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Ultra-thin Carbon Layer Stabilized Metal Catalysts towards Oxygen Reduction

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Table S1 Pt content of the catalysts determined by inductively coupled plasma optical emission spectrometry.

	Pt/C	Pt-SS/C	Pt/C-H	Pt-UTCL/C
Pt content	19.69%	20.06%	21.86%	22.63%

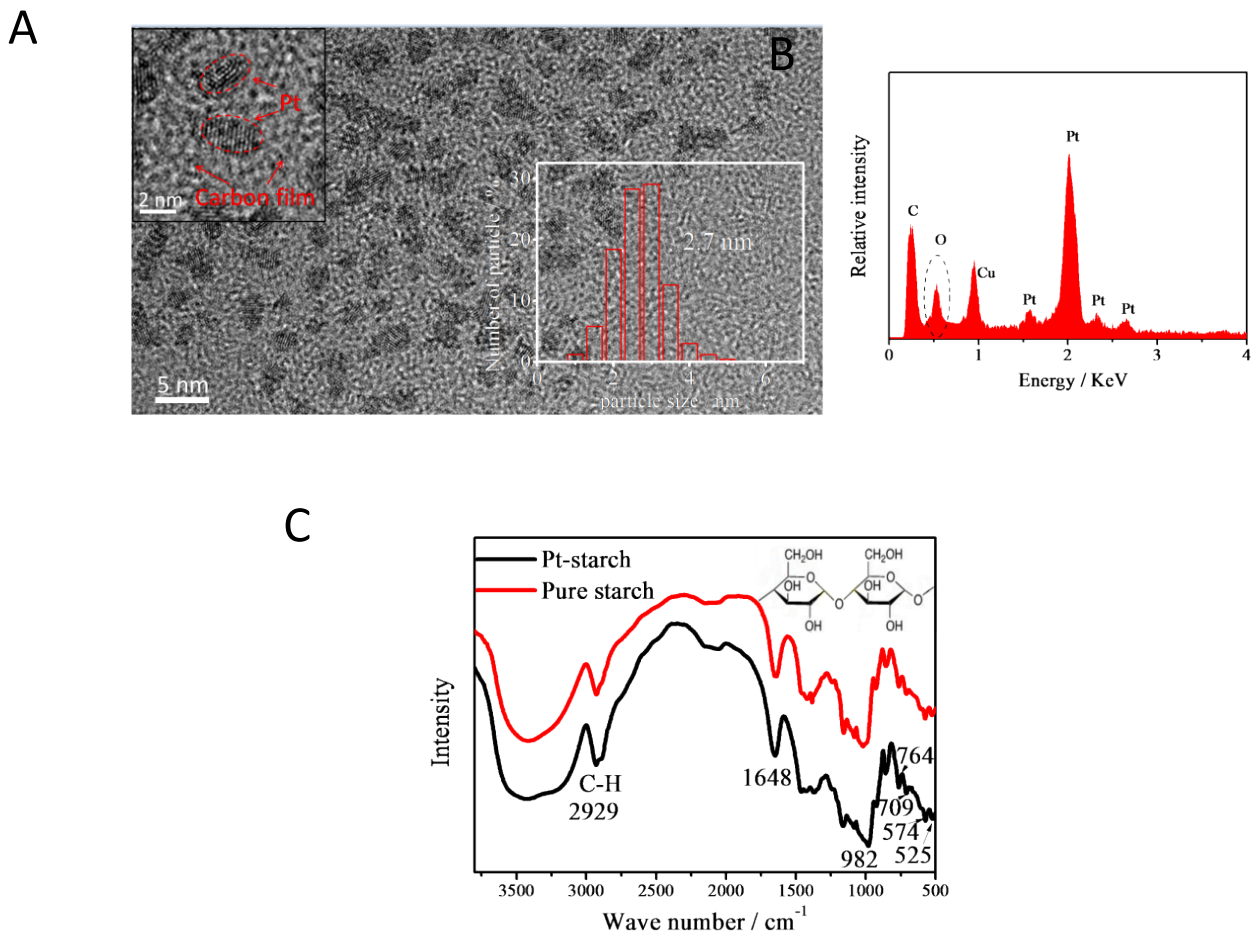

Figure S1 (A) TEM image of colloidal Pt NPs with insets of an enlarged image of Pt NPs (left) and a Pt size distribution graph (right). (B) A corresponding EDX spectra of the TEM image. (C) comparison of FTIR spectra of pure starch vs. Pt-starch with some characteristic peaks of starch are marked out. The inset is a typical chemical structural formula of starch.

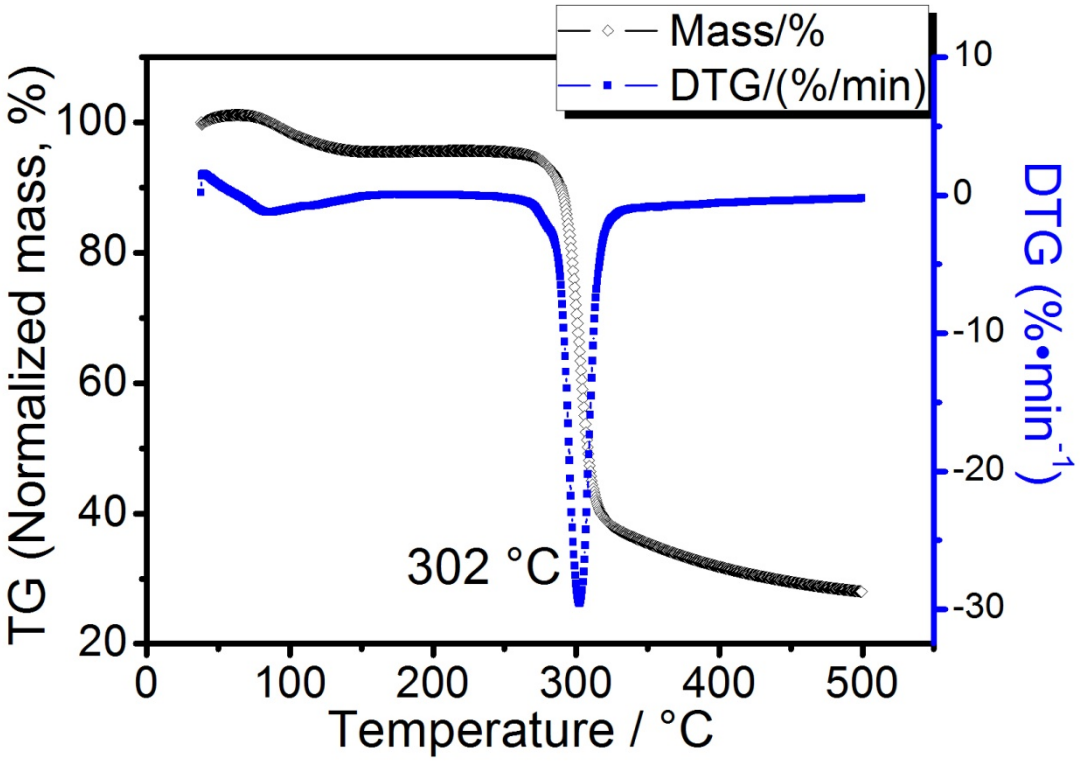

Figure S2 TG analysis for pure starch recorded in nitrogen atmosphere. The DTG curve show that the carbonization temperature of pure starch was at around 302 °C .

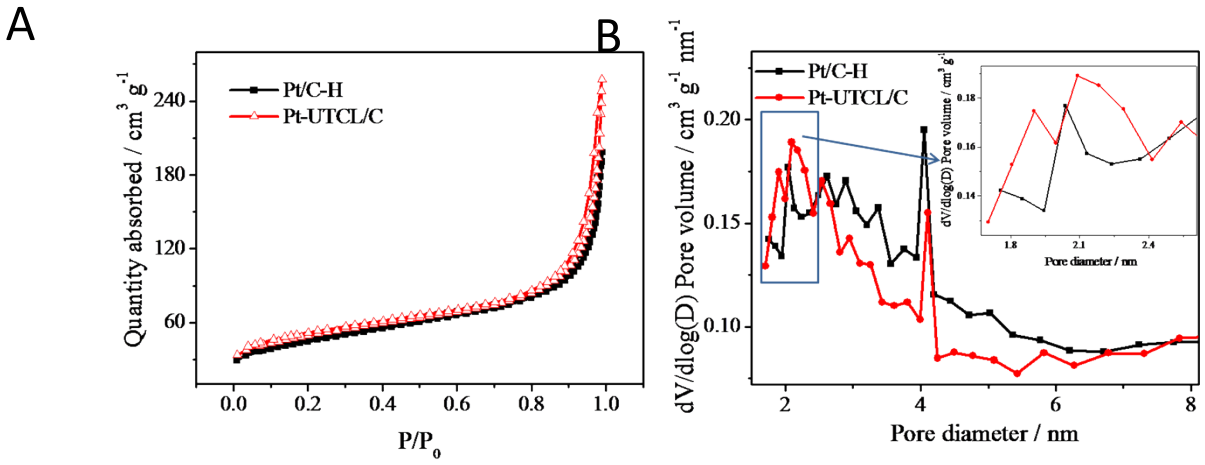

Figure S3 (A) Low-temperature N_2 (77.4 K) adsorption/desorption isotherms of Pt/C-H and Pt-UTCL/C; (B) Pore size distribution of Pt/C-H and Pt-UTCL/C from the BET analysis.

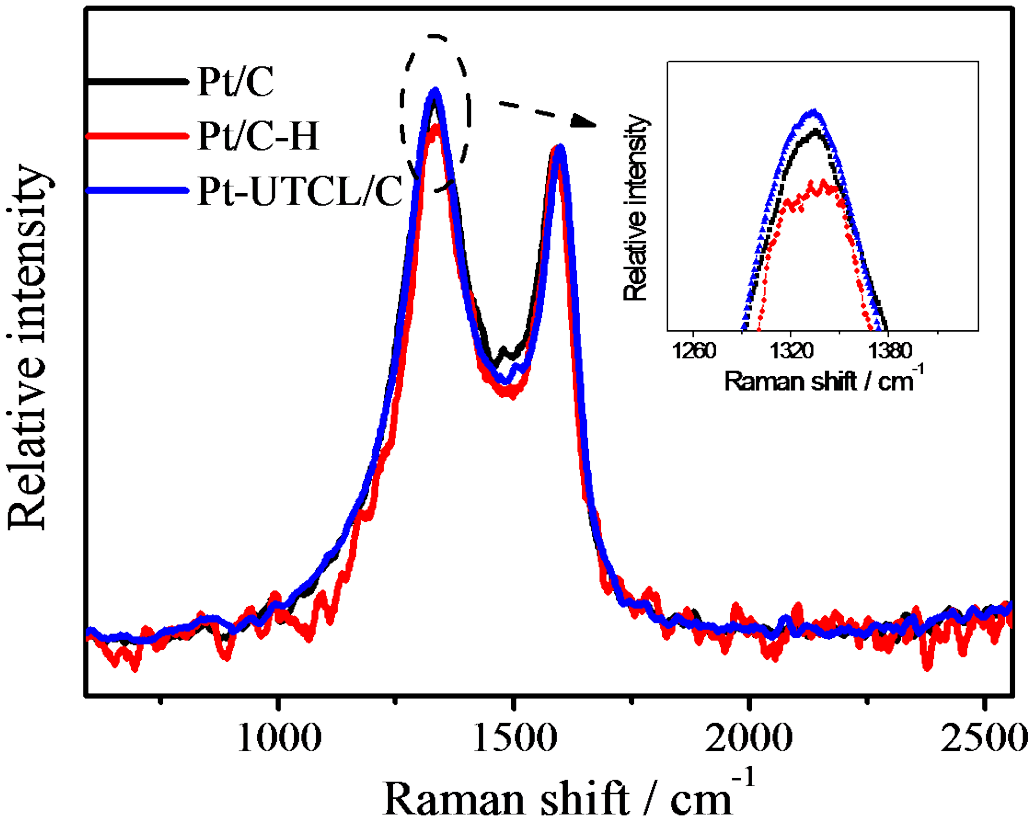

Figure S4 Raman spectra for Pt/C, Pt/C-H, Pt-UTCL/C catalysts with the intensities normalized by G band (1596 cm^{-1}). The insert is an enlarged image of D band (1328 cm^{-1}).

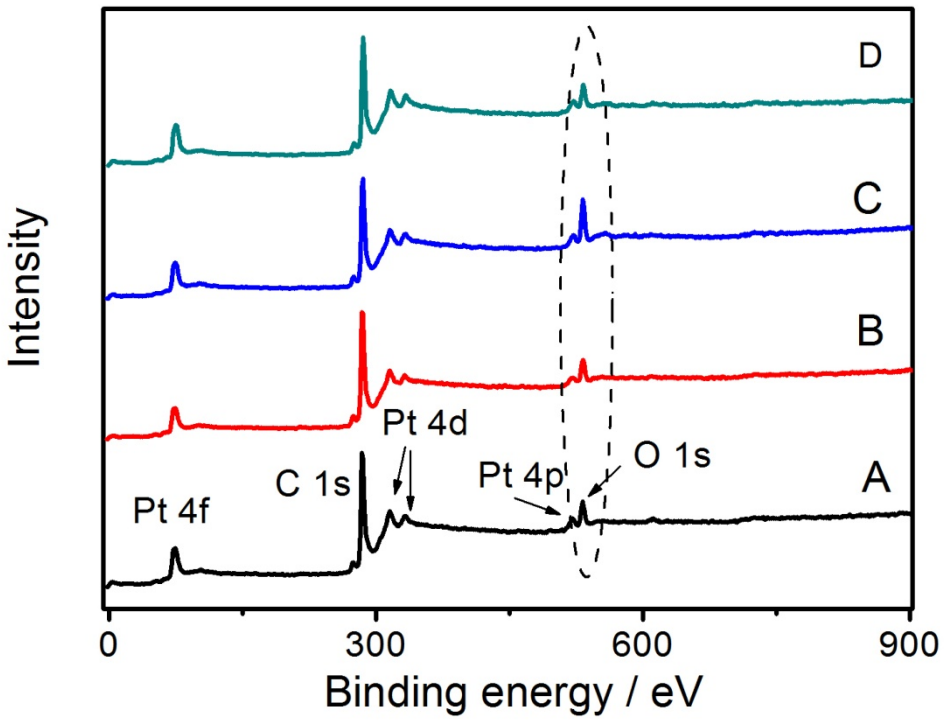

Figure S5 XPS spectra of Pt/C (A), Pt/C-H (B), Pt-SS/C (C) and Pt-UTCL/C (D) catalysts. As shown C(1s) signal at 284.2 eV and the O(1s) signal at 543.1 eV, the Pt(4f), Pt(5s), Pt(4p), and Pt(4d) signals appear in samples. It is noteworthy that the O(1s) signal of Pt-SS/C is stronger than that of other catalysts, which is ascribed to the contribution of oxygen element in SS. This confirms the successful introduction of SS into Pt-SS/C.

Table S2 The surface elemental composition of C, O, and Pt elements in each catalyst originated from XPS.

Sample	C	O	Pt
Pt/C	87.63	9.34	3.03
Pt/C-H	88.61	9.04	2.35
Pt-SS/C	83.35	14.22	2.44
Pt-UTCL/C	88.24	8.65	3.11

It is noteworthy that the oxygen content of Pt-SS/C is larger than that of other catalysts due to the contribution of SS. In addition, it can been seen that the contents of C and O for Pt/C-H rarely change compared with those of Pt/C, indicating that the heat treatment rarely to the surface structure of Pt/C catalyst.

Table S3 The fitted peaks of Pt4f and C1s and their relative atomic ratio along with their binding energies.

Pt4f		$Pt4f_{7/2}$ (Pt 0)	$Pt4f_{5/2}$ (Pt 0)	$Pt4f_{7/2}$ ($Pt\ 2^+$)	$Pt4f_{5/2}$ ($Pt\ 2^+$)	$Pt4f_{7/2}$ ($Pt\ 4^+$)	$Pt4f_{5/2}$ ($Pt\ 4^+$)
Pt/C	at.%	31.59	23.69	12.39	9.29	11.52	11.52
	eV	71.94	75.27	73.12	76.67	74.74	77.93
Pt/C-H	at.%	33.33	25.00	13.56	10.17	10.25	7.69
	eV	71.94	75.43	72.99	76.89	74.68	78.74
Pt-UTCL/C	at.%	32.64	24.48	13.34	10.01	11.16	8.37
	eV	72.29	75.69	73.66	77.38	75.09	79.14

C1s		sp2 C	sp3 C	C-O carbon (C(epoxy)/ C-OH)	carbonyl carbon (C=O)	carboxylate carbon (O-C=O)
Pt/C	at.%	50.58	30.72	11.54	4.65	2.51
	eV	284.32	284.96	286.02	287.15	288.88
Pt/C-H	at.%	59.36	21.93	9.27	6.26	3.19
	eV	284.35	285.02	285.99	286.83	288.63
Pt-UTCL/C	at.%	53.30	26.56	10.71	6.59	2.85
	eV	284.09	284.68	285.66	286.58	288.68

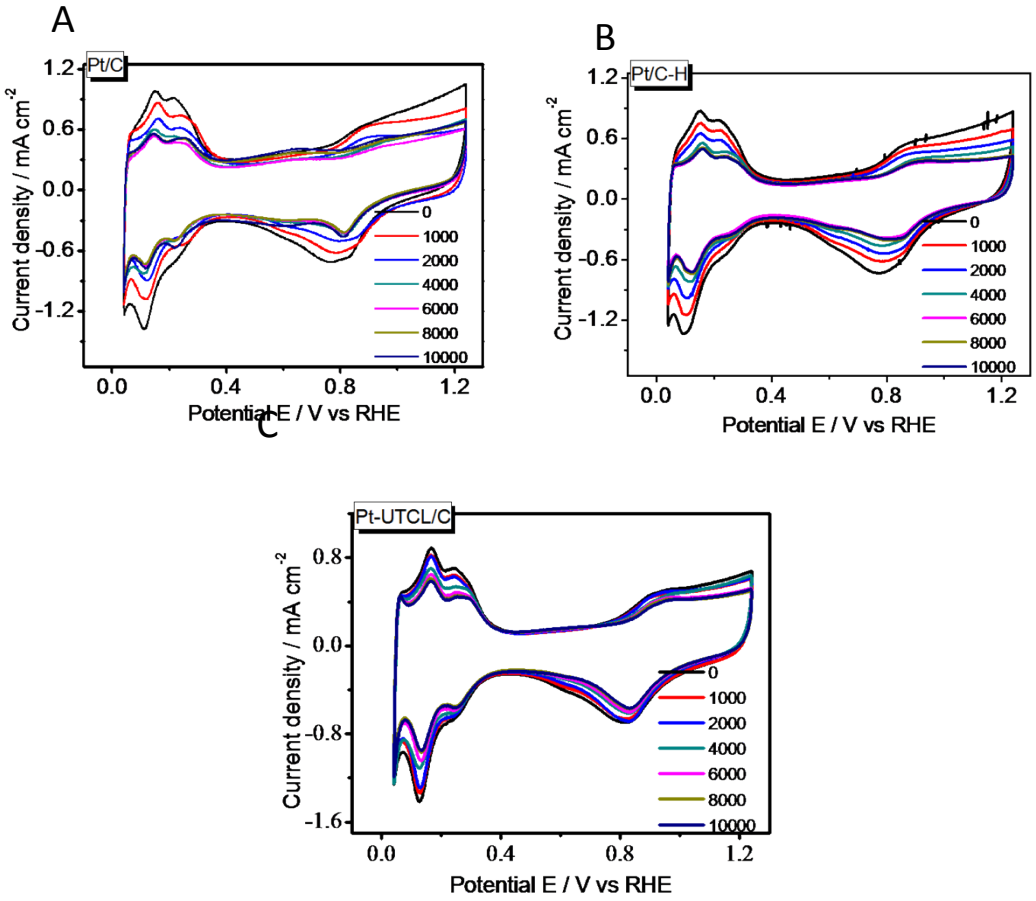

Figure S6 A group of CV curves after certain numbers of potential cycling for (A) Pt/C, (B) Pt/C-H, (C) Pt-UTCL/C in 0.1 mol L^{-1} $HClO_4$ at the scan rate of 50 mV/s.

Table S4 The mass activity, onset potential, half-wave potential, transfered electron number **(n)** and Tafel slope values for the catalysts.

Sample	mass activity (A/g)	onset potential (V vs. RHE)	half-wave potential (V vs. RHE)	**n**※	Tafel slope (mV dec^{-1})
Pt /C	123.8	1.022	0.865	4	-63
Pt-UTCL/C	112.5	1.021	0.861	4	-65

※ "**n**" refers to the number of electron in the reduction process of one oxygen molecule.

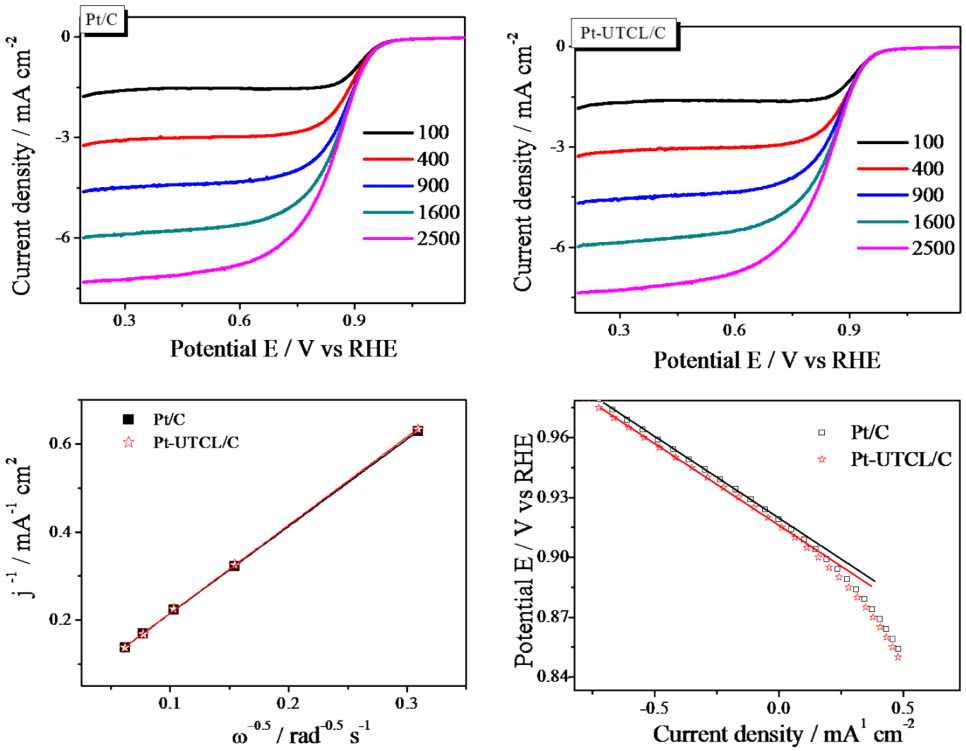

Figure S7 The RDE voltammograms of Pt/C (A) and Pt-UTCL/C (B) at different rotating rates (100-2500 rpm) in O_2-saturated 0.1 mol L^{-1} $HClO_4$ at the scan rate of 10 mV/s. (C) Koutecky´ –Levich plot of j^{-1} vs $\omega^{-1/2}$ obtained from the RDE data of (A, B) at 0.3 V vs. RHE. (D) Tafel plots for Pt/C and Pt-UTCL/C extracted from (A, B).