Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Bifunctional Pt-SnO_x Nanorods for Enhanced Oxygen Reduction and Hydrogen Evolution Reactions

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Table S1. ICP-OES determined composition ratios and preparation process of experimental catalysts.

Samples	Preparation Process	Morphology	Pt (at. %)	Sn (at. %)
Pt-NRs	FAM method	Pt Nanorods	100	0
Pt-SnO_x NRs	FAM method	SnO_2 capped Pt-nanorods	81	19

Table S2. XRD determined structural parameters of experimental samples.

Sample	$d_{(hkl)}$ (Å)			$D_{(hkl)}$ (nm)			$H_{(111)}/H_{(200)}$	$H_{(111)}/H_{(220)}$
	(111)	(200)	(220)	(111)	(200)	(220)		
J.M.-Pt/C	2.261	1.966	1.380	3.82	4.09	3.68	3.24	5.46
Pt NRs	2.265	1.963	1.384	7.77	4.64	4.54	2.95	5.88
Pt-SnO_x NRs	2.254	1.950	1.380	6.19	5.36	5.51	2.73	5.05

* $d_{(hkl)\_Pt}$ = lattice spacing
* $D_{(hkl)\_Pt}$ = particle size

Table S3 XPS analysis results for experimental samples and standards

Samples	Catalysts	Pt $4f_{7/2}$ (eV)		Sn $3d_{3/2}$ (eV)	
		Pt	Pt n+	Sn 2+	Sn 4+
Experiment samples	J.M.-Pt/C	71.07	73.19	N/A	
	Pt NRs	71.10	73.32		
	Pt-SnO_x NRs	70.50	72.62	495.34	496.01
Standard*	Pt	70.90 – 71.10	N/A	N/A	
	PtO	N/A	72.40 – 74.60		
	PtO_2		74.10 – 74.90		
	PtOSn		72.30		
	SnO	N/A		495.37	N/A
	SnO_2			N/A	494.50

* Data obtained from the standard XPS data base of NIST website.

Table S4. Comparison of ORR activities of various low Pt loading catalysts.

Samples	Pt loading (wt.%)	Electrolyte	$MA_{0.85}$ (mA/mg_{Pt})	Reference
Pt-SnO_x NRs	36	0.5 M $HClO_4$	160	This study
Pt 20s/SC CoO NRs	9.41	1.0 M KOH	156	1
75% $Pd_{80}Co_{20}$ +25% Pt	5	0.5 M H_2SO_4	150	2
Pt/C	2.54	0.5 M H_2SO_4	6.5	3
$Pt_{0.5}Pd_{0.5}$/C	3.11		8.5	
Ag@$Pt_{0.1}Pd_{0.1}$/C	1.87		23.5	
H-Pt/$CaMnO_3$	8.06	0.1 M KOH	380	4
Pt/$Na_4Ge_9O_{20}$	4.97	0.1 M KOH	380	5
		0.1 M $HClO_4$	150	

Table S5. Comparison of HER activities of various low Pt loading catalysts.

Samples	Pt loading ($\mu g/cm^{-2}$)	Electrolyte, Scan rate	η^* (mV) @ 10 mA/cm^{-2}	References
Pt-SnO_x NRs	351	0.5 M H_2SO_4, 2 mVs^{-1}	48	This Study
Pt/MoS_2/CFs	5.7	0.5 M H_2SO_4, 5 mVs^{-1}	80	6
$Pd_{60}Pt_{40}$	13	0.5 M H_2SO_4, 5 mVs^{-1}	130	7
5 ALD cycles Pt-WC	0.55	0.5 M H_2SO_4, 2 mVs^{-1}	438	8
10 ALD cycles Pt-WC	3.1		408	
30 ALD cycles Pt-WC	5.5		306	
Pt/C	25		296	
Pt-MoS_2	27	0.5 M H_2SO_4, 2 mVs^{-1}	80	9
Pt-MoS_2	18	0.1 M H_2SO_4, 2 mVs^{-1}	150	10

* η: Overpotential

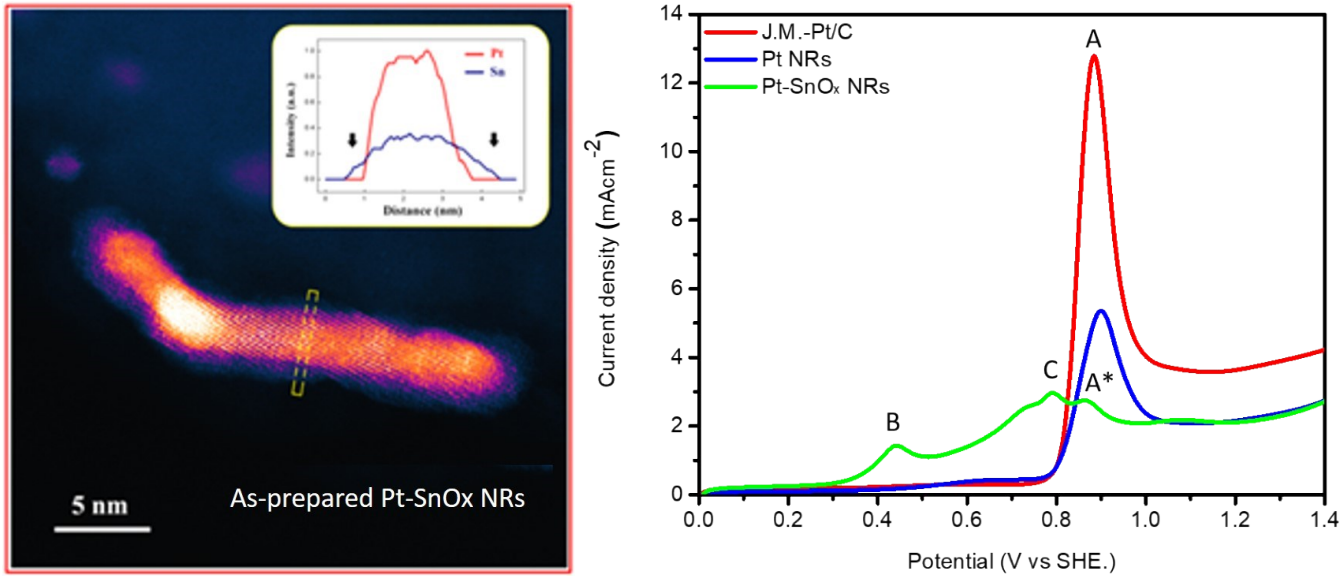

Figure S1. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) of Pt-SnOx NR with Energy-dispersive X-ray spectroscopy (EDS) elemental mapping (right) and its CO stripping curve compared with that of J.M.-Pt/C and Pt NRs.

The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) of Pt-SnOx NR with Energy-dispersive X-ray spectroscopy (EDS) elemental mapping is presented in **Figure S6** and **Figure R1 (left)**. Accordingly, the Sn atoms are decorated in the Pt NR surface in Pt-SnOx NR. The **Figure R1 (right)** compares the CO stripping curves of commercial Pt catalyst (J.M.-Pt/C), Pt NRs and Pt-SnOx NRs. In this curve, peak A correspond to the current responses of CO oxidation in the Pt surface and the intensity corresponds to the specific surface area for chemical reaction. Compared to that of Pt NRs, the offset of peak A to A* (by -0.02 V) reveals the reduction of energy barrier for CO oxidation due to the presence of Sn atoms neighboring to Pt atoms in the Pt-SnOx NR surface and the broad current density from 0.3 to 0.9 V vs. RHE is the CO oxidation current from Sn oxide surface (T. Matsui et al. / Journal of Power Sources 155 (2006) 152–156). In this region, the sharp current peaks B and C can be attributed to the characteristic reactions of Pt/Sn sites in different crystal facts of the Pt-SnOx NRs surface. Given that the redox reaction peaks for H_2 remaining exist in UPD_H region (**Figure 5a**), the results of CO stripping curve and the EDX mapping analysis complementarily reveals the formation of SnOx decoration in the Pt-SnOx surface. Meanwhile, compared with that of Pt NR, a broad double layer region with higher current density (H_{DL}) reveals the prevailing OH adsorption by SnOx, therefore, revealing the facilitation of ORR in hydration step in the Pt-SnOx NRs surface.

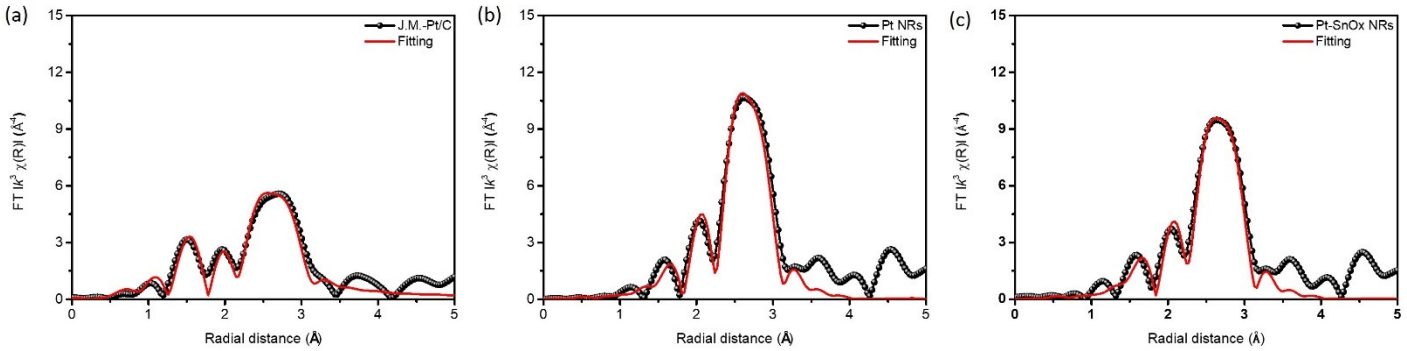

Figure S2. Model analysis fitting curves compared with experimental FT-EXAFS spectra at Pt L_3-edge of (a) J.M.-Pt/C, (b) Pt NRs and (b) Pt-SnO_x NRs.

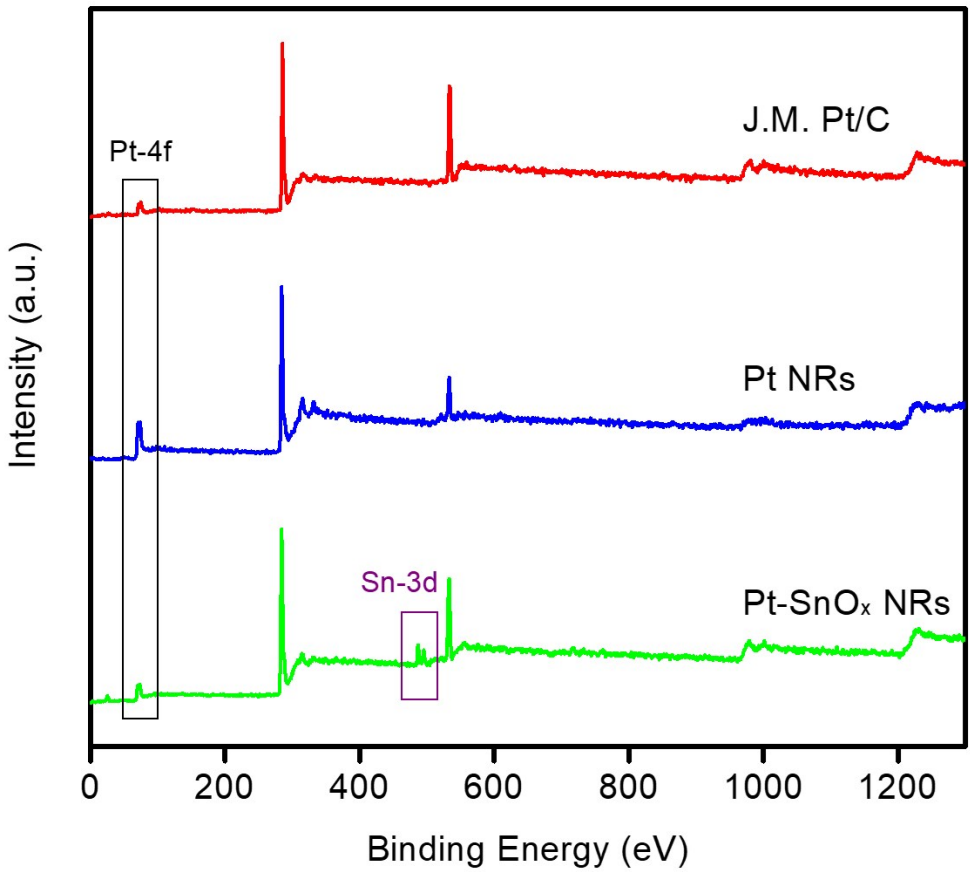

Figure S3. XPS survey spectra of J.M.-Pt/C, Pt NRs, and Pt-SnO_x NRs catalysts. The black, and purple regions represent the core level spectra of Pt 4f, and Sn 3d, respectively.

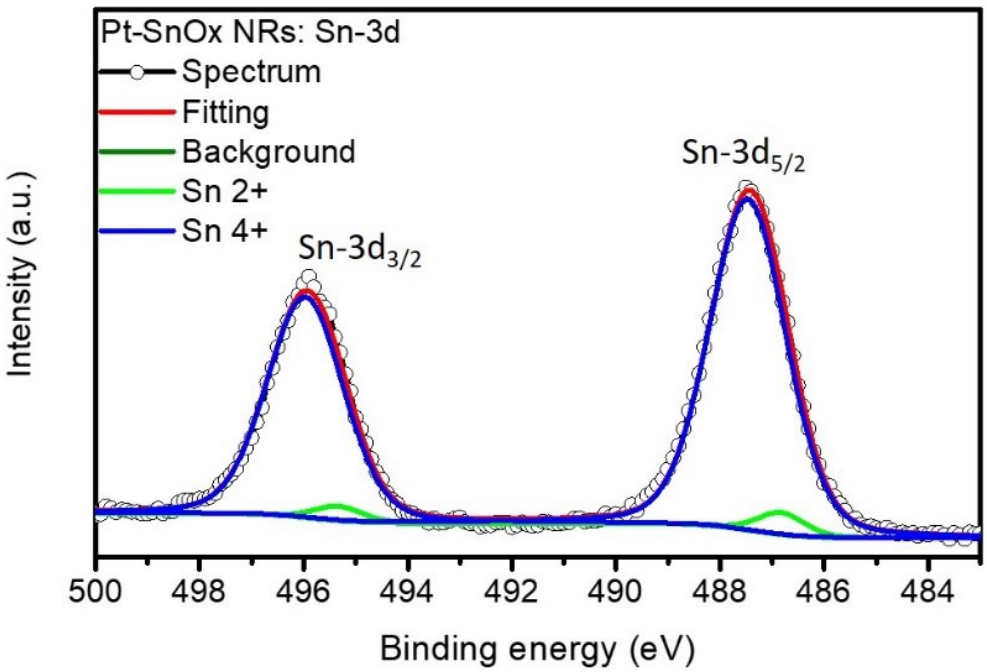

Figure S4. XPS spectra in the Sn-3d regions of the Pt-SnO_x NRs.

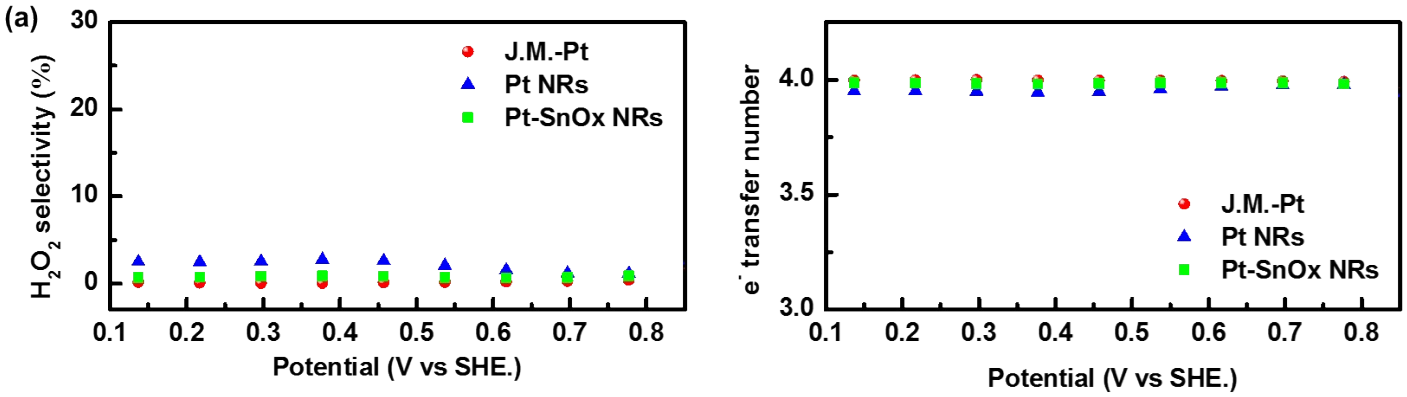

Figure S5. (a) The H_2O_2 selectivity and (b)electron transfer number (n) of J.M.-Pt/C, Pt NRs, and Pt-SnO_x NRs catalysts.

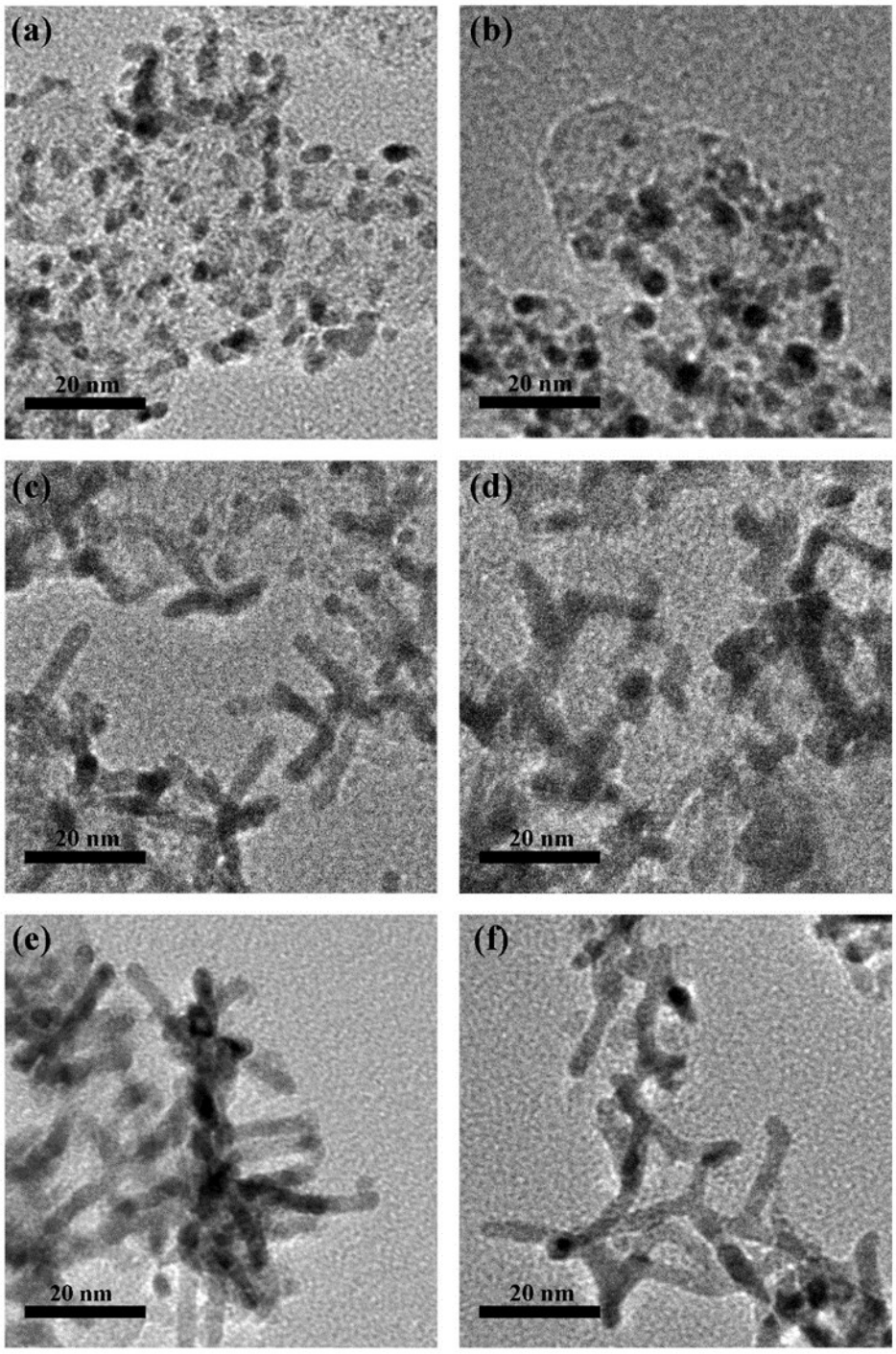

Figure S6. The morphologies of as-prepared (a) J.M.-Pt/C, (c) Pt NRs, and (e) Pt-SnOx NRs catalysts, and (b) J.M.-Pt/C, (d) Pt NRs, and (f) Pt-SnOx NRs after ADT.

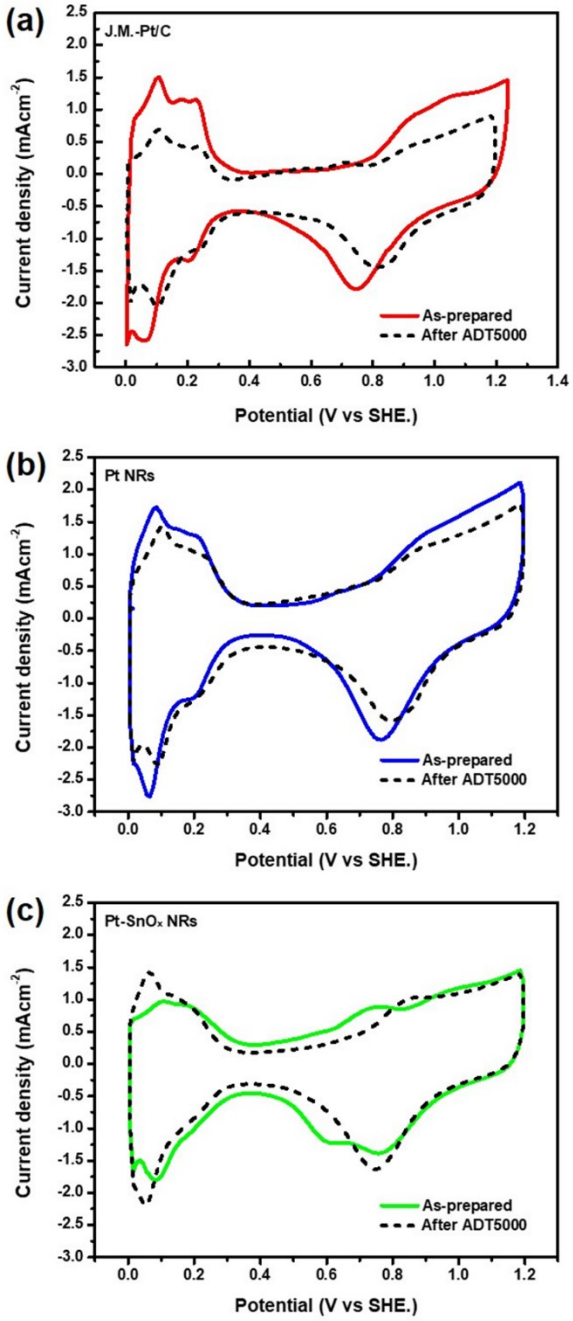

Figure S7. CV curve before and after ADT for (a) J.M.-Pt/C, (b) Pt NRs, and (c) Pt-SnO_x NRs in N_2-saturated 0.5 M $HClO_4$ solution at room temperature.

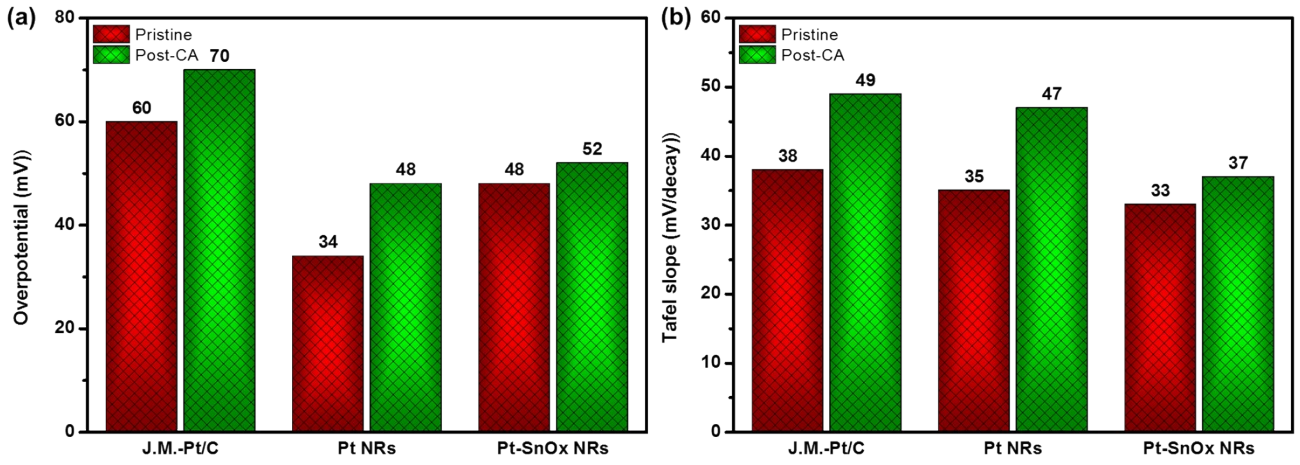

Figure S8. Pristine and after CA for 10 hours. (a) overpotentials and (b) Tafel slopes of J.M.-Pt/C, Pt NRs, and Pt-SnO_x NRs.

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