Supporting Information

Structurally ordered PtSn intermetallic nanoparticles supported on ATO for methanol oxidation reaction

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EXPERIMENTAL SECTION

The preparation of ATO: The method for preparing ATO nanoparticles is similar to that described by Lee et al. [1] $SnCl_4 \cdot 5H_2O$ (10.6 g), $SbCl_3$ (0.35 g), HCl (4.6 mL) , and 50 mL deionized water were added to a three-neck flask equipped with a condenser. The NaOH (6 g) dissolved in 100 mL deionized water were poured into above solution. The mixtures were heated upto 100 ℃ with mild stirring under an N_2 atmosphere, and kept at 100 ℃ for 2 h. After the mixture cooled down to room temperature, the resulting solid were washed three times with deionized water. The powder freeze dried for 12 h and then calcined at 500 ℃ for 2 h. Finally the powder was ground to obtain ATO support.

The preparation of catalysts: Using a polyol reduction method, ATO (100 mg) , $H_2PtCl_6 \cdot 6H_2O$ (66 mg) and NaOH (500 mg) were added to a three-necked flask containing 80 mL ethylene glycol. The solution was heated to 200 ℃ under N_2 atmosphere for 5 minutes, 0.5 hours, 2 hours, 3 hours (the samples were labeled as Pt/ATO-200-5min, Pt/ATO-200-0.5h, Pt/ATO-200-2h, Pt/ATO-200-3h). After cooling to room temperature, the as-prepared catalysts were collected by centrifugation and were washed three times with deionized water, and then freeze-dried. For comparision, we also prepared catalyst using same method at 160 ℃ (labeled as Pt/ATO-160-2h).

The synthesis of PtSn/ATO catalysts: $H_2PtCl_6 \cdot 6H_2O$ (0.127 mmol), $SnCl_4 \cdot 5H_2O$ (0.127 mmol) as precursors were added to a three-necked flask containing 60 mL ethylene glycol. The solutions were heated to 200 ℃ and the solution changed to black. After reaction for 2 h at 200 ℃ and then cooling to the room temperature, ATO (100 mg) was added into black solution and stired for 1 h, the PtSn/ATO catalyst was collected by centrifugation and was washed three times with deionized water, and then freeze-dried.

Electrochemical Characterization: Electrochemical experiments were carried out

on a CHI 660E electrochemistry station using a three electrode system at room temperature. Ag/AgCl (saturated KCl) electrode, Pt wire and glassy-carbon electrode (GCE, diameter 5 mm) coated with catalysts were used as the counter, reference electrode and working electrode respectively. Catalyst ink for electrochemical study was prepared by ultrasonically mixting of 2 mg catalyst, 1 mg carbon balck (Vulcan XC-72), 1 mL 2-propanol and 20 μL Nafion solution (5 wt %). 4 μg_{pt} of catalyst ink was deposited onto the GCE, and dried in the air. Cyclic voltammetry was tested in a 0.5 M N_2-saturated H_2SO_4 electrolyte and the methanol oxidation reaction was performed in 0.5 M H_2SO_4 + 1 M methanol between 0.05 V and 1.2 V at a scan of 50 mV s^{-1} . For CO stripping experiment, CO was bubbled through the 0.5 M H_2SO_4 electrolyte for 20 min when the electrode potential was held at 0.05 V vs. RHE. N_2 was then bubbled to remove the free CO in the electrolyte. Then, the CO stripping voltammetry was performed between 0.05 V and 1.2 V at a scan of 50 mV s^{-1}.

Catalysts characterization: The morphology of the samples were characterized by aberration correction field emission transmission electron microscope (Titan G2 60-300 with image corrector). X-ray powder diffraction (XRD) was measured on Rigaku ULTIMA Ⅲ. X-ray photoelectron spectroscopy (XPS) characterization was obtained on VG ESCALAB 250 (corrected by referencing the energies of the C 1s peak at 284.6 eV). The Pt content of catalysts were tested through inductively coupled plasma-optical emission spectrometer (ICP-OES, iCAP7000).

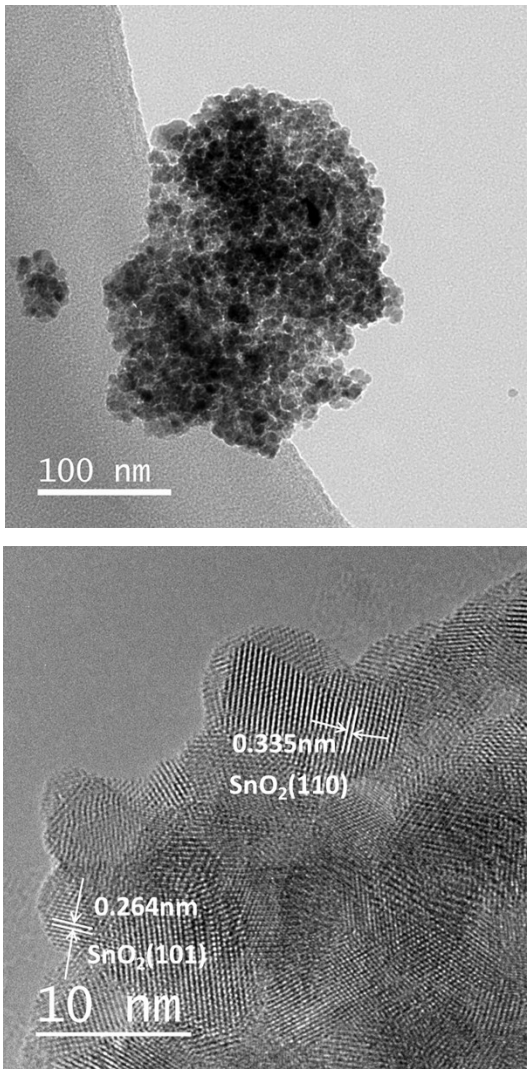

Figure S1. TEM of ATO support.

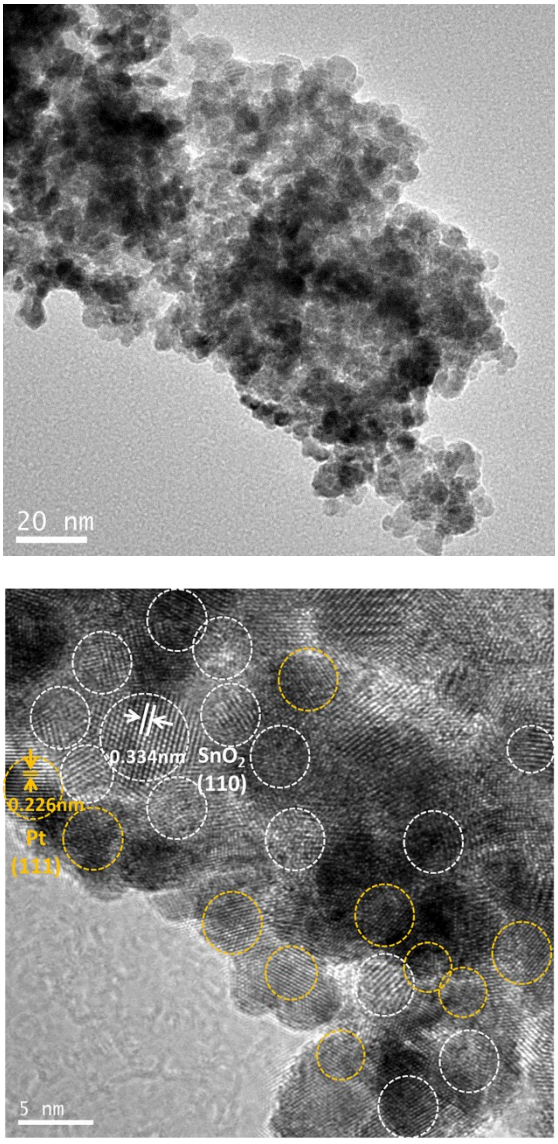

Figure S2. TEM of Pt/ATO-200-5min.

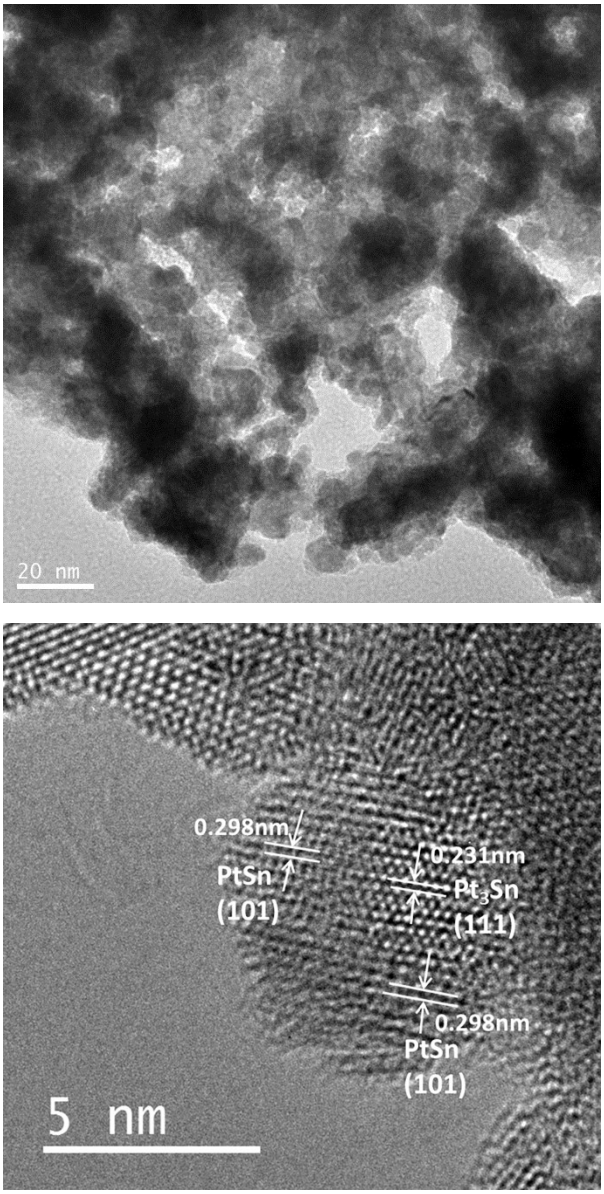

Figure S3. TEM of Pt/ATO-200-2h.

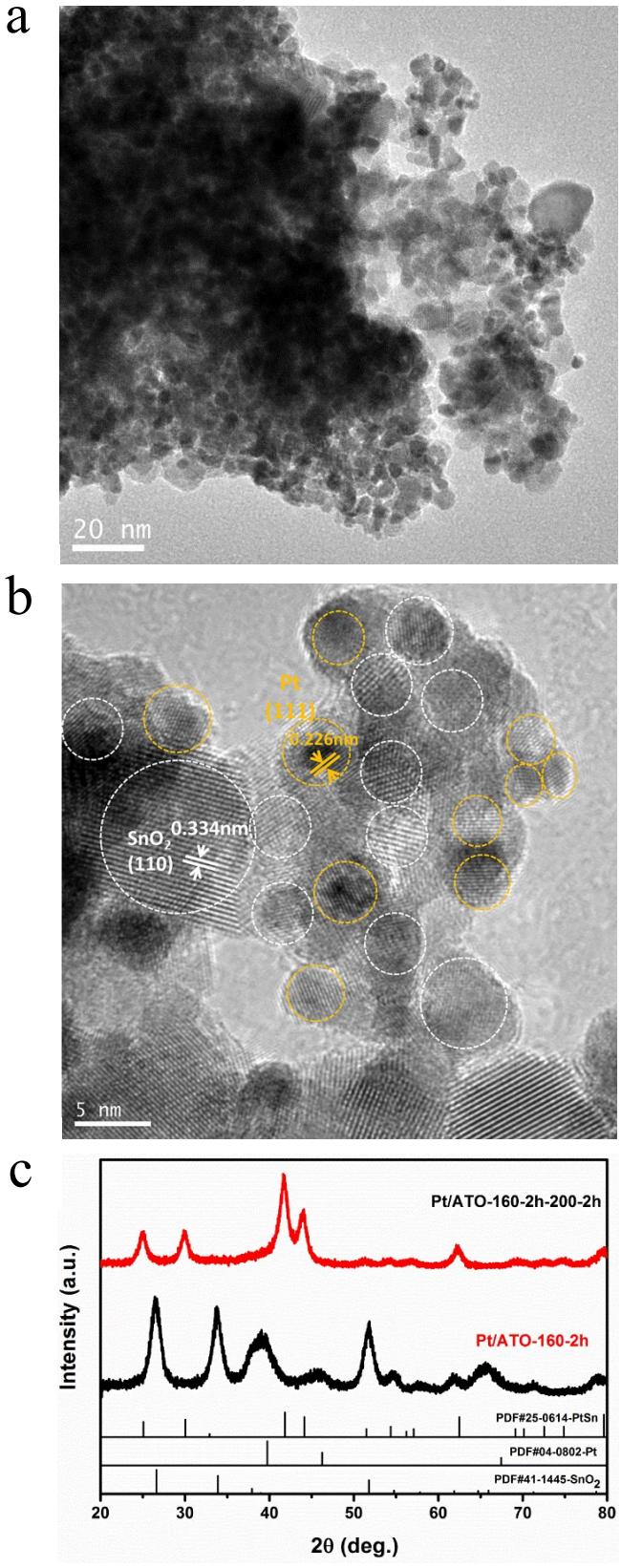

Figure S4. (a) and (b)TEM of Pt/ATO-160-2h. (C) XRD of Pt/ATO-160-2h and Pt/ATO-160-2h heated up to 200 ℃ for 2 h in EG solution.

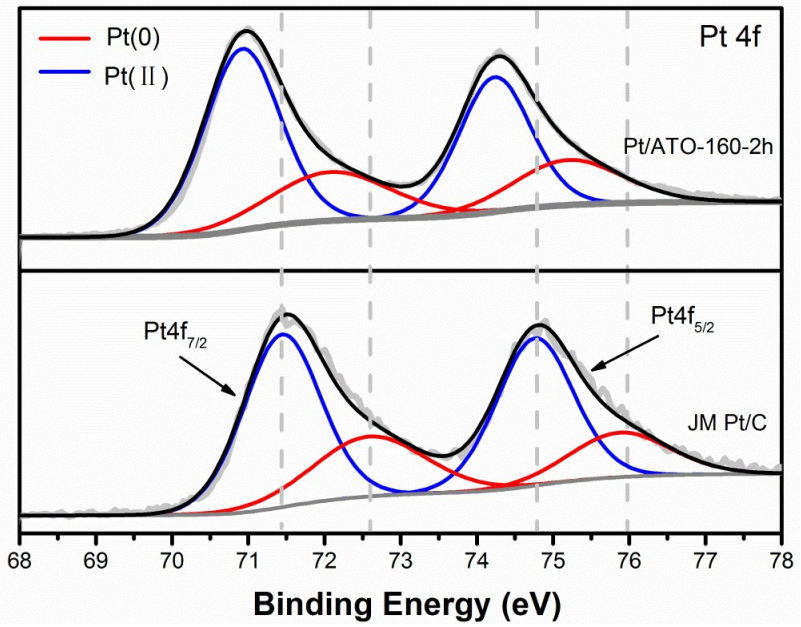

Figure S5. XPS spectra of Pt 4f for JM Pt/C and Pt/ATO-160-2h catalysts.

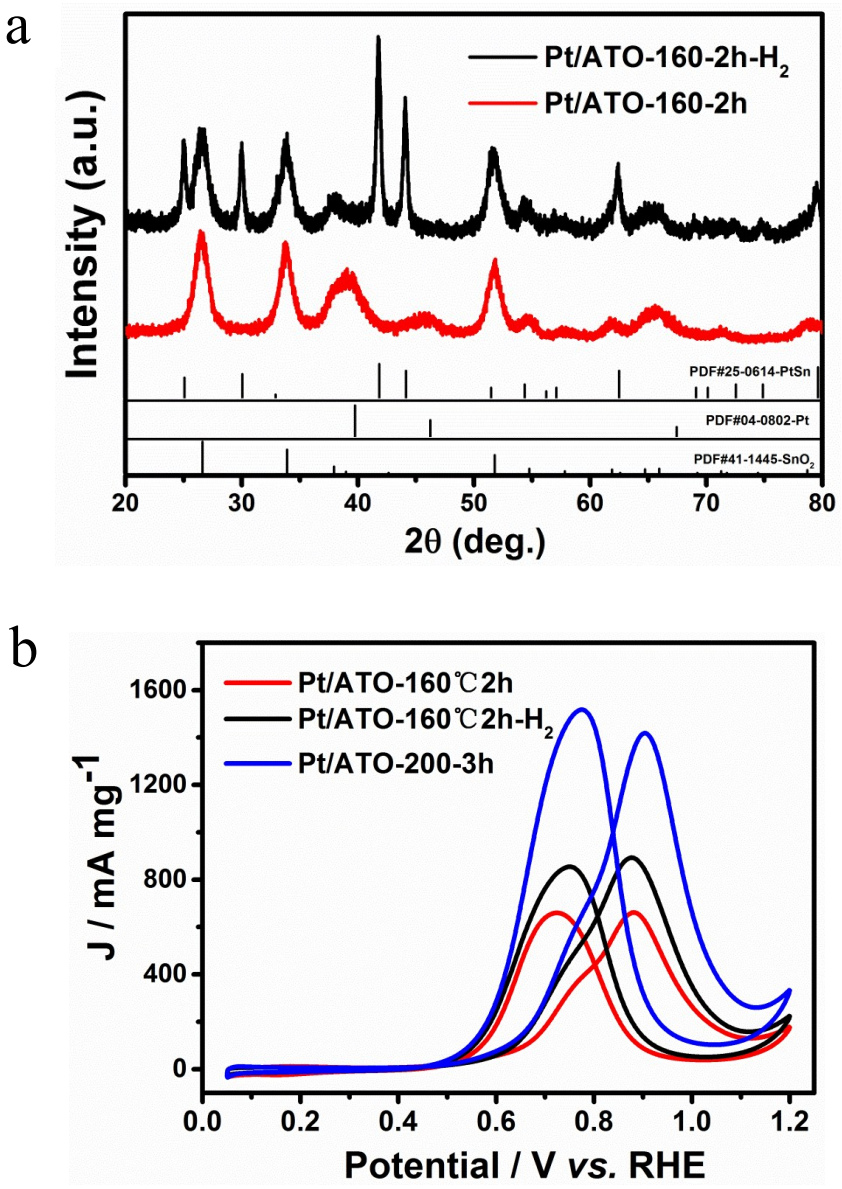

Figure S6. (a) XRD of Pt/ATO-160-2h and Pt/ATO-160-2h annealing at 300℃ in H_2/N_2 (denoted as Pt/ATO-160-2h-H_2) for 2h. (b) CV curves of Pt/ATO-160-2h, Pt/ATO-160-2h-H_2 and Pt/ATO-200-3h catalysts in 0.5 M H_2SO_4 + 1 M CH_3OH solution with a sweep rate of 50 mV s^{-1}.

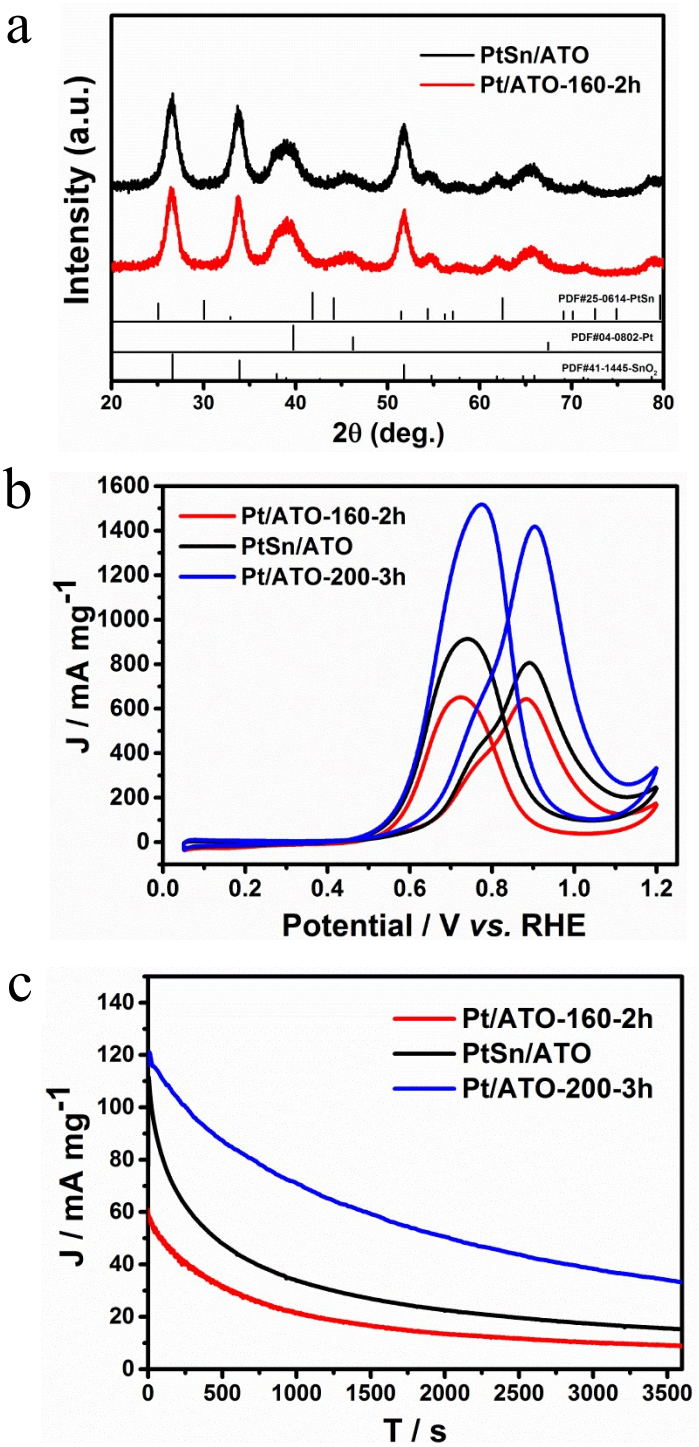

Figure S7. (a) XRD of Pt/ATO-160-2h, PtSn/ATO catalysts. (b) CV curves of Pt/ATO-160-2h, PtSn/ATO and Pt/ATO-200-3h catalysts in 0.5 M H_2SO_4 + 1 M CH_3OH solution with a sweep rate of 50 mV s^{-1}. (c) Chronoamperometric curves of Pt/ATO-160-2h, PtSn/ATO and Pt/ATO-200-3h catalysts in N_2-saturated 0.5 M H_2SO_4 + 1 M CH_3OH solution at constant voltage 0.6 V for 60 mins.

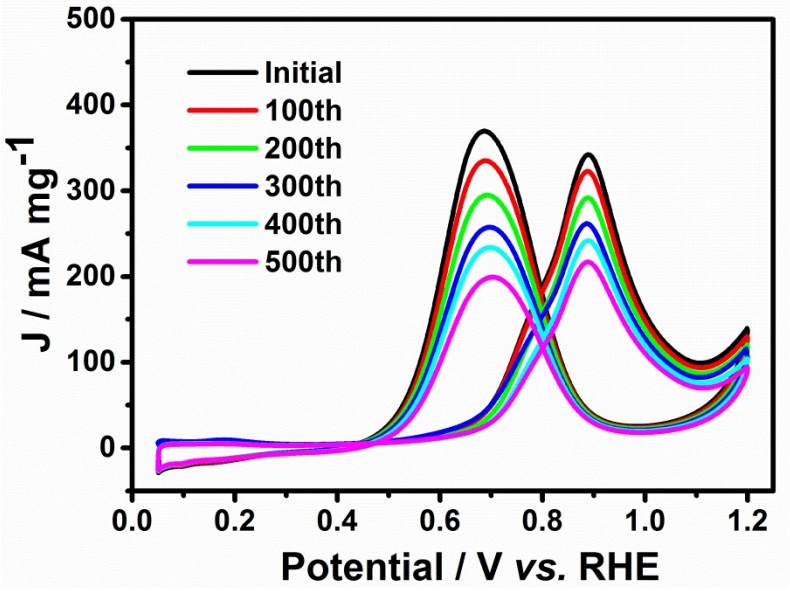

Figure S8. Cyclic voltammogram of Pt/C catalyst in N_2-saturated 0.5 M H_2SO_4 + 1 M CH_3OH solution at scan rate of 50 mV s^{-1} during the durability tests.

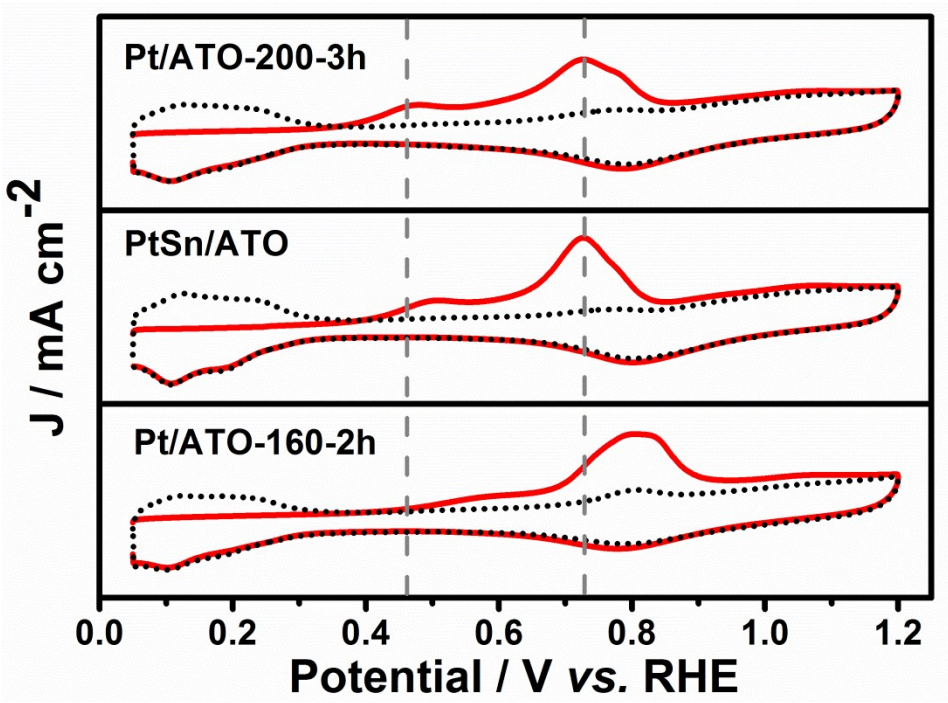

Figure S9. CO stripping patterns of Pt/ATO-160-2h, PtSn/ATO and Pt/ATO-200-3h catalysts in 0.5 M of H_2SO_4.

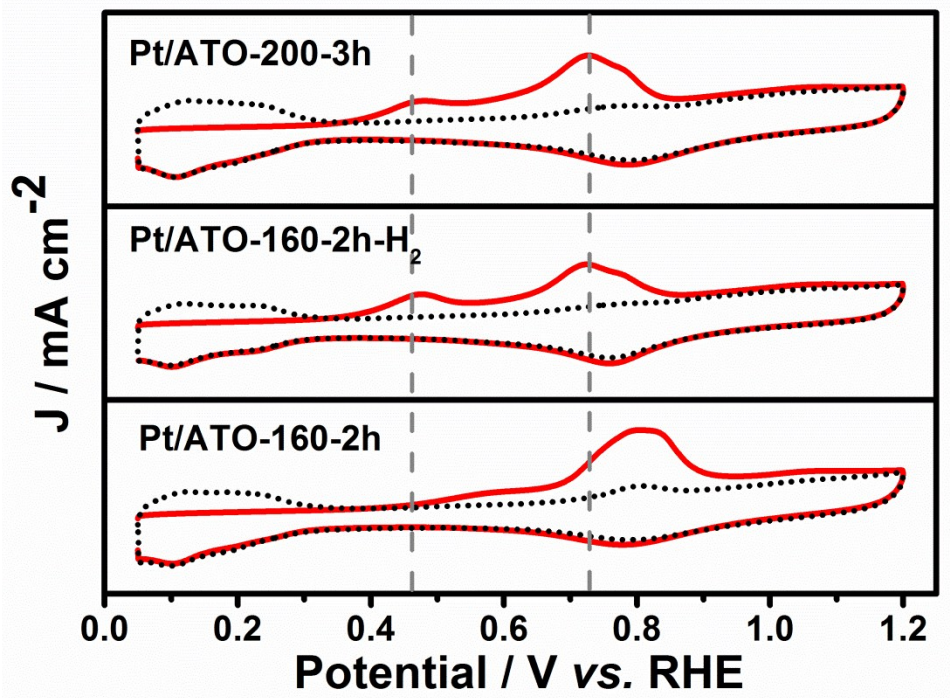

Figure S10. CO stripping patterns of Pt/ATO-160-2h, Pt/ATO-160-2h-H_2 and Pt/ATO-200-3h catalysts in 0.5 M of H_2SO_4.

Table S1. ICP-OES of Pt and Sn mass percentage of different catalysts.

Samples	Pt/ATO-200 -5min	Pt/ATO-200 -0.5h	Pt/ATO-200 -2h	Pt/ATO-200 -3h
Pt	18	21	29	35
Sn		5	12	21

Table S2. XPS spectra of different catalysts with Sn 3d.

Samples	$Sn^{4+}3d_{5/2}$	$Sn^{0}3d_{5/2}$	$Sn^{4+}3d_{3/2}$	$Sn^{0}3d_{3/2}$
ATO	486.8	-	495.2	-
Pt/ATO-200-5min	487.04	485.38	495.45	493.79
Pt/ATO-200-0.5h	486.99	485.35	495.43	493.87
Pt/ATO-200-2h	486.9	485.28	495.31	493.78
Pt/ATO-200-3h	486.63	485.2	494.95	493.55

Table S3. XPS spectra of different catalysts with Pt 4f.

Samples	$Pt^{0}4f_{7/2}$	$Pt^{2+}4f_{7/2}$	$Pt^{0}4f_{5/2}$	$Pt^{2+}4f_{5/2}$
JM Pt/C	71.45	72.60	74.77	75.91
Pt/ATO-200-5min	70.78	71.82	74.06	75.22
Pt/ATO-200-0.5h	70.84	71.93	74.21	75.37
Pt/ATO-200-2h	71.18	72.32	74.54	75.7
Pt/ATO-200-3h	71.23	72.36	74.56	75.74

Table S4. ECSA of Pt/C and Pt/ATO-200 series catalysts.

Samples	Pt/C	Pt/ATO-200 -5min	Pt/ATO-200 -0.5h	Pt/ATO-200-2h	Pt/ATO-200 -3h
ECSA (m^2 g^{-1})	52	41.2	32.7	28.7	25.4

Table S5. Electrochemical activity of the catalysts reported in the literature currently and compared with our Pt/ATO-200-3h catalyst.

Catalysts	Onset Potential (V vs. RHE) from CO	Peak currents MA (mA mg_{Pt}^{-1})	Electrolytes	Ref.
Pt/ATO-200-3h	0.36	1520	0.5M H_2SO_4 + 1M CH_3OH	This work
Pt_3V/C	~0.42	~490	0.1 M $HClO_4$ + 1 M CH_3OH	2
Pt_3Ti/C	~0.42	~380	0.1 M $HClO_4$ + 1 M CH_3OH	2
PtRu NWs	-	820	0.1 M $HClO_4$ + 0.5 M CH_3OH	3
JM-PtRu/C	~0.4	1253.5	0.5 M H_2SO_4 + 1 M CH_3OH	4
Pt/CeO2-P	~0.6	714	0.5 M H_2SO_4 + 1 M CH_3OH	5
PtFe@PtRuFe	0.39	690	0.1 M $HClO_4$ + 0.5 M CH_3OH	6
PtPb CNCs	-	970	0.1 M $HClO_4$ + 0.5 M CH_3OH	7
$PtPb_{0.27}$ NWs	-	1210	0.1 M HClO4 + 0.15 M CH3OH	8
PtSn	-	350	0.5 M H_2SO_4 + 0.5 M CH_3OH	9
PtRuCu/C	~0.6	1350	0.1 M $HClO_4$ + 1 M CH_3OH	10
Pd@PtNi NPs	~0.65	782	0.5 M H_2SO_4 + 0.5 M CH_3OH	11
$Pt_{94}Zn_6$ NWs	~0.65	511.3	0.1 M $HClO_4$ + 0.2 M CH3OH	12

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