Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

The enhanced orygen reduction reaction performance on PtSn nanowires: the importance of segregation energy and morphological effect

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Table S1 Computed Δ*E* and *Ea* in eV of the five elementary steps on the (111) surface of Pt,[a] $PtSn_{o*}$ and PtSn. The corresponded structures are shown in Fig. S1 and the related minimum energy pathway are compared in Fig. 2.

		Pt	$PtSn_{o*}$	PtSn
OH1: O_2*+ H^+ + e^- → OOH*	Δ*E*	-0.04	-0.46	-0.18
	Ea	0.71	0.64	0.51
OH2: O*+ H^+ + e^- → OH*	Δ*E*	-0.02	-0.94	-0.51
	Ea	0.78	0.30	0.46
OH3: OH*+ H^+ + e^- → H_2O*	Δ*E*	-0.45	-0.42	-0.35
	Ea	0.46	0.54	0.61
OO1: OOH* → O* + OH*	Δ*E*	-1.43	-1.73	-2.12
	Ea	0.13	0.18	0.09
O_2* → O* + O*	Δ*E*	-1.54	-1.21	-2.17
	Ea	0.85	1.05	0.72

[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 S2 The L/D decay, MA, ECSA, SA, and ORR decay of various catalysts.

Samples	L/D decay (%)[a]	MA (mA/mg_{Pt})	[(111)+(220)]/(200)[b]	ECSA (m^2/g_{Pt})	SA (mA/cm^2)	ORR decay during ADT (%)
Pt7	49.5	112	3.13	47	0.24	83
PtSn1	-	95	2.83	40	0.24	77
PtSn5	35.1	100	3.09	35	0.29	55
PtSn7	24.2	112	3.22	31	0.37	42
PtSn9	19.2	119	3.46	27	0.44	24

[a] L/D decay: $(L/D_{as\text{-}prepared} - L/D_{after\ ADT})/L/D_{as\text{-}prepared}*100$

[b] The area ratio of [(111)+(220)]/(200) peaks in XRD patterns

Table S3 The EXAFS fitting results of as-prepared PtSn catalysts for Pt L_{III} edge.

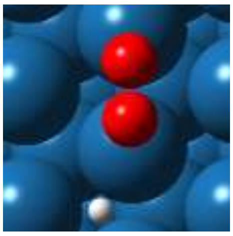
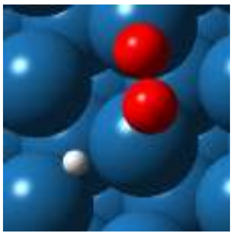
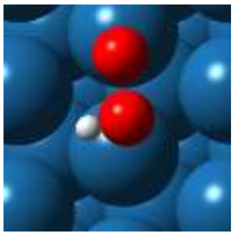
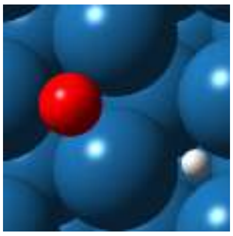
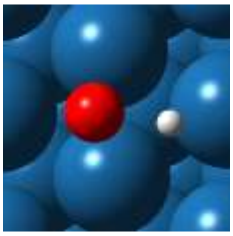
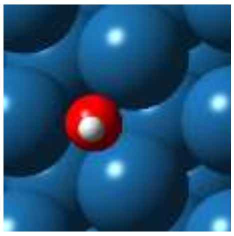
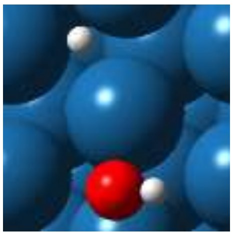
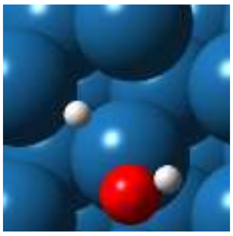
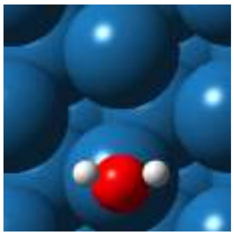
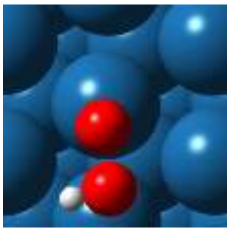
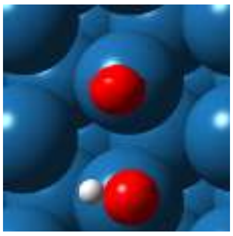
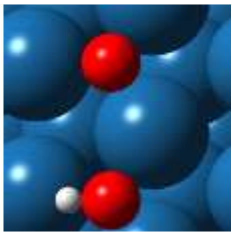
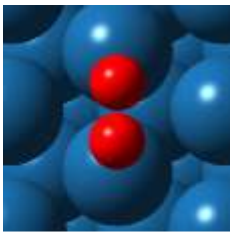
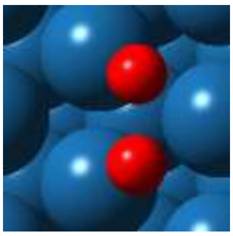
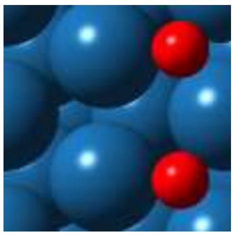
Sample	H_{Ts}	shell	CN[a]	R[b] [Å]	σ^2(x10^{-3})[c] [Å ^{2}]	ΔE_0[d] [eV]	R factor[e]
PtSn1	0.3156	Pt-Pt	6.4	2.76	6.2	9.7	0.006
		Pt-O	0.9	2.04			
		Pt-Sn	0.5	2.91			
PtSn5	0.3129	Pt-Pt	7.2	2.76	5.8	9.8	0.007
		Pt-O	0.7	2.02			
		Pt-Sn	0.3	2.95			
PtSn7	0.3024	Pt-Pt	7.3	2.76	5.9	9.8	0.006
		Pt-O	0.6	2.00			
		Pt-Sn	0.3	2.94			
PtSn9	0.3002	Pt-Pt	7.6	2.75	6.1	9.0	0.005
		Pt-O	0.5	2.02			
		Pt-Sn	0.2	2.86			

Table S4 The EXAFS fitting results of as-prepared PtSn catalysts for Sn K edge.

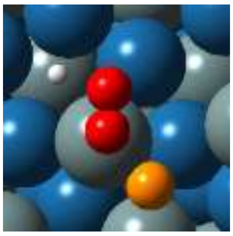
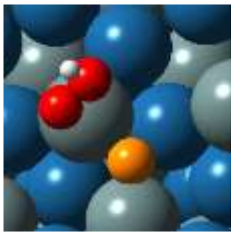
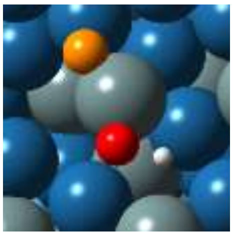
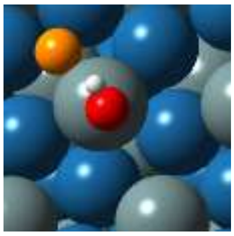
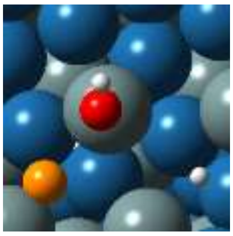
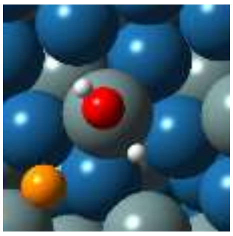
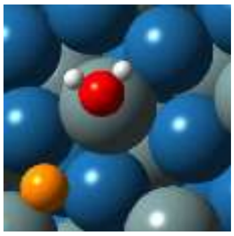
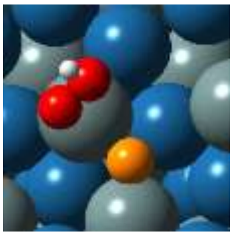
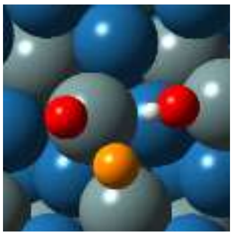
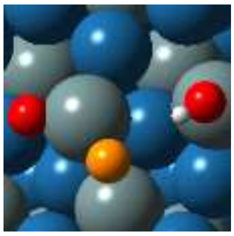
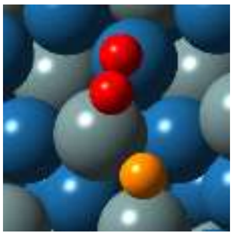
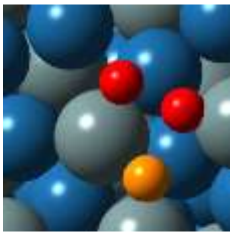
Sample	shell	CN[a]	R[b] [Å]	σ^2(x10^{-3})[c] [Å ^{2}]	ΔE_0[d] [eV]	R factor[e]
PtSn1	Sn-Sn	0.2	2.01	4.2	5.4	0.002
	Sn-O	4.4	2.05			
	Sn-Pt	4.0	2.88			
PtSn5	Sn-Sn	0.2	2.04	4.4	5.3	0.004
	Sn-O	5.7	2.06			
	Sn-Pt	3.7	2.94			
PtSn7	Sn-Sn	0.1	2.05	4.1	5.2	0.001
	Sn-O	6.0	2.07			
	Sn-Pt	4.7	2.87			
PtSn9	Sn-Sn	0.1	2.05	4.0	5.4	0.003
	Sn-O	6.4	2.06			
	Sn-Pt	5.0	2.89			

[a] CN: coordination number.
[b] R: bond distance.
[c] σ^2: Debye–Waller factor.
[d] ΔE_0: inner potential correction.
[e] R factor: residual error.

(a) Pt

reactant	transition state	product
OH1: $O_2^* + H^+ + e^- \rightarrow OOH^*$		
		
OH1: $O^* + H^+ + e^- \rightarrow OH^*$		
		
OH3: $OH^* + H^+ + e^- \rightarrow H_2O^*$		
		
OO1: $OOH^* \rightarrow O^* + OH^*$		
		
$O_2^* \rightarrow O^* + O^*$		
		

(b) $PtSn_{o*}$

reactant	transition state	product
OH1: O_2*+ H^+ + e^- → OOH*		
		
OH1: O*+ H^+ + e^- → OH*		
		
OH3: OH*+ H^+ + e^- → H_2O*		
		
OO1: OOH* → O* + OH*		
		
O_2* → O* + O*		
		

(c) PtSn

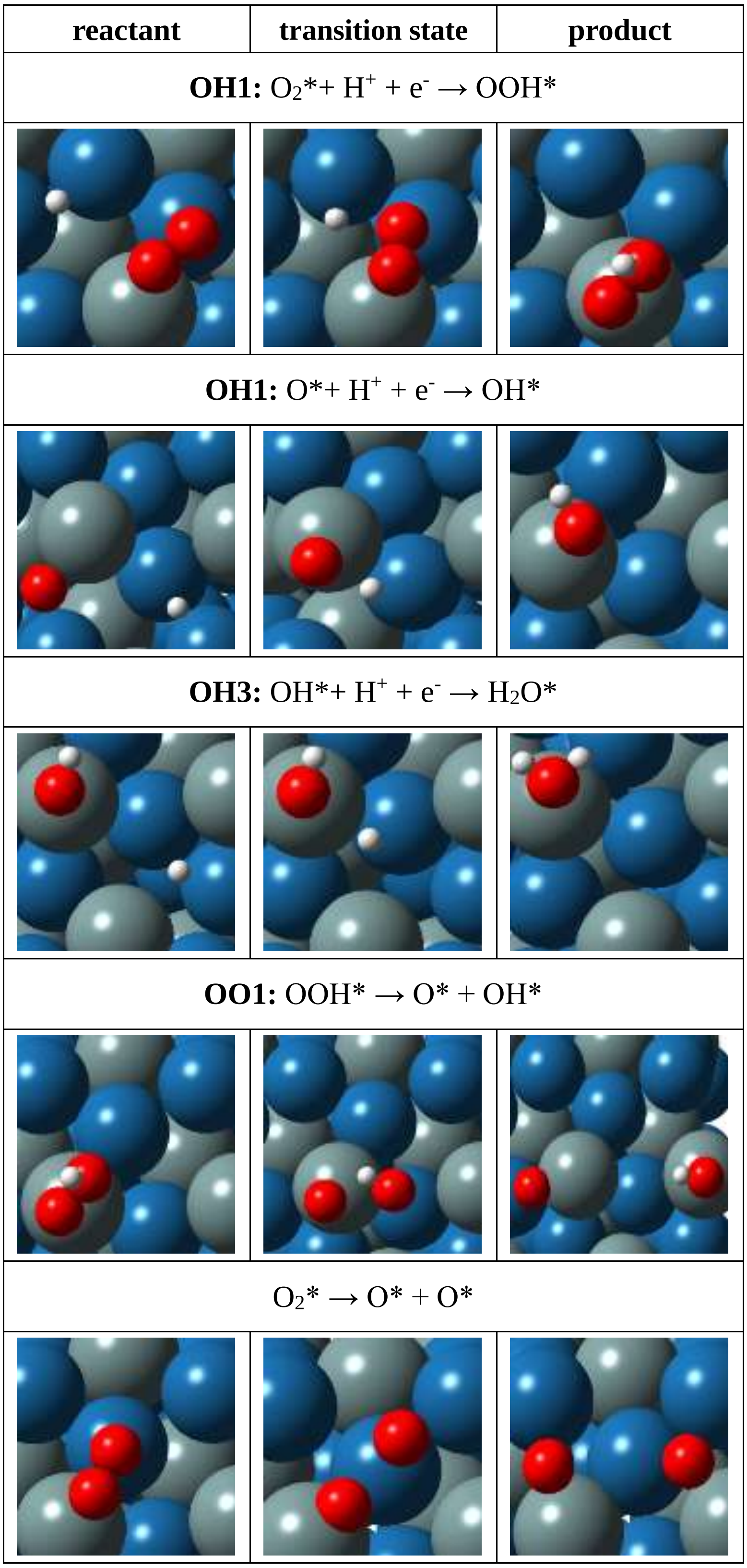
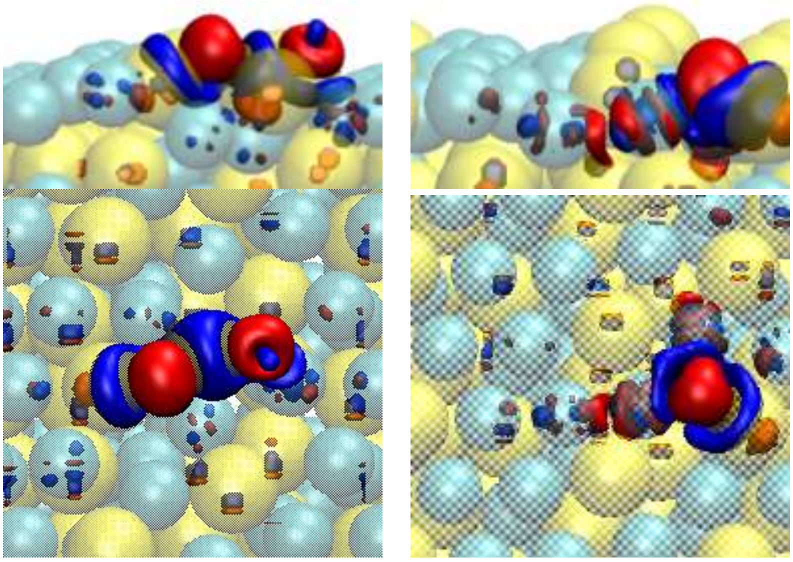


Fig. S1. Optimized structures for local minimums and transition states of the five elementary steps in ORR on (a) Pt, (b) $PtSn_{O*}$ and (c) PtSn. The corresponding energetic results are listed in Table S1 and the related potential energy surfaces are compared in Fig. 1. Cyan, tan, red and white spheres are represented as Pt, Sn, O and H atoms, respectively. The spectator O* in $PtSn_{O*}$ surface is marked by orange sphere.



O*/PtSn$_{OH*}$ **O*/PtSn**

Fig. S2 Induced charge of O* on PtSn$_{OH*}$ (denoted as a spector OH* on the PtSn) and PtSn. The isosurface of +/- 0.02 |e| are shown in the opaque blue/red lobes. The Pt, Sn and O atoms are represented as transparent cyan, yellow and orange spheres, respectively. Less induced charge in O*/PtSn$_{OH*}$ interface indates the weaker E_{ads}(O*) on PtSn$_{OH*}$ due to the lateral repulsion between the adsorbed O* and spectator OH*.

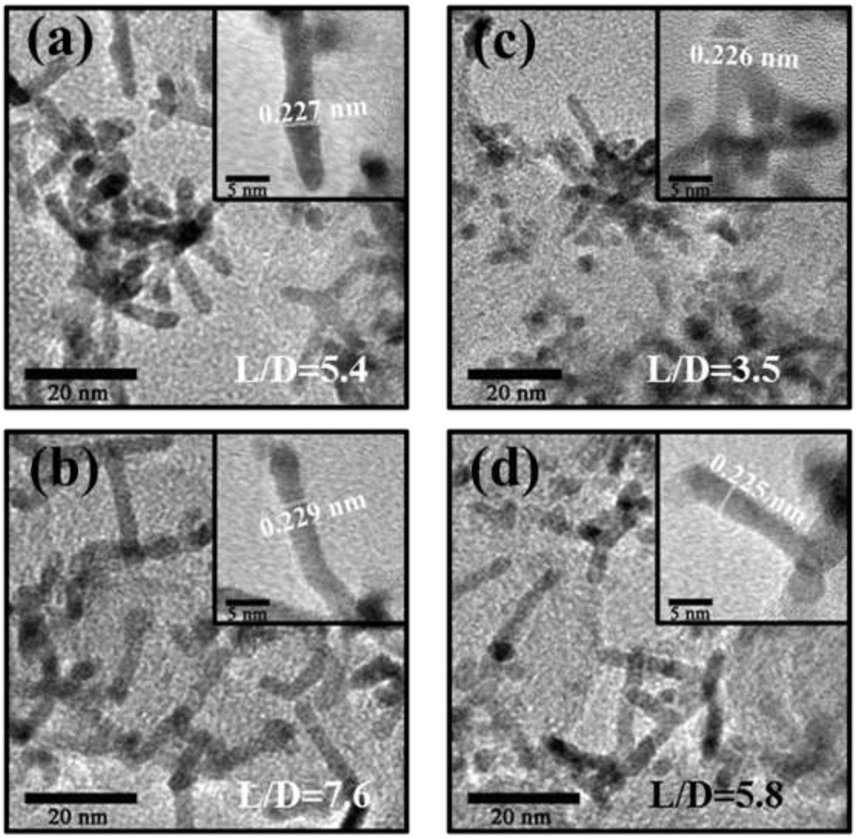


Fig. S3 HRTEM micrographs of catalysts before and after ADT for PtSn5 (a) and (c), and PtSn7 (b) and (d), respectively.

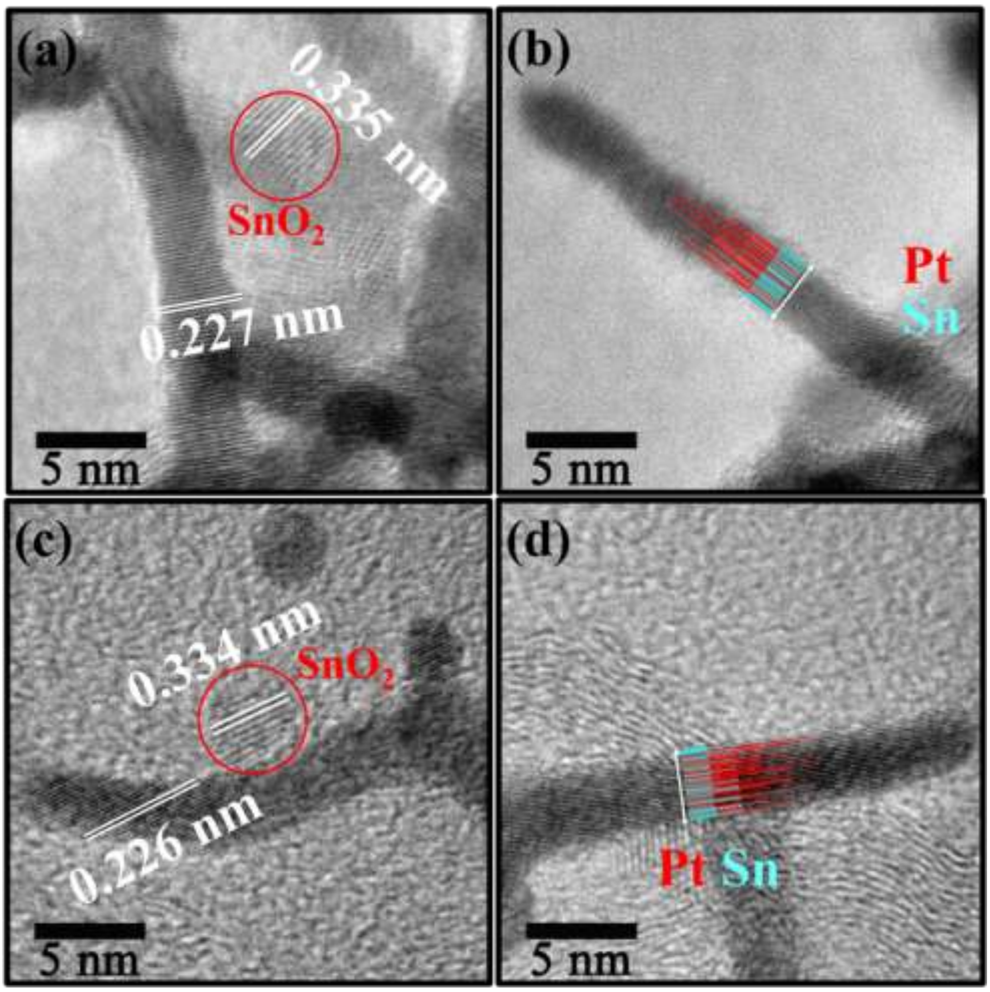


Fig. S4 The local TEM micrographs and line scans results for as-prepared PtSn9 (a) and (b), and PtSn9 after ADT (c) and (d), respectively.

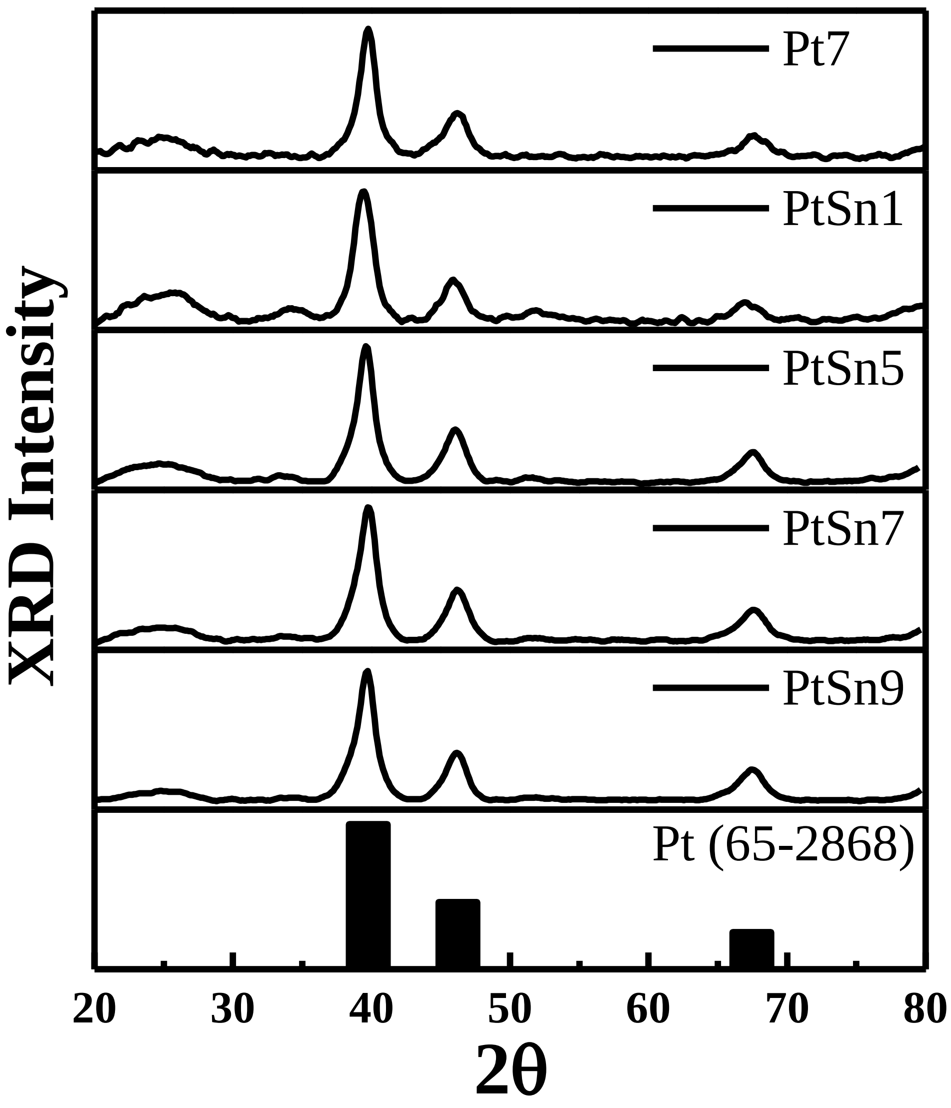


Fig. S5 XRD patterns of Pt7 and various PtSn samples.

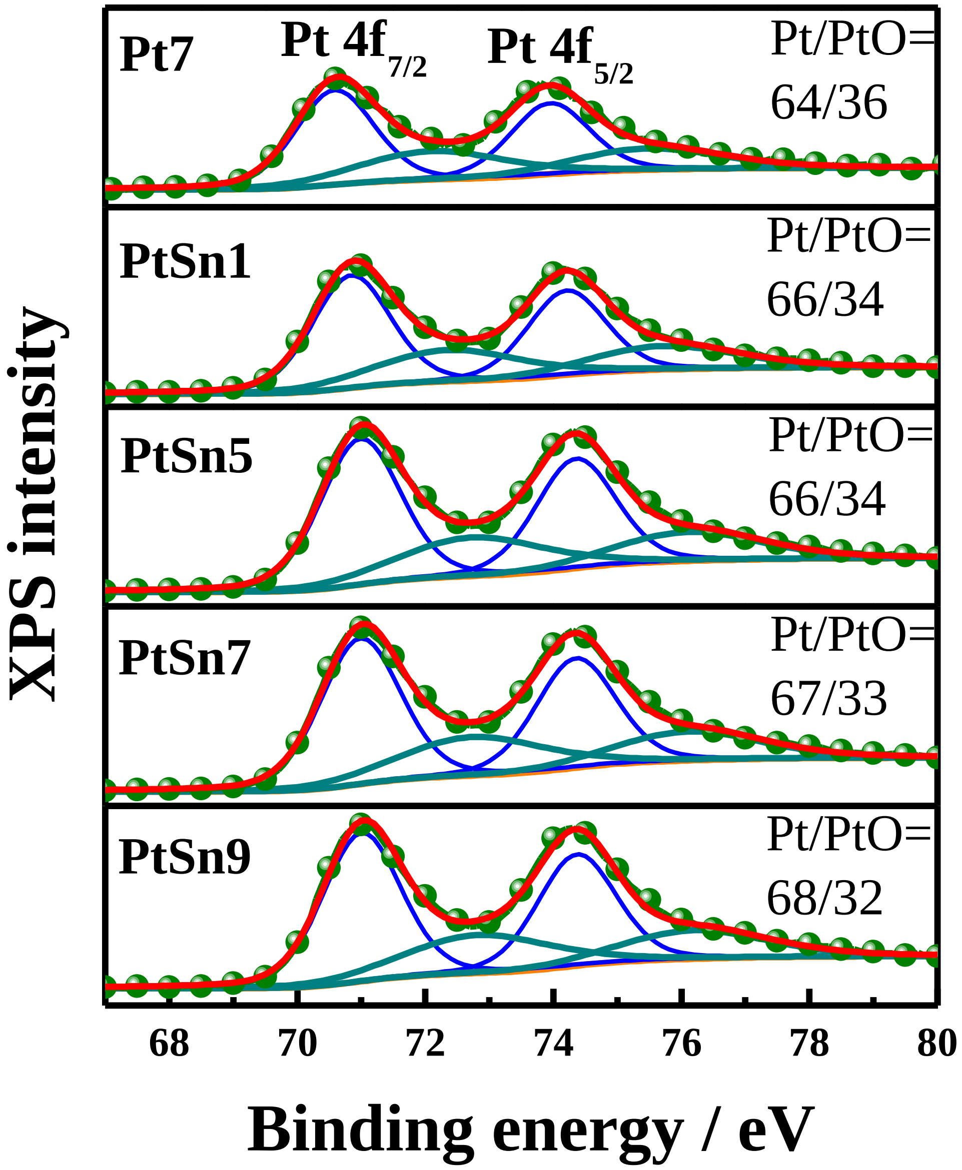


Fig. S6 XPS spectra of Pt and fitting results for Pt7 and various PtSn samples.

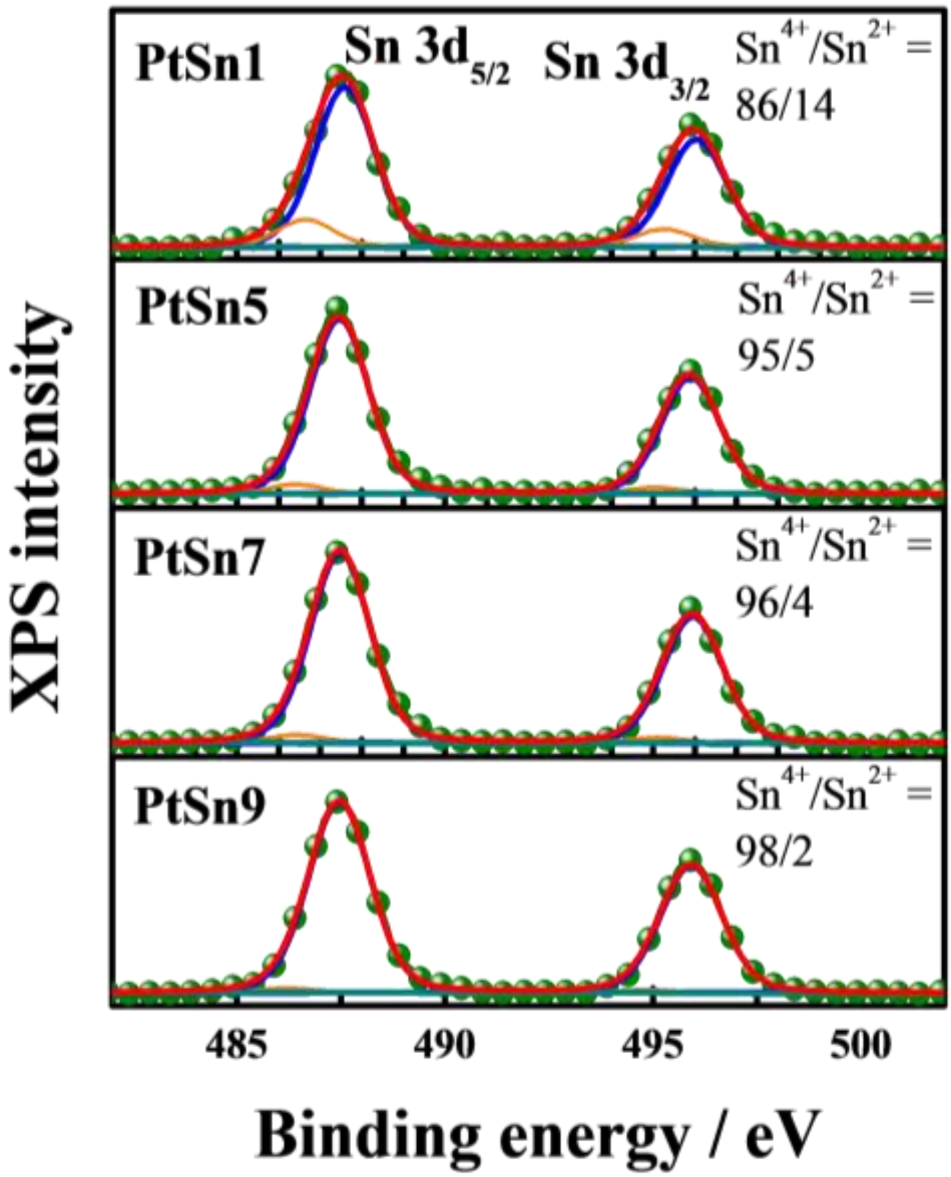


Fig. S7 XPS spectra of Sn and fitting results for various PtSn samples.

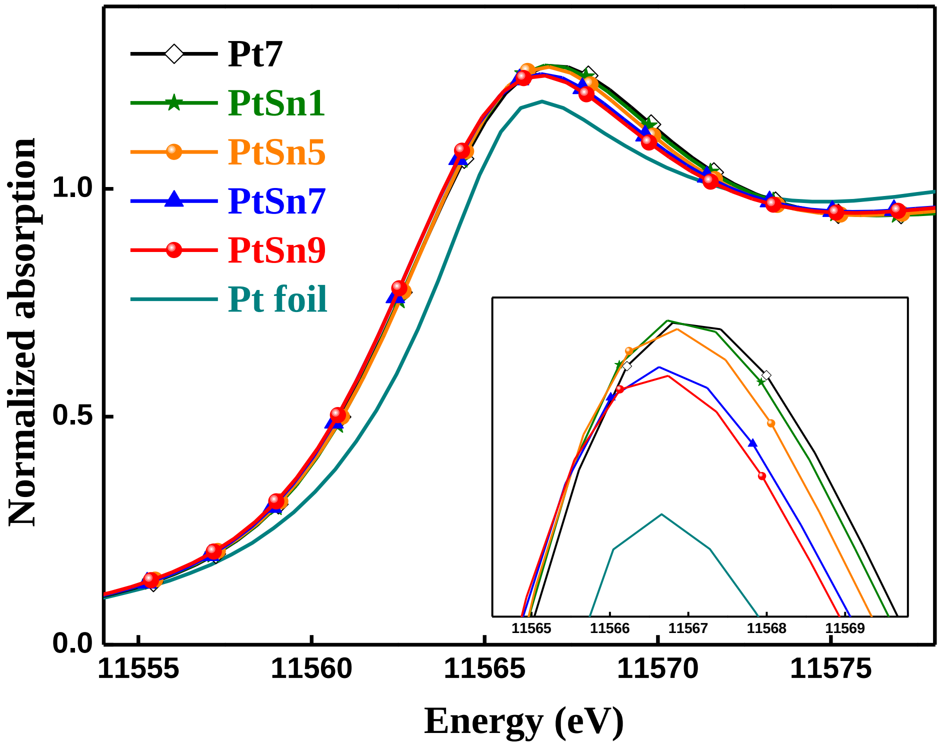


Fig. S8 The XANES spectra of as-prepared PtSn samples for Pt L_{III} edge.

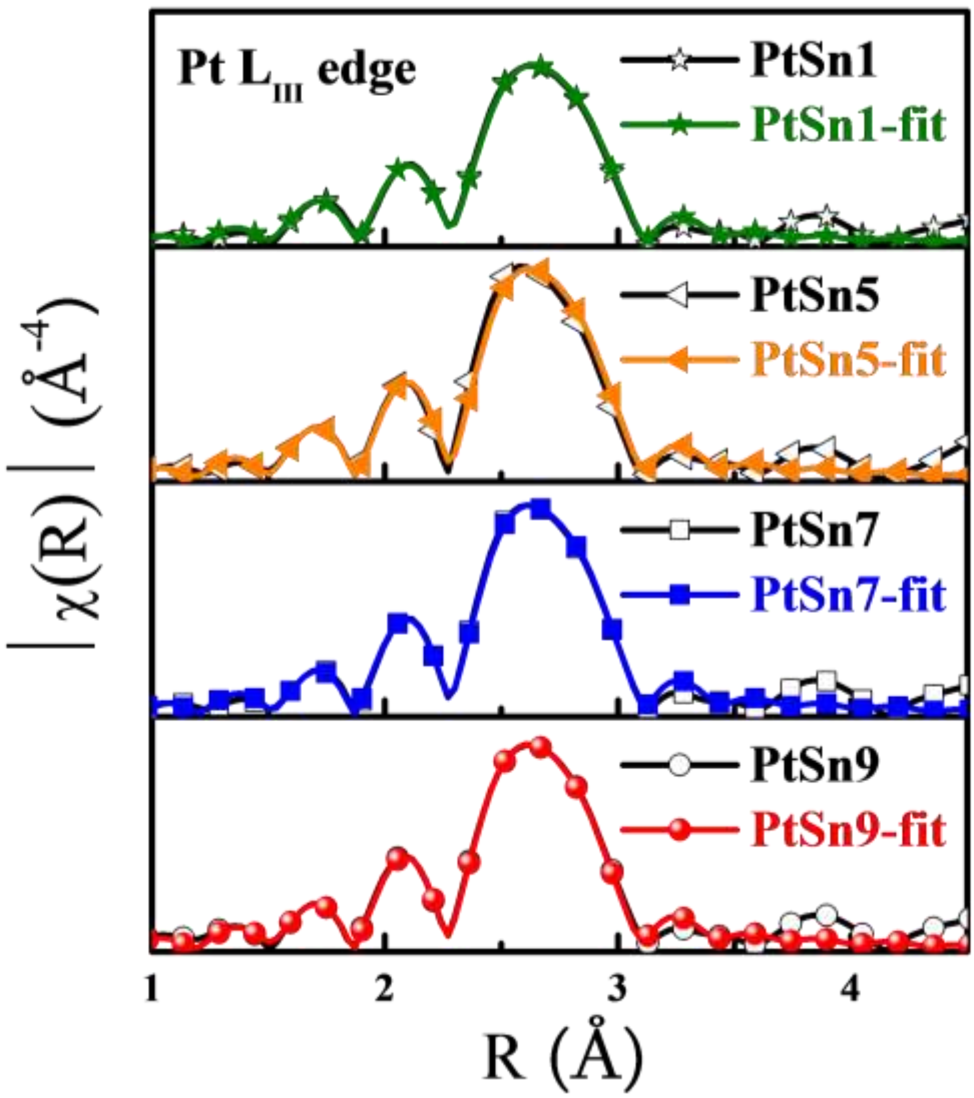


Fig. S9 The EXAFS fitting results of as-prepared PtSn samples for Pt L_{III} edge.

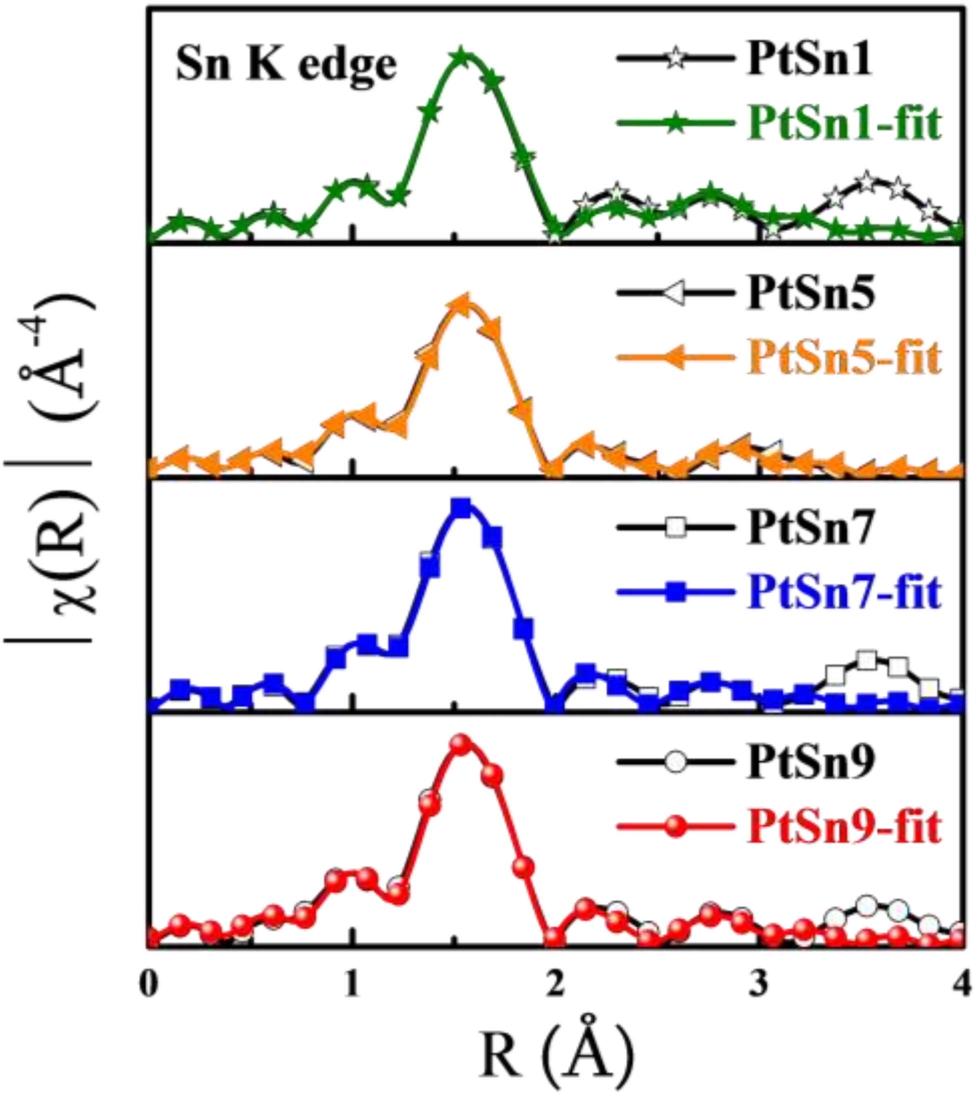


Fig. S10 The EXAFS fitting results of as-prepared PtSn samples for Sn K edge.