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Supporting information

Well-controlled Pt-CeO_2-nitrogen doped carbon triple-junction catalysts with enhanced activity and durability for oxygen reduction reaction

Qizi Lu,[#] Zhili Wang,[#] Yuanting Tang, Chaojun Huang, Aimin Zhang, Feng Liu, Xiao Liu,[*] Bin Shan, Rong Chen,[*]

# Qizi Lu and Zhili Wang contributed equally to this work.

* Corresponding authors: *xiaoliu@hust.edu.cn* (Xiao Liu); *rongchen@mail.hust.edu.cn* (Rong Chen)

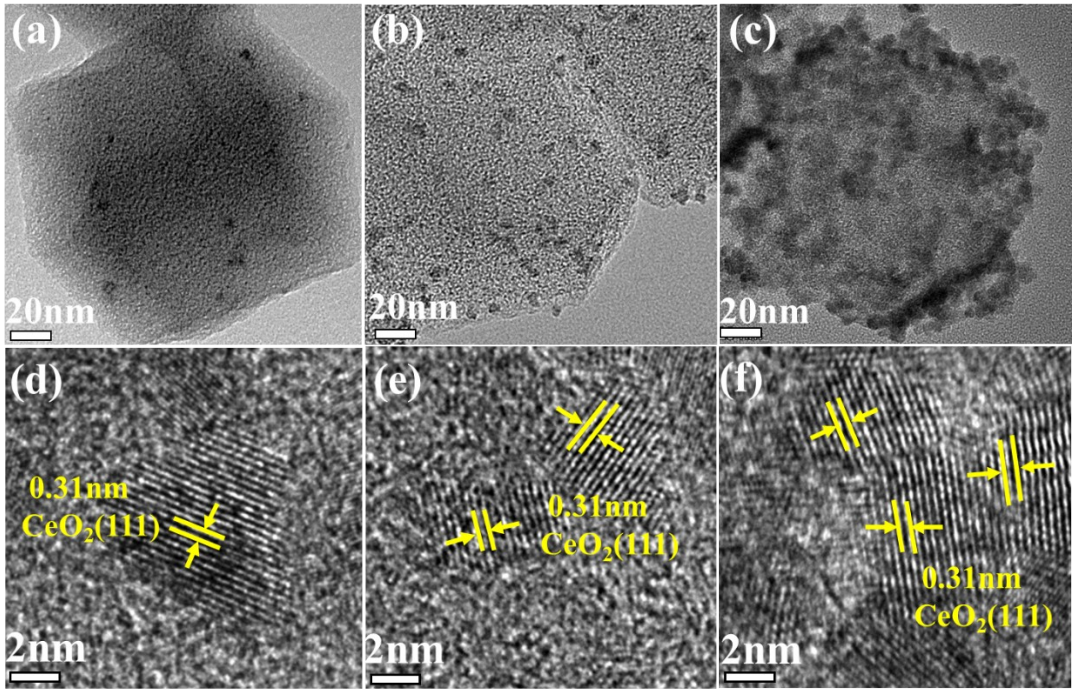

Fig. S1. TEM images of different contents of CeO_2 on the nitrogen-doped carbon (NC) substrate. (a) $0.2CeO_2$/NC, (b) $0.3CeO_2$/NC, (c) $1.0CeO_2$/NC. The average size of CeO_2 on the surface of NC became larger with the increase of the mass ratio of CeO_2 and NC. High resolution TEM images of (d) $0.2CeO_2$/NC, (e) $0.3CeO_2$/NC, (f) $1.0CeO_2$/NC. The specific lattice fringe of 0.31 nm corresponding to CeO_2(111) was labeled.

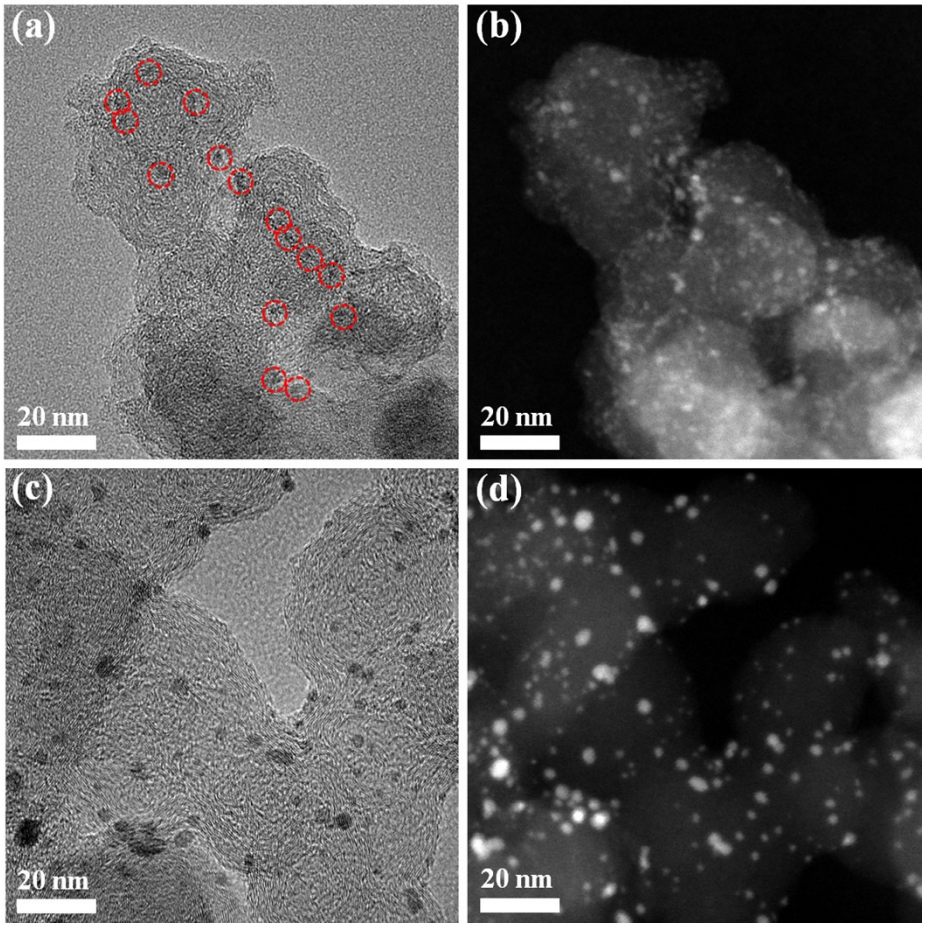

Fig. S2. TEM and HADDF images of (a-b) 0.3CeO_2/C; (c-d) Pt/0.3CeO_2/C.

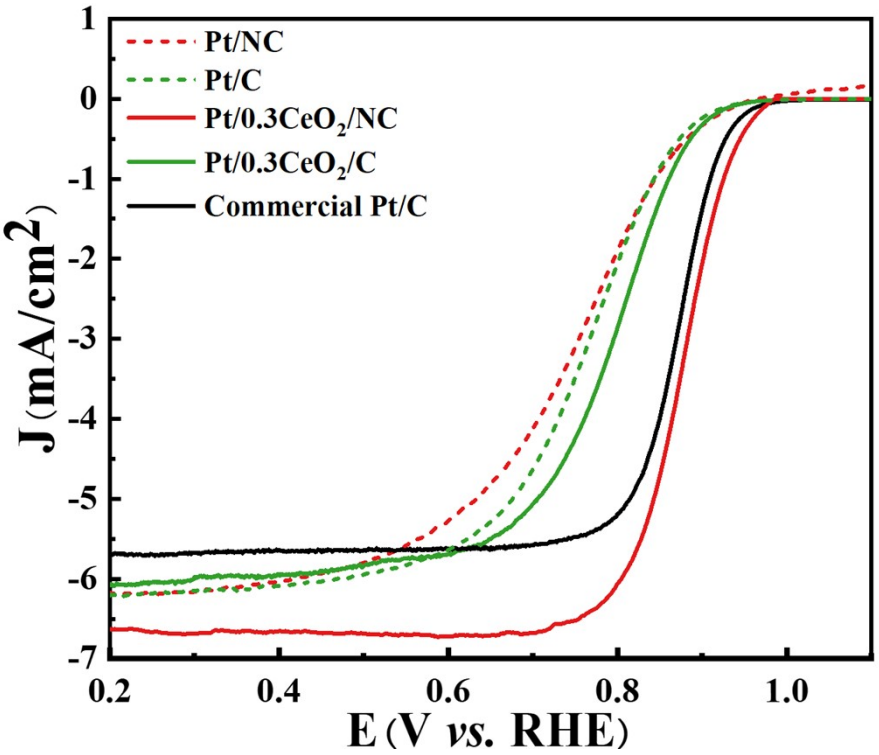

Fig. S3. LSV curves of Pt/NC, Pt/C, Pt/0.3CeO_2/NC, Pt/0.3CeO_2/C and commercial Pt/C for ORR obtained at a rotating rate of 1600 rpm in 0.1 M $HClO_4$ solution.

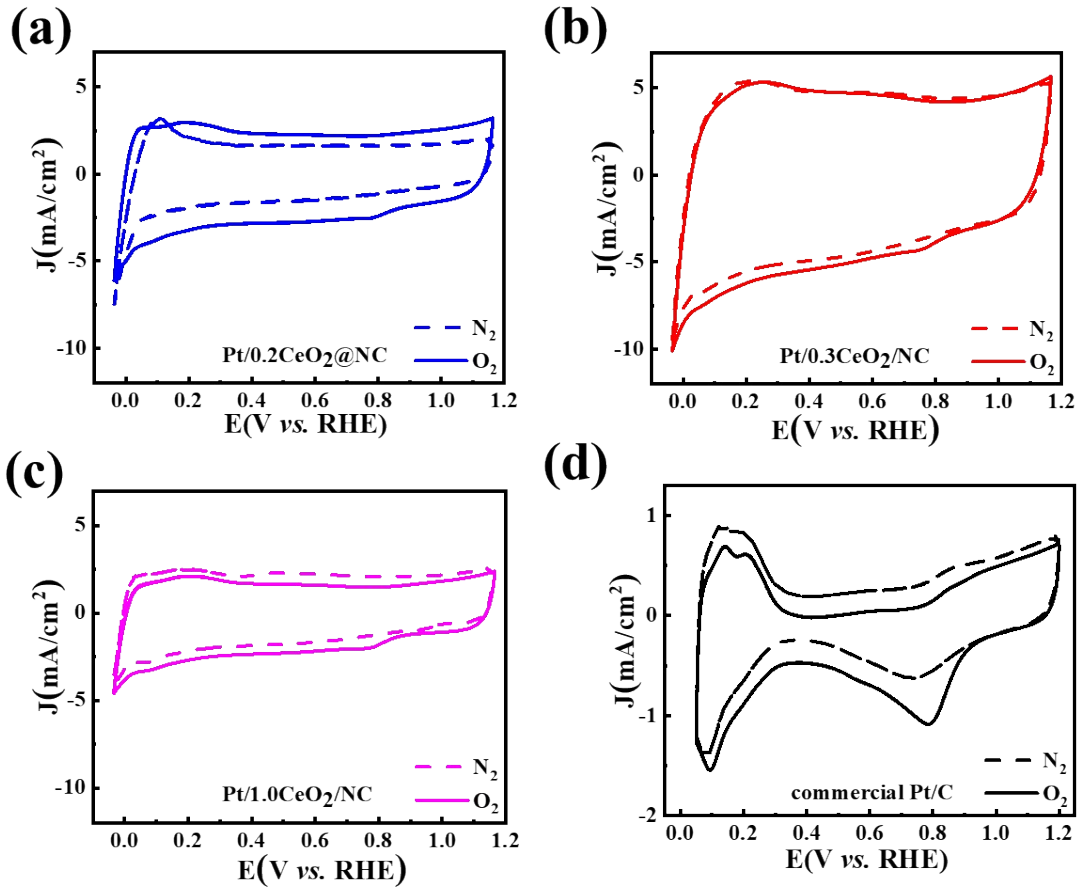

Fig. S4. Electrochemical performance test. Cyclic voltammogram (CV) curves of the catalysts Pt/xCeO_2/NC (x = 0.2, 0.3, 1.0) and commercial Pt/C in N_2-saturated and O_2-saturated 0.1 M $HClO_4$ solution. The electrochemical measurements were performed in a CHI 760E electrochemical workstation from 0 to 1.2 V vs. RHE with scan rate of 50 mV s^{-1}.

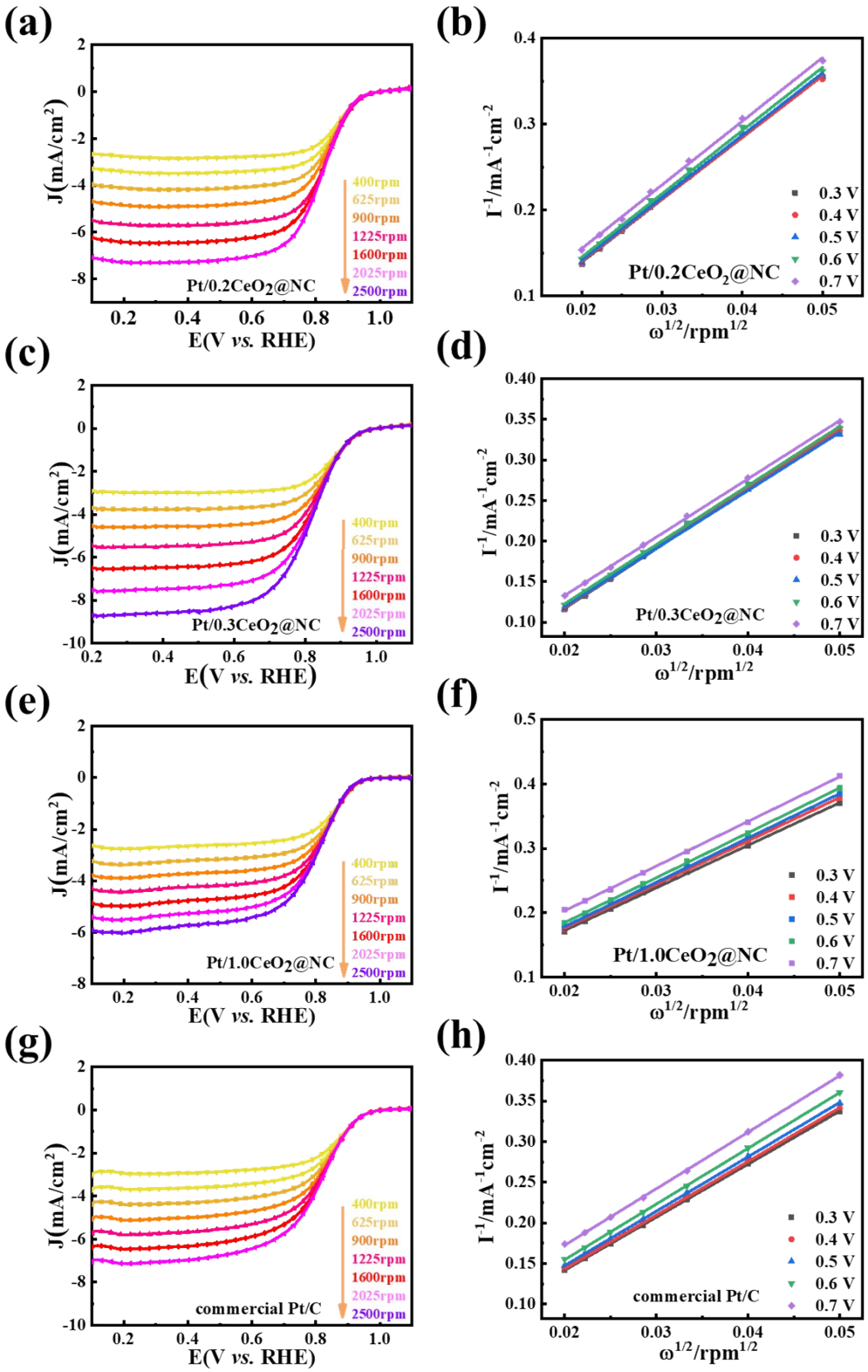

Fig. S5. Linear scan voltammetry (LSV) curves from 400 to 2500 rpm and the corresponding K-L curves of ((a) and (b)) Pt/0.2CeO_2/NC, ((c) and (d)) Pt/0.3CeO_2/NC, ((e) and (f)) Pt/1.0CeO_2/NC and ((g) and (h)) commercial Pt/C from 0 to 1.2 V vs. RHE with scan rate of 10 mV s^{-1} in O_2-saturated 0.1 M $HClO_4$ solution.

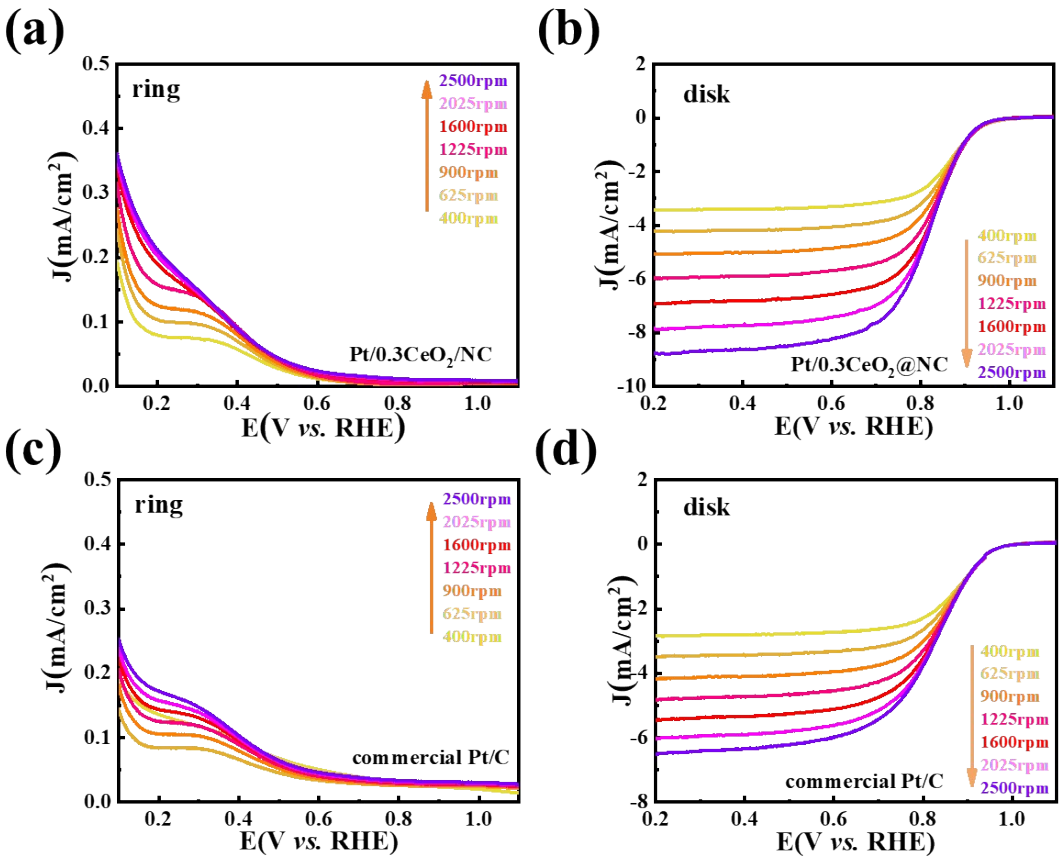

Fig. S6. The ring and disk LSV curves on RRDE of ((a) and (b)) Pt/0.3CeO_2/NC ((c) and (d)) commercial Pt/C in O_2-saturated 0.1 M $HClO_4$ solution at 400-2500 rpm.

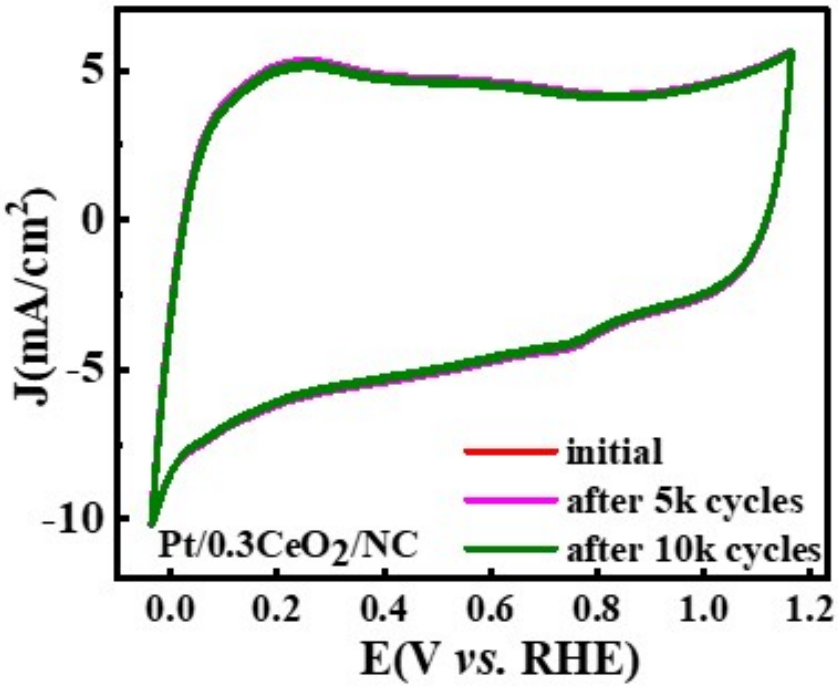

Fig. S7. Accelerated durability test CV curves of the catalyst Pt/0.3CeO_2/NC in O_2-saturated 0.1 M $HClO_4$ solution after 10000 cycles of ADT at 0.6-1.0 V *vs.* RHE with the scanning rate of 100 mV s^{-1}.

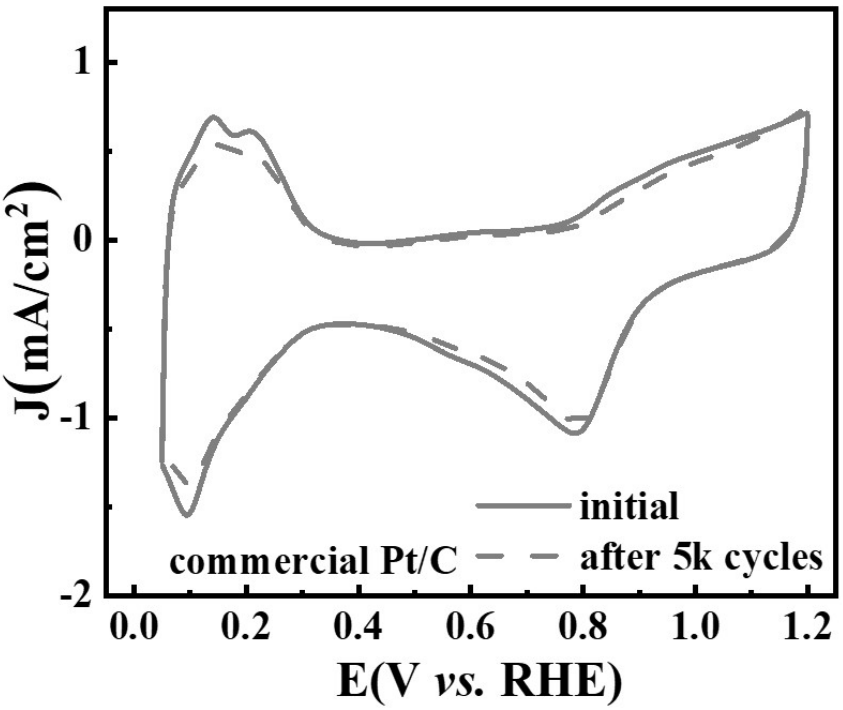

Fig. S8. Accelerated durability test CV curves of commercial Pt/C in O_2-saturated 0.1 M $HClO_4$ solution after 5000 cycles of ADT at 0.6-1.0 V *vs.* RHE with the scanning rate of 100 mV s^{-1}.

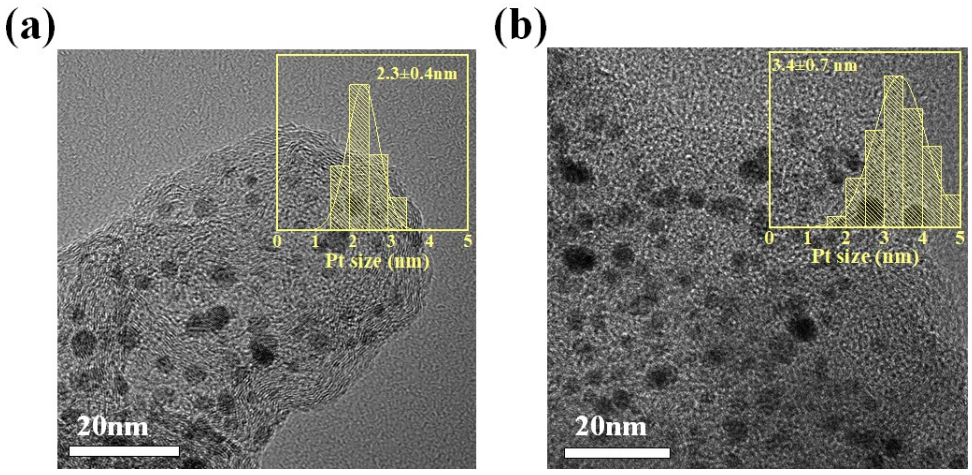

Fig. S9. TEM image of (a) commercial Pt/C; (b) commercial Pt/C after 10000 cycles ADT with corresponding size distribution is inserted.

Table S1. The ratios of different valence states of O 1s, Ce 3d and Pt 4f for the catalysts Pt/xCeO_2/NC (x = 0.2, 0.3, 1.0), 0.3CeO_2/NC and Pt/NC. The XPS spectra of O 1s were split into three O species including O_a (lattice oxygen), O_b (chemically adsorbed oxygen), and O_c (physically adsorbed oxygen), respectively. And the relative content of O_b has a positive influence on the ORR performance. The XPS spectra of Ce 3d were split to Ce^{3+} and Ce^{4+} into the prepared catalysts, the presences of which help with the swift transition of electrons. The XPS spectra of Pt 4f were split into Pt^{4+}, $Pt^{2+}$and Pt^0. The content of Pt^{2+} in Pt/0.3CeO_2/NC is larger than that of Pt/0.2CeO_2/NC and Pt/1.0CeO_2/NC.

		Pt/0.2CeO_2/NC	Pt/0.3CeO_2/NC	Pt/1.0CeO_2/NC	0.3CeO_2/NC	Pt/NC
O 1s	O_a	16.46%	10.39%	20.43%	18.64%	/
	O_b	56.80%	70.79%	54.51%	60.14%	/
	O_c	26.74%	18.82%	25.06%	21.22%	/
Ce 3d	Ce^{3+}	40.79%	59.75%	51.35%	44.4%	/
	Ce^{4+}	59.21%	40.25%	48.65%	55.6%	/
Pt 4f	Pt^0	27.55%	21.46%	30.10%	/	44.15%
	Pt^{2+}	58.18%	68.07%	57.05%	/	41.63%
	Pt^{4+}	14.27%	10.47%	12.85%	/	14.22%

Table S2. The ORR performance of the prepared catalysts. Pt loading is the specific figure of the relative content of Pt on the working electrode. $E_{1/2}$ represents the half-wave potential and J_m is the limited diffusion current density in O_2-saturated 0.1 M $HClO_4$ solution. MA is the mass activity at 0.9 V vs. RHE.

Catalyst	Pt loading ($\mu g\ cm^{-2}$)	$E_{1/2}$ (V *vs.* RHE)	Jm ($mA\ cm^{-2}$)	MA ($mA\ mg_{Pt}^{-1}$)
Pt/NC	10.02	0.757	6.15	47.8
Pt/0.2CeO_2/NC	6.2	0.846	5.57	188.8
Pt/0.3CeO_2/NC	4.98	0.876	6.65	593.6
Pt/1.0CeO_2/NC	5.42	0.834	4.78	104.1
Commercial Pt/C	20	0.872	5.64	97.0

Table S3. The performance comparison towards ORR of the Pt/CeO_2 catalysts in the relative references with our prepared catalysts.

Catalysts	Pt loading ($\mu g\ cm^{-2}$)	$E_{1/2}$ (V)	MA ($mA\ mg^{-1}$)	$\Delta E_{1/2}$ after ADT	ADT (cycles)	Ref.
$Pt/0.3CeO_2/NC$	4.98	0.876	593.6	5mV	10000	This work
Pt/C	20	0.872	97.0	43mV	10000	
$Pt/CeO_2/CNT$-A	26.2	0.865	186	7mV	5000	[1]
$Pt/CeO_2/CNT$-W	39.3	0.85	396	22mV	5000	
$Pt\text{-}CeO_2$-CN	20.4	0.79	122.5	/	/	[2]
$Pt@CeO_2@CNT$	120	0.884	/	16mV	2000	[3]
$Pt/20CeO_2/C$	17	0.86	52.09	/	/	[4]
$Pt\text{-}CeO_2$-C	20	0.86	165	30	6000	[5]
$Pt\text{-}CeO_x$ NW/C	5.6	0.75	159	/	/	[6]
$20Pt\text{-}10CeO_2/C$	2038	0.785	/	/	/	[7]

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