Supporting Information

The Structure-dependent Enhancement of Oxygen Reduction Reaction Performance for Co-based low Pt catalysts through Au Addition

Zi-Jun Lin [a], Tsung-Fu Chou[b], Chen-Wei Liu [c],Po-Hsiang Huang [a], Yao-Zhang Guo[a], Jeng-Han Wang[b,*] and Kuan-Wen Wang [a,*]

[a] Institute of Materials Science and Engineering, National Central University, Taoyuan 320, Taiwan

[b] Department of Chemistry, National Taiwan Normal University, Taipei 116, Taiwan.

[c] Green Energy and Environment Research Laboratories, Industrial Technology Research Institute, Hsinchu 310, Taiwan

*To whom correspondence should be addressed,

E-mail: kuanwen.wang@gmail.com

E-mail: jenghan@ntnu.edu.tw.

Table S1. Computed E_{ads}[a] (eV) of H*, O*, OH*, O_2*, OOH* and H_2O* on CoPt/C, CoPtAu-1/C and CoPtAu-4/C, in comparison with Pt.

	Co	CoPt/C	CoPtAu-1/C	CoPtAu-4/C	Pt[b]
H*	-2.85	-2.63	-2.67	-2.41	-2.78
O*	-5.90	-5.15	-5.28	-4.46	-4.52
OH*	-3.62	-2.89	-2.87	-2.38	-2.46
O_2*	-1.68	-1.06	-1.21	-0.93	-0.67
OOH*	-2.05	-1.66	-1.71	-1.56	-1.21
H_2O*	-0.26	-0.22	-0.21	-0.18	-0.14

[a] $E_{ads}(A^*) = E(A^*) - E(\text{surface}) - E(A_{(g)})$

where $E(A^*)$ is the total energy for the surface with adsorbed A*, E(surface) is the total energy for the clean surface, and $E(A_{(g)})$ is the energy for gas-phase $A_{(g)}$. The coverage of the computed E_{ads} is 1/16 as each adspecies is on a 4 × 4 surface unit**.**

[b] Previous work: S. P. Lin, K. W. Wang, C. W. Liu, H. S. Chen, J. H. Wang, *Phys. Chem. C*, 2015, **119**, 15224.

Table S2 Computed *Ea* and Δ*E* in parentheses (eV) of the five elementary steps on CoPt/C, CoPtAu-1/C and CoPtAu-4/C, in the comparison with Pt.[a]

		Co	CoPt/C	CoPtAu-1/C	CoPtAu-4/C	Pt
$O_2^* \rightarrow O^* + O^*$	*Ea*	0.06	0.19	0.15	0.63	0.89
	Δ*E*	-3.45	-2.87	-2.90	-1.98	-1.55
$OOH^* \rightarrow O^* + OH^*$	*Ea*	0.03	0.05	0.05	0.10	0.16
	Δ*E*	-3.56	-3.10	-3.15	-2.52	-1.44
$O_2^* + H^+ + e^- \rightarrow OOH^*$	*Ea*	0.85	0.76	0.73	0.73	0.75
	Δ*E*	0.30	0.24	0.20	0.01	-0.09
$O^* + H^+ + e^- \rightarrow OH^*$	*Ea*	1.05	0.81	0.80	0.80	0.81
	Δ*E*	0.57	0.07	0.13	0.05	-0.14
$OH^* + H^+ + e^- \rightarrow H_2O^*$	*Ea*	0.82	0.58	0.55	0.52	0.49
	Δ*E*	0.37	-0.38	-0.35	-0.63	-0.53

[a] Previous work: S.P. Lin, K.W. Wang, C.W. Liu, H.S. Chen, J.H. Wang, *Phys. Chem. C*, **2015,** *119*, 15224

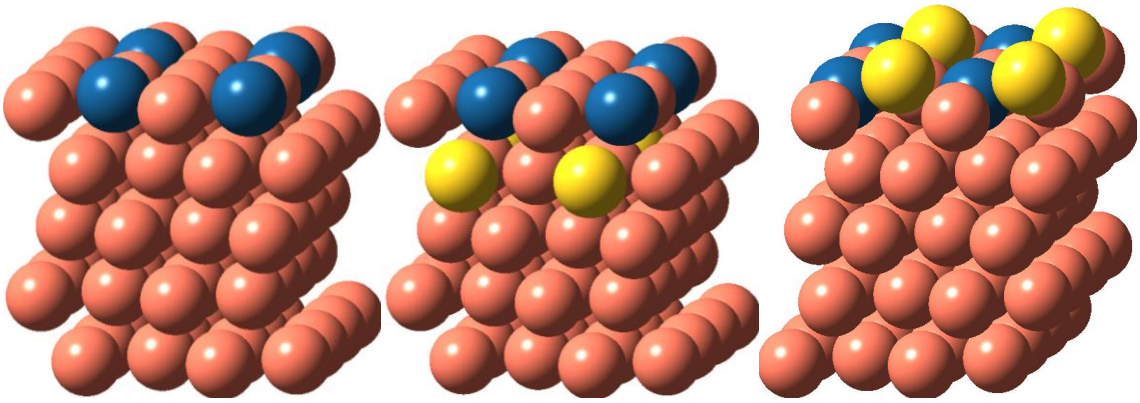
Table S3 The Pt metal loading, electrochemical results of Pt/C, CoPt/C, and various CoPtAu/C catalysts.

Samples	Pt loading (%)	[a] S_{Pt}	MA_{085} (mA/mg_{Pt})		1000^{th} Decay (%)
			1^{st}	1000^{th}	
Pt/C	46.0	1.00	83.4	19	76.90
CoPt/C	7.3	1.00	718.0	252	64.81
CoPtAu-1/C	6.7	0.99	764.1	653	14.60
CoPtAu-2/C	7.3	0.86	664.3	282	57.46
CoPtAu-3/C	6.1	0.60	594.9	80	86.44
CoPtAu-4/C	4.5	0.27	213.6	0	100

[a] $S_{Pt} = A_{Pt} / (A_{Pt}+A_{Au})$ where A_{Pt} and A_{Au} is the surface areas of Pt and Au oxide peaks in CV

Table S4. The surface compositions of CoPt/C, CoPtAu-1/C and CoPtAu-2/C sample characterized by XPS before and after ADT

sample	Surface compositions (at %)			
	Co	Pt	Au	Au/Pt
CoPt/C	92.9	7.1	0	0
CoPt/C-ADT	0	100	0	0
CoPtAu-1/C	88.1	7.1	4.8	0.68
CoPtAu-1/C-ADT	50.1	29.5	20.4	0.69
CoPtAu-2/C	79.8	7.7	12.5	1.62
CoPtAu-2/C-ADT	0	41.7	59.3	1.42



CoPt/C **CoPtAu-1/C** **CoPtAu-4/C**

Figure S1. Surface models of CoPt/C, CoPtAu-1/C and CoPtAu-4/C electrodes. Blue, yellow and orange spheres are represented as Pt, Au and Co atoms, respectively.

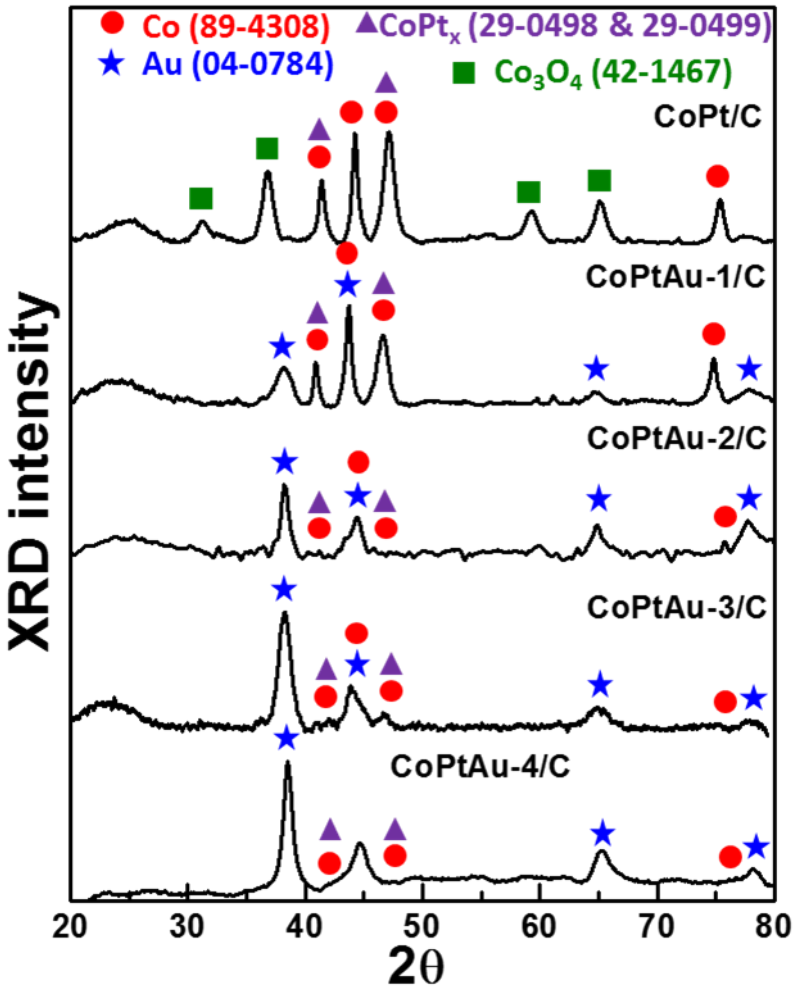


Figure S2. XRD patterns of CoPt/C and CoPtAu/C samples catalysts. Besides the peak of C support located at around 25°, characteristic peaks of Co_3O_4 (JCPDS 42-1467) noted at 31.3, 36.9, 59.4, and 65.2° are attributed to the diffractions of (220), (311), (511), and (440), respectively. When Au is added, strong Au peaks are noted at 38.2, 44.4, 64.6, and 77.5° (04-0784).

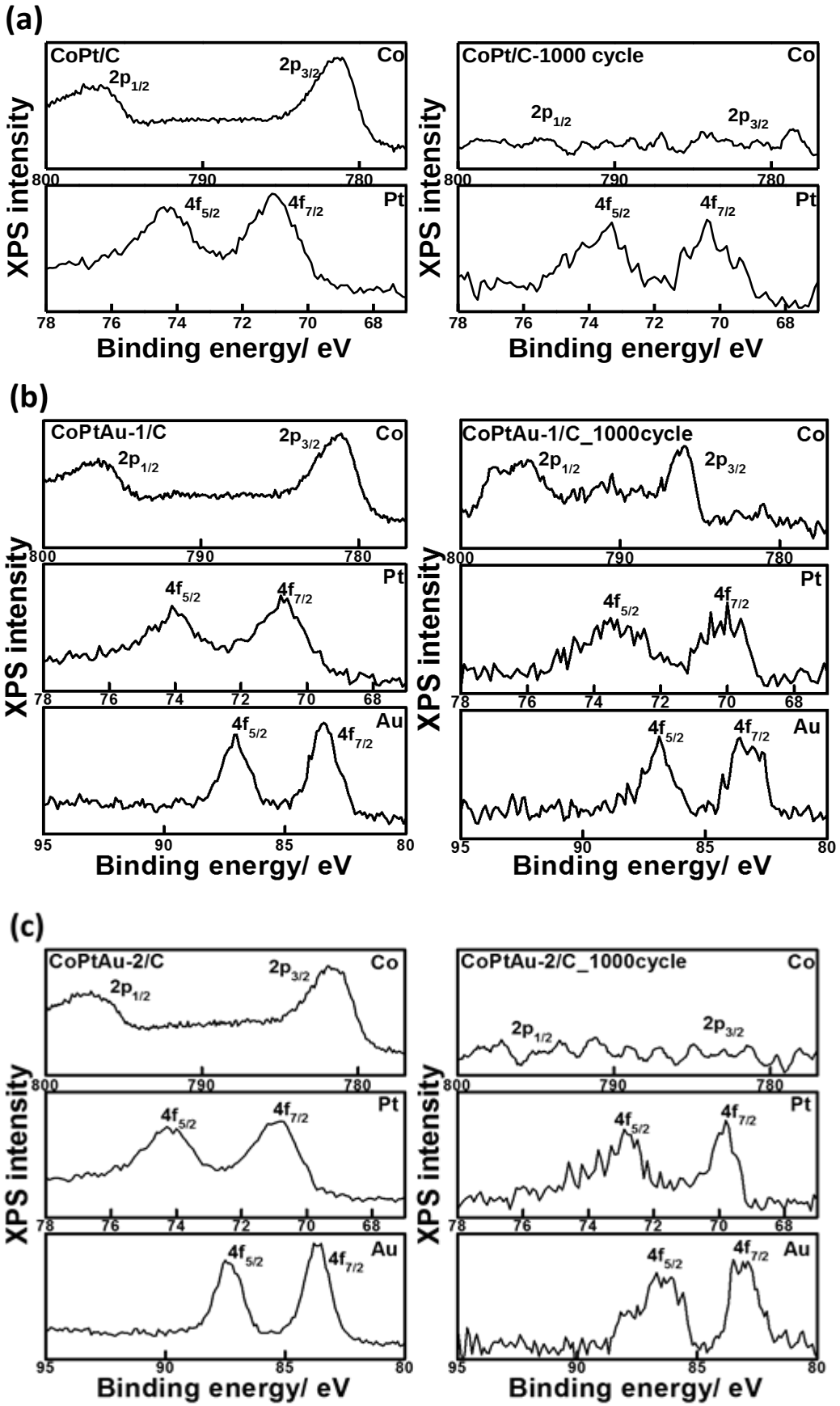


Figure S3. The XPS spectra of (a)CoPt/C, (b) CoPtAu-1/C, and (c) CoPtAu-2/C samples before and after ADT.

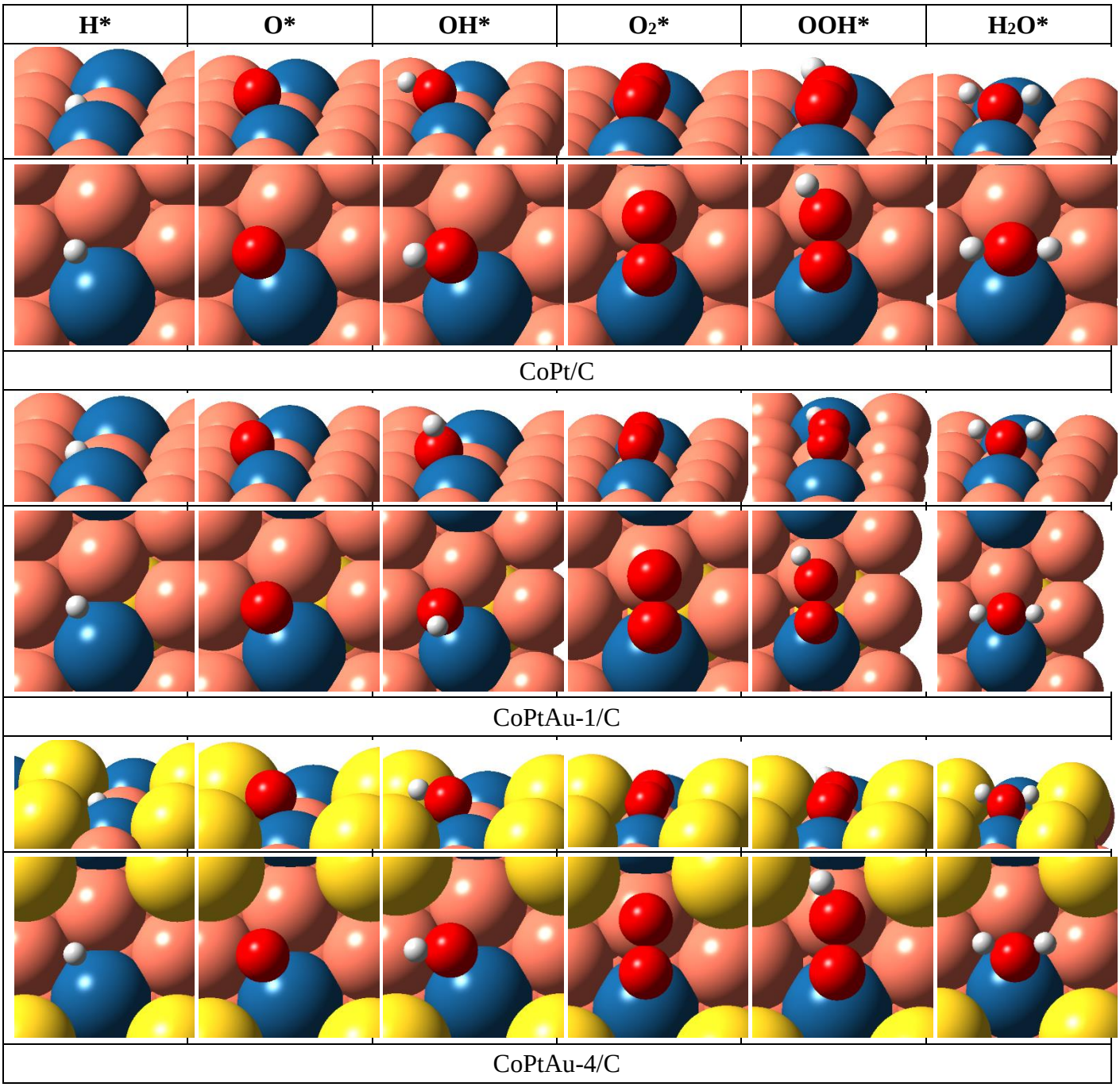


Figure S4. Optimized structures for H*, O*, OH*, O_2*, OOH* and H_2O* on CoPt/C, CoPtAu-1/C and CoPtAu-4/C. The corresponding E_{ads} are listed in Table S2. Blue, yellow, orange, red and white spheres are represented as Pt, Au, Co, O and H atoms, respectively.

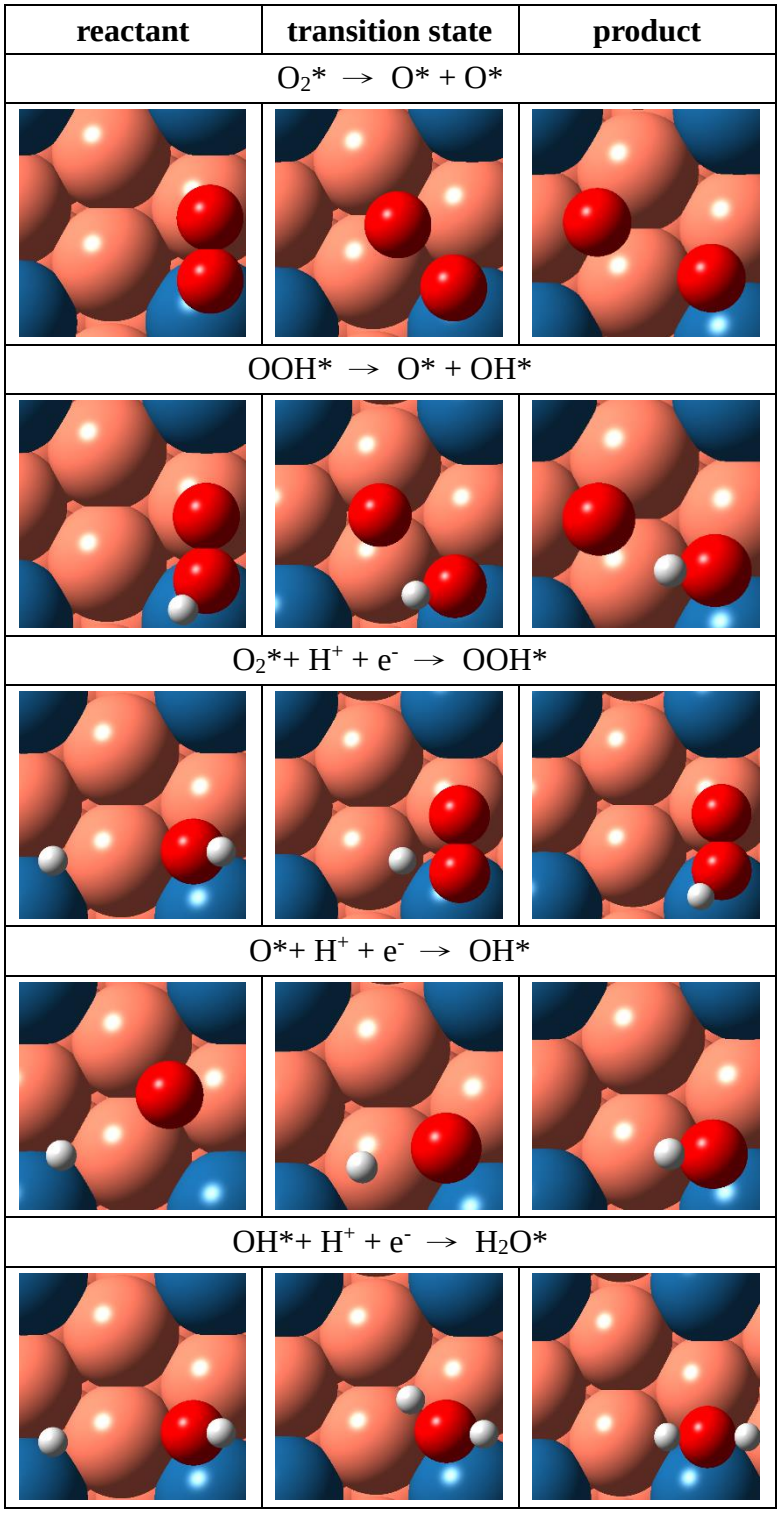


Figure S5. Optimized structures for local minimums and transition states of the five elementary steps in ORR on CoPt/C. The corresponding *Ea* and ΔE are listed in Table S2. Blue, yellow, orange, red and white spheres are represented as Pt, Au, Co, O and H atoms, respectively.

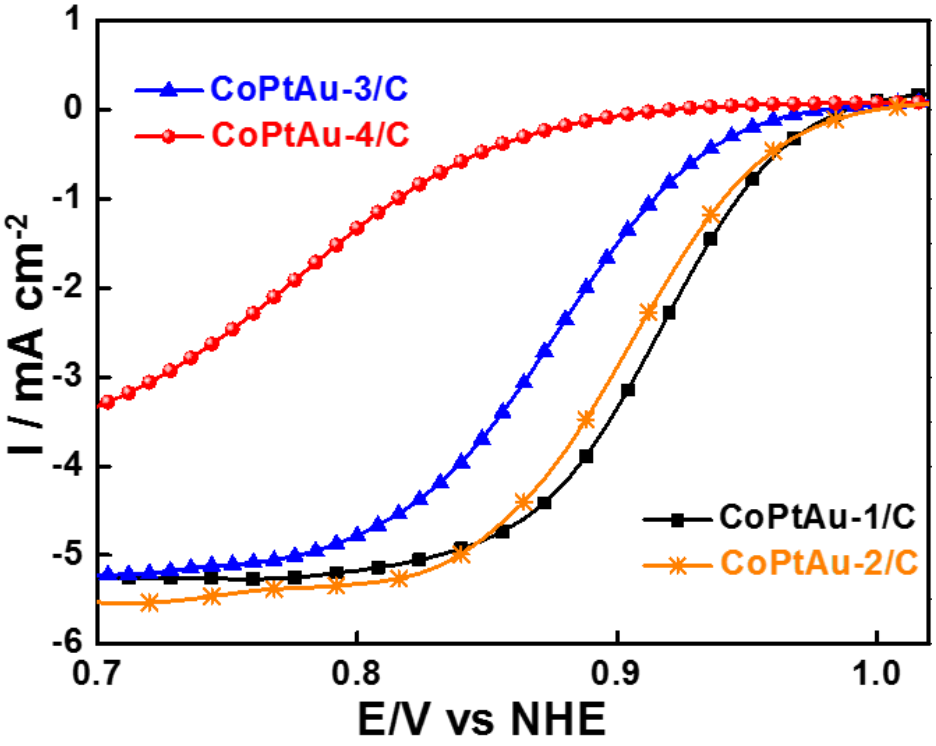


Figure S6. The LSV results of various CoPtAu/C samples recorded in 0.5 M $HClO_4$ saturated with O_2.

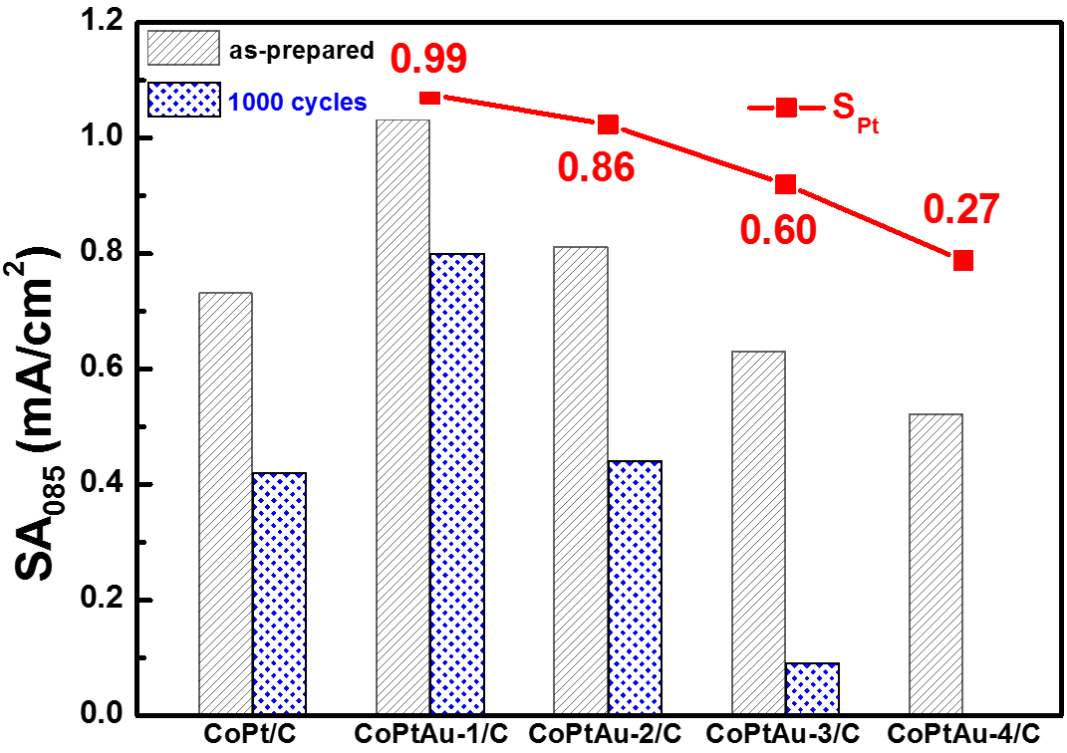


Figure S7 The SA before and after ADT and S_{Pt} of CoPt/C and CoPtAu/C samples.