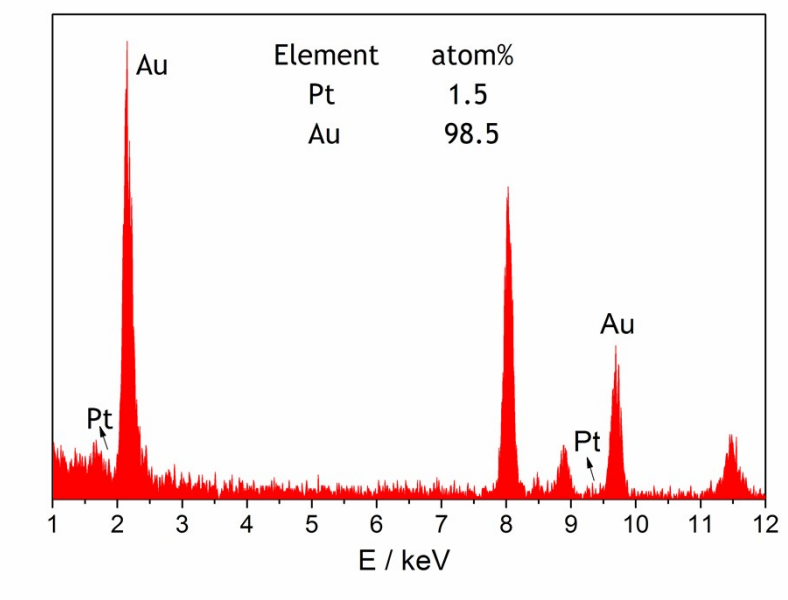

Figure S9 The EDS element analysis of (Pt_{AC}-Au)-1 electrode.

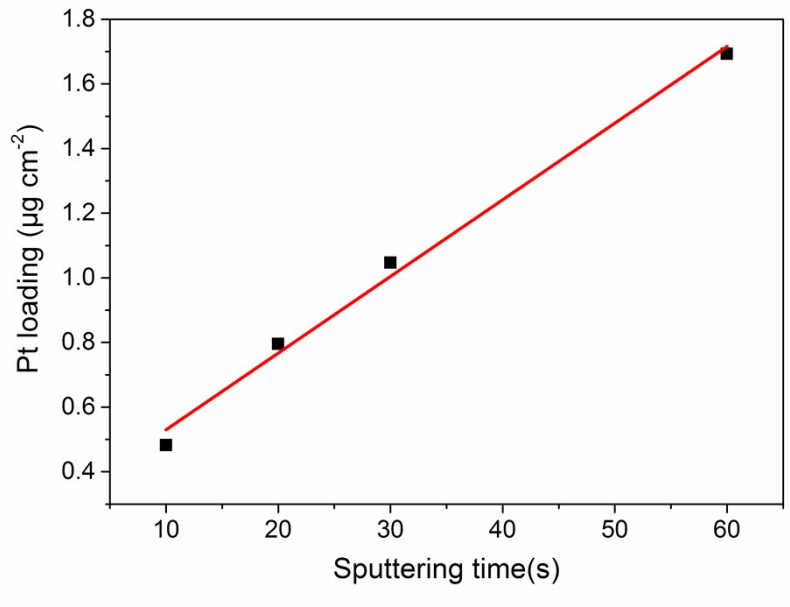

Figure S10 Relationship between the sputtering time and Pt loading

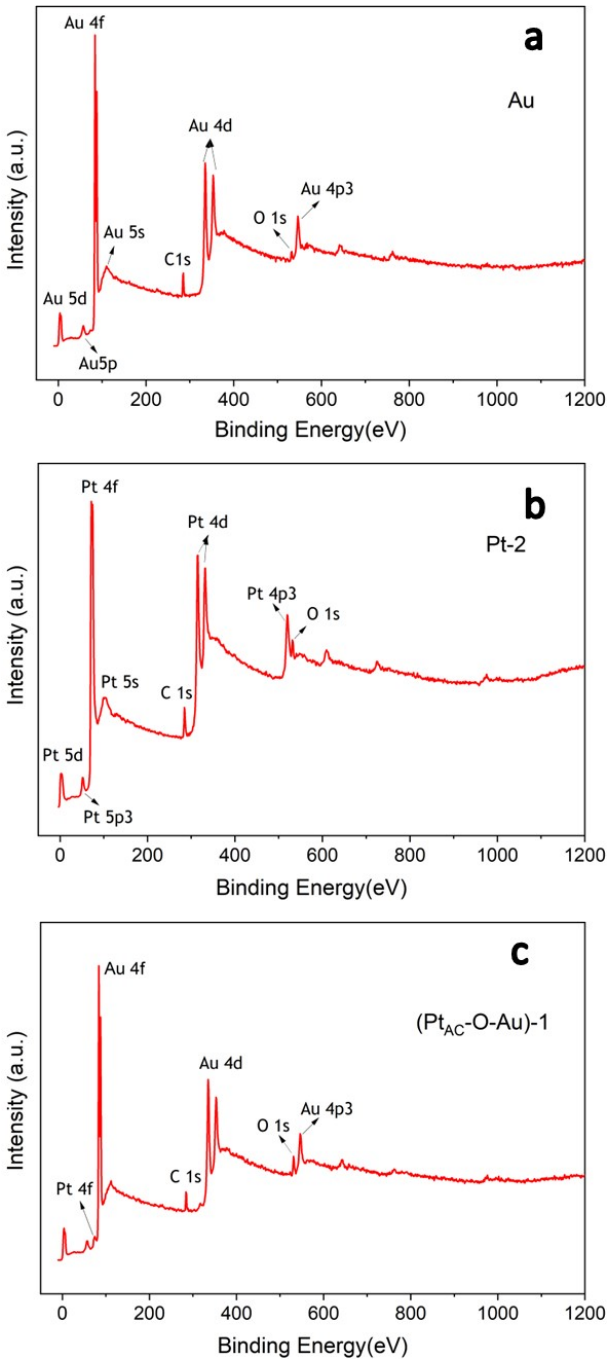

Figure S11 The survey XPS analysis of the Au (a), Pt-2 (b) and (Pt_{AC}-O-Au)-1 (c) electrodes.

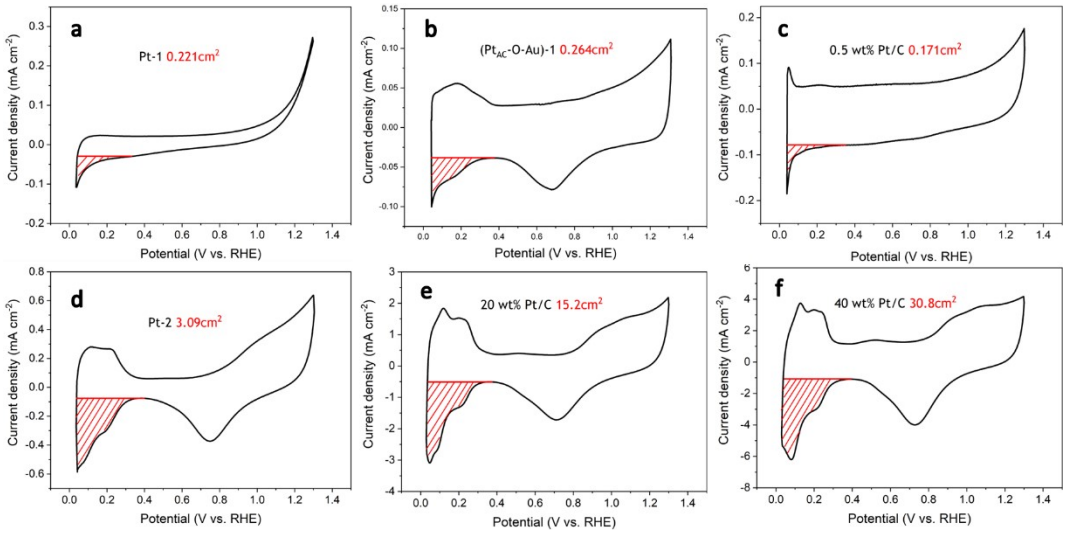

Figure S12 Cyclic voltammograms of Pt-1 (a), (Pt_{AC}-O-Au)-1 (b), 0.5 wt% Pt/C (c), Pt-2 (d), 40 wt% Pt/C (e) and 20 wt% Pt/C (f).

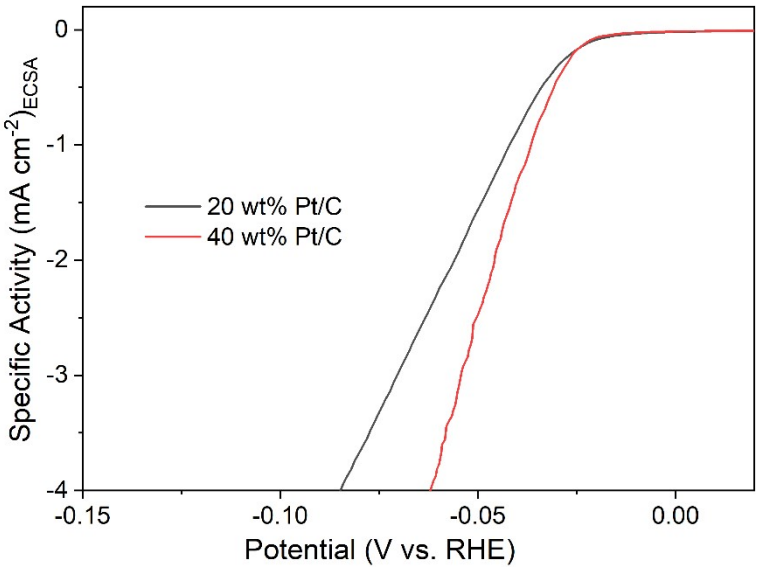

Figure S13 The specific activities (SAs) of 20 wt% Pt/C and 40 wt% Pt/C.

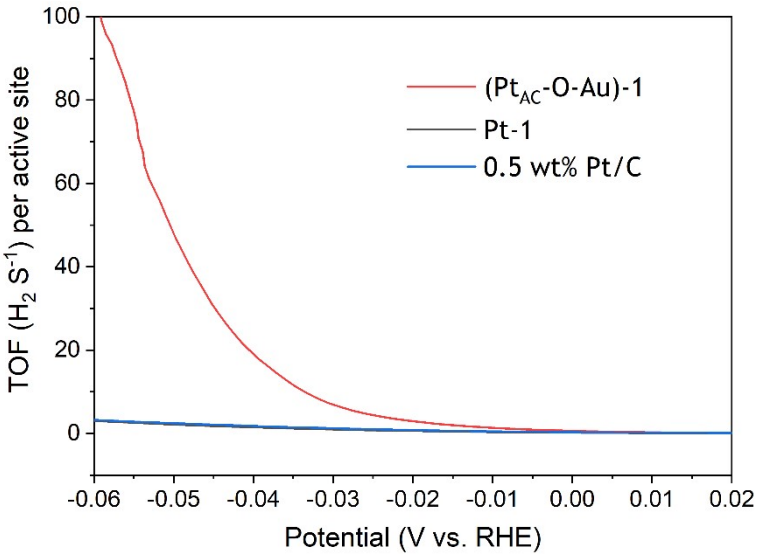

Figure S14 The turnover frequency (TOF) of (Pt_{AC}-O-Au)-1, Pt-1 and 0.5 wt% Pt/C.

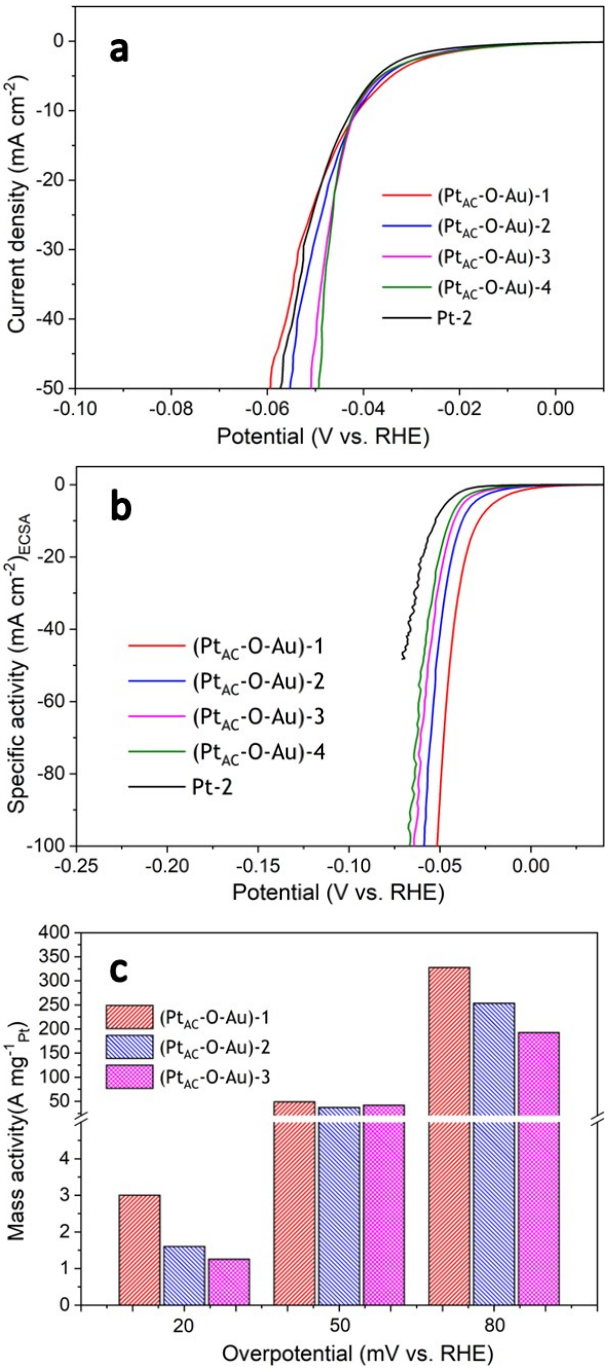

Figure S15 HER apparent activity (a), specific activity (b) and mass specific activity (c) of (Pt_{AC}-O-Au)-x (x=1, 2, 3, 4) with different Pt loading.

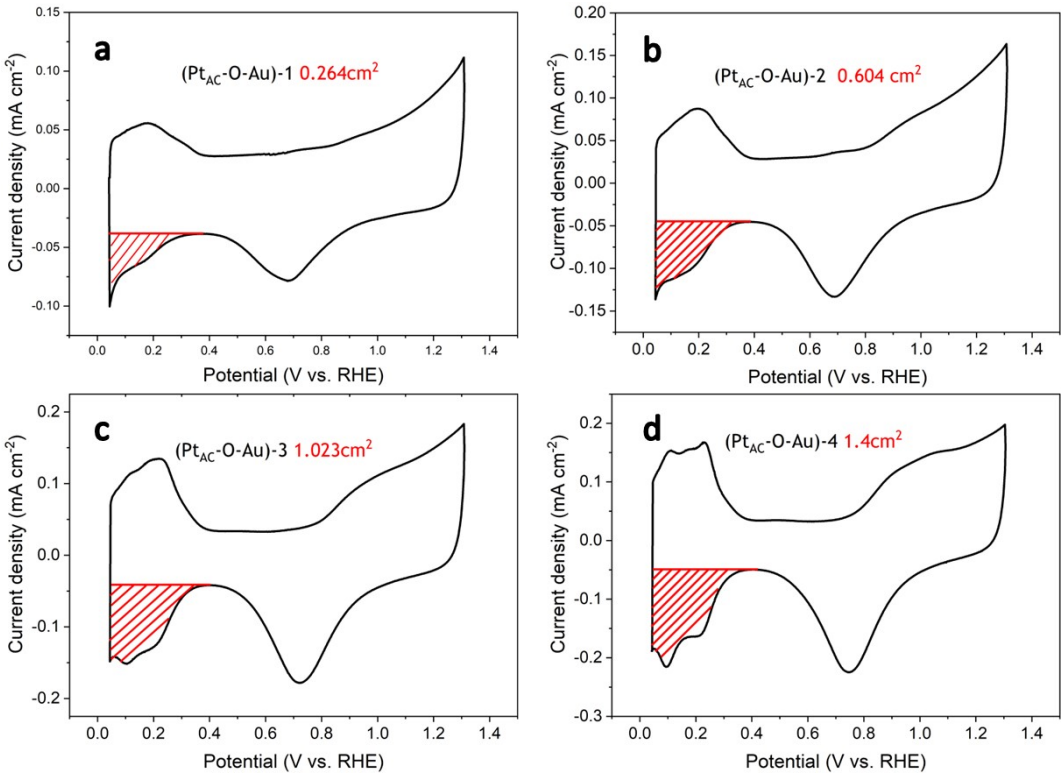

Figure S16 Cyclic voltammograms of (Pt$_{AC}$-O-Au)-1 (a), (Pt$_{AC}$-O-Au)-2 (b), (Pt$_{AC}$-O-Au)-3 (c) and (Pt$_{AC}$-O-Au)-4 (d).

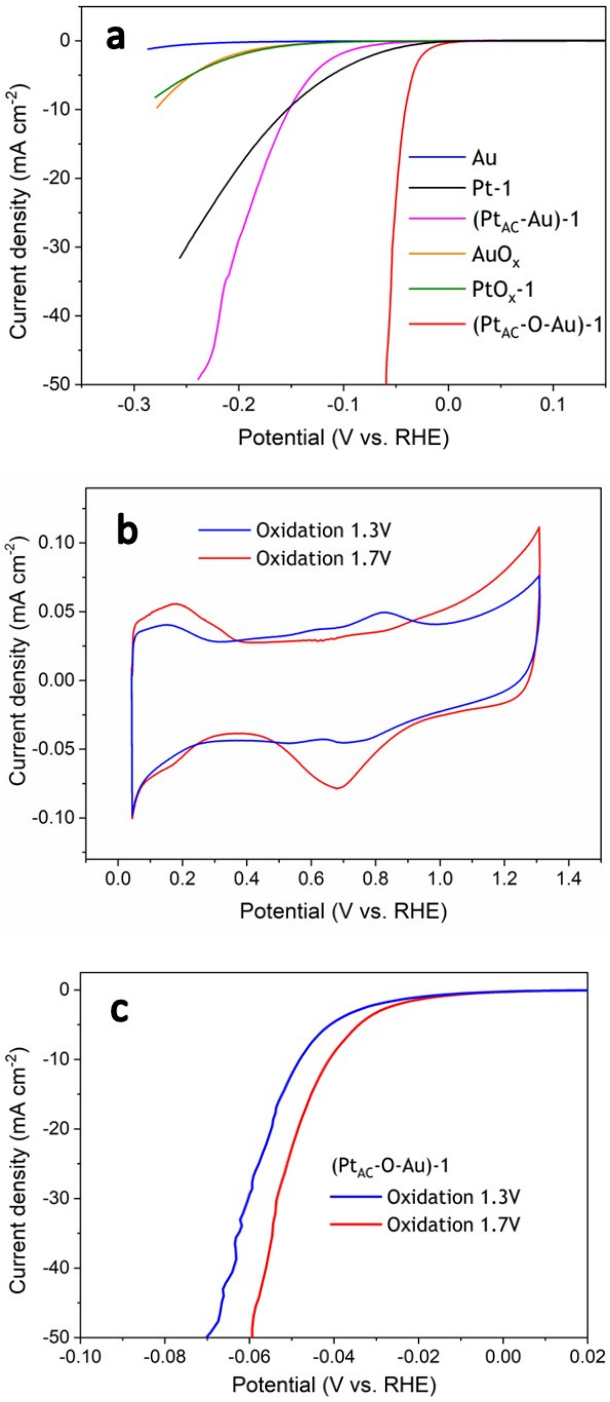

Figure S17 The apparent activity of (Pt_{AC}-O-Au)-1, (Pt_{AC}-Au)-1, PtO_x-1, Pt-1, AuO_x and Au (a). Cyclic voltammograms (b) and linear sweep voltammetry curves (c) of (Pt_{AC}-O-Au)-1 at anodic oxidation potentials of 1.3 and 1.7 V.

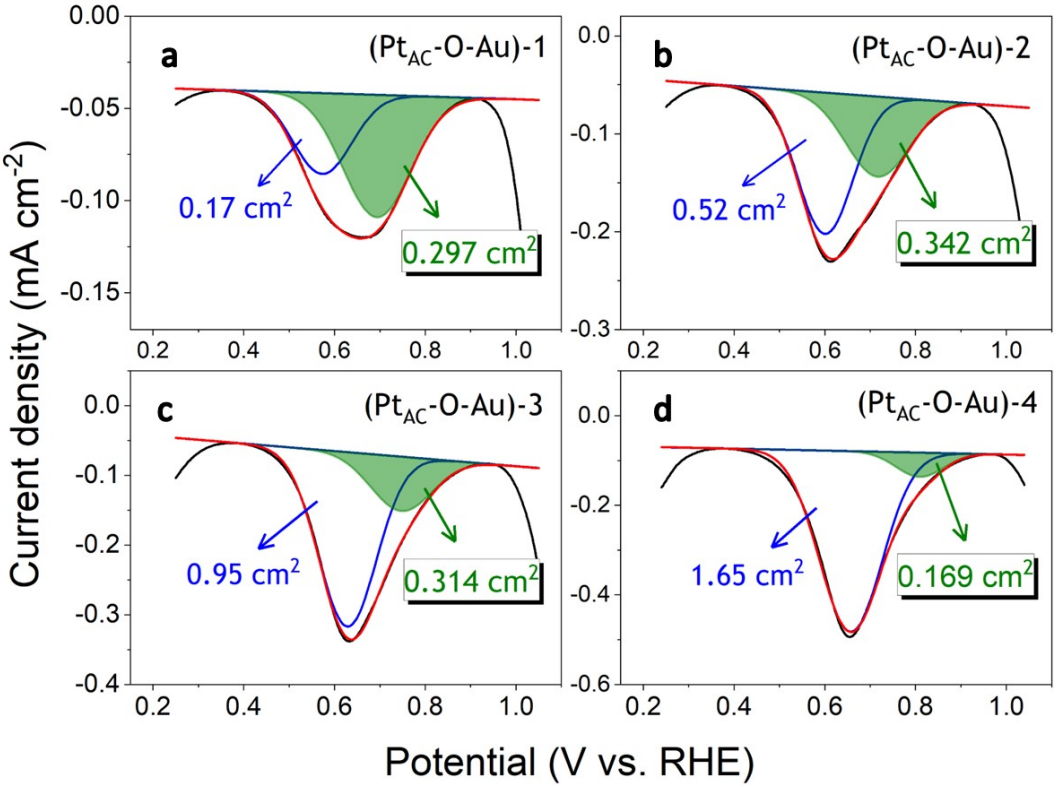

Figure S18 Peak fitting of Au-O-Pt and PtO_x reduction peaks of (Pt_{AC}-O-Au)-1 (a), (Pt_{AC}-O-Au)-2 (b), (Pt_{AC}-O-Au)-3 (c) and (Pt_{AC}-O-Au)-4 (d).

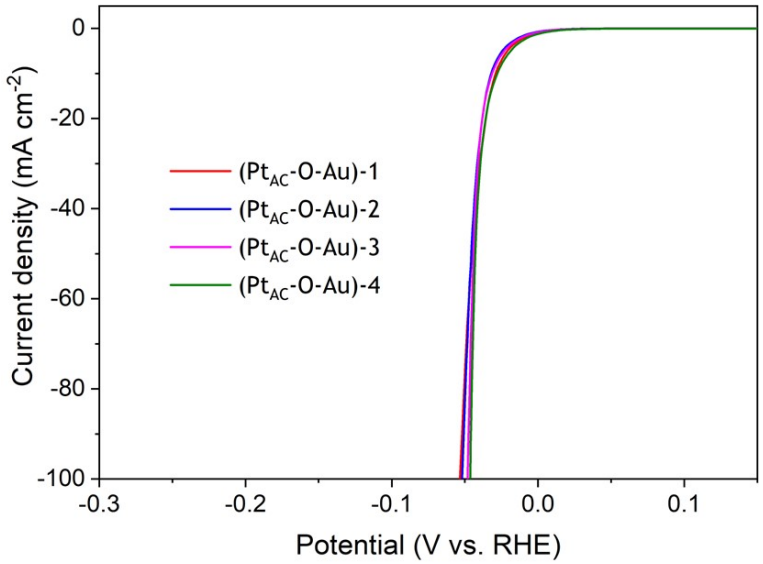

Figure S19 The specific activity of (Pt_{AC}-O-Au)-x (x=1, 2, 3, 4) with different Pt loading (The calculation of ECSA is based on the reduction peak area of Au-O-Pt at 0.72V).

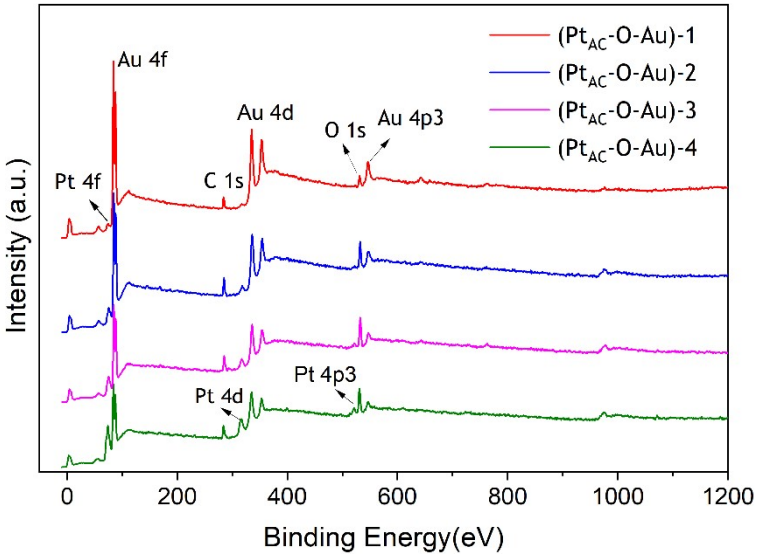

Figure S20 The survey XPS analysis of the (Pt_{AC}-Au)-x (x=1, 2, 3, 4) electrodes with different Pt loading.

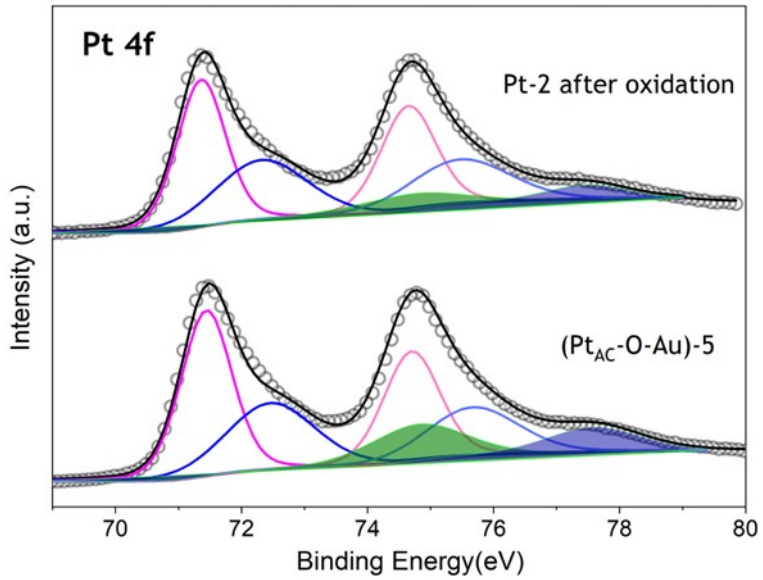

Figure S21 The XPS core-level spectra of Pt 4f obtained from the (Pt_{AC}-O-Au)-5 and Pt-2 (after oxidation) electrodes.

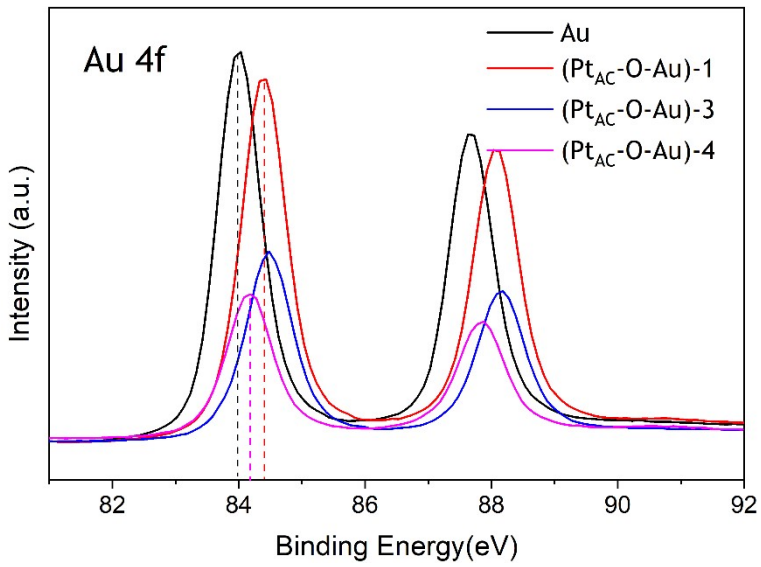

Figure S22 The XPS core-level spectra of Au 4f obtained from Au and (Pt_{AC}-Au)-x (x=1, 3, 4) electrodes with different Pt loading.

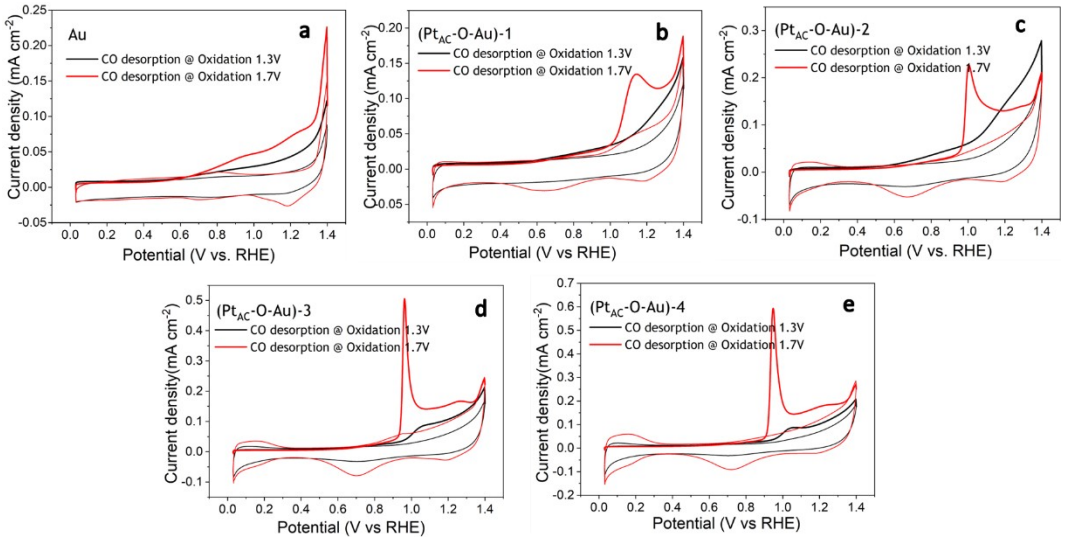

Figure S23 The CO adsorption-stripping curves of (Pt_{AC}-Au)-x (x=1, 2, 3, 4) electrodes with anodic oxidation potential at 1.3 V and 1.7 V (Au (a), (Pt_{AC}-Au)-1 (b), (Pt_{AC}-Au)-2 (c), (Pt_{AC}-Au)-3 (d) and (Pt_{AC}-Au)-4 (e)).

Supplementary Tables

Table S1 Pt loading with different sputtering times using ICP-OES

Sputtering time(s)	Electrode	Pt(μg cm^{-2})	Au(μg cm^{-2})	Pt(atom%)
10	(Pt_{AC}-O-Au)-1	0.482	100	0.484
20	(Pt_{AC}-O-Au)-2	0.795	104	0.766
30	(Pt_{AC}-O-Au)-3	1.047	109	0.961
60	(Pt_{AC}-O-Au)-4	1.693	101	1.664
600	(Pt_{AC}-O-Au)-5	17.58	105	14.44

Table S2 Pt loading with different sputtering times using XPS

Sputtering time(s)	Electrode	Pt(atom%)	Au(atom%)
	Au		100
10	(Pt_{AC}-O-Au)-1	4.79	95.21
20	(Pt_{AC}-O-Au)-2	15.3	84.7
30	(Pt_{AC}-O-Au)-3	23.9	76.1
60	(Pt_{AC}-O-Au)-4	42.4	57.6
600	(Pt_{AC}-O-Au)-5	99	1

Table S3 The Pt loading capacity, apparent activity and mass specific activity of different low Pt loading electrocatalysts in the references and this work.

Electrodes	Loading ($\mu g_{Pt}\ cm^{-2}$)	η at 10 mA cm^{-2} (mV)	Mass activity (A mg^{-1})	Tafel slope (mv dec^{-1})	Ref
Pt/VS_2/CP	379.2	77	22.88 @ 200mV	39.46	1
Pt/Ni-Mo-N-O	243.75	89.5@100	10.05 @ 134mV	31.5	2
Pt-a-MoS3 NDs	84.99	11.5	3.23 @ 20mV	25.4	3
Pt SASs/AG	31.1	12	22.4 @ 50mV	29.33	4
Pt/WO_3-600	29.94	8	7.015 @ 50mV	35	5
Pt_{doped}@WC_x	22.9	2.4	14.28 @ 100mV	20	6
PtW NP s/C[a]	20.4	19.4	0.566 @ 20mV	27.8	7
$Pt_{0.04}$/Ni-DA	17.72	19	2.13 @ 50mV	34	8
Pt/def-WO_3@CFC	15.9	42	0.764 @ 50mV	61	9
Pt_3Ni_2 NWs-S/C	15.0	~23	-----	-----	10
Pt@MoS_2/NiS_2	~13.68	34	-----	40	11
MXene/B-Pt	13.4	14	-----	78.6	12
$Mo_2TiC_2T_x$-Pt_{SA}	~12	30	8.3 @ 77mV	30	13
Pt-MoO_2@PC	11.6	20	11.34 @ 50mV	22	14
Pt/TiO_2-O_V	10.45	18	14.82 @ 50mV	12	15
Pt/MOF-C	10.191	28	0.97 @ 50mV	24.4	16
Pt@VNC	9.802	5	-----	21	17
Pt_1Ru_1/NMHCS-A	9.58	22	3.49 @ 50mV	38	18
CDs/Pt-PANI	8.1	30	1.22 @ 30mV	41.7	19
Pt_5/HMCS[a]	7.6	20.7	12.8 @ 30 mV	28.3	20
Pt_1/N-C	6.25	19	-----	14.2	21
Pt_{at}–CoP MNSs/CFC	5.89	13	-----	30.28	22
Pt@mh-3D MXene[a]	4.8	12	19.45 @ 100mV	24.2	23
Pt-GDY-2	4.65	~ 66	23.64 @ 100mV	46.6	24
Pt-HNCNT	~3.8	15	20.4 @ 50mV	29.1	25
0.66% Pt-WC/CNT	3.4	42	8.9 @ 50mV	-----	26
PtNC/S-C	2.55	11	26.1 @ 20mV	24	27
$Ti_3C_2T_x$-Pt_{SA}	2.38	38	23.21 @ 50mV	45	28

Pt Cs/MoO_2 NSs-L	1.79	47	7.43 @ 50mV	32.6	29
AL-Pt/Pd_3Pb[a]	~1.6	13.8	7.834 @ 50mV	18	30
CNT/Pt@CdSe-OCPs	~1.58	-----	166.2 @ 150mV	61.3	31
Pt_C(250)	1.41	37.4	107.7 @ 50mV	30	32
Pt-GT-1	1.4	15	-----	24	33
Pt-Ru dimer	1.38	50	23.1 @ 50mV	28.9	34
F-SnO_2@Pt	1.2	42	≈10 @ 50mV	34	35
CoPt-Pt_{SA}/NDPCF	1.18	31	74.31 @ 50mV	43.65	36
Pt-Ti_vC	1	24.9	49.69 @ 50mV	22.3	37
Pt/MPNC	0.9	18.6±1.6	56±3 @ 50mV	-----	38
Pt SA/m-WO_{3-x}	0.86	47	12.8 @ 50mV	45	39
Pt-SAs/CoNC	0.45	57	18.8 @ 50mV	64.5	40
Pt-SAs/WS_2	0.415	32	54 @ 100 mV	28	41
PtO_x/TiO_2	~0.21	~110	8.68 @ 50mV	40	42
Pt/TiB_xO_y	0.191	-----	37.8 @ 50mV	32	43
(Pt_{AC}-O-Au)-1	0.48	41	3.02 @ 20mV 49.2 @ 50mV 329 @ 80mV	28.6	This work

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