Electronic Supplementary Information

Stabilizing ultra-close Pt clusters on all-in-one CeO_2/Al_2O_3 fibril-in-tubes against sintering

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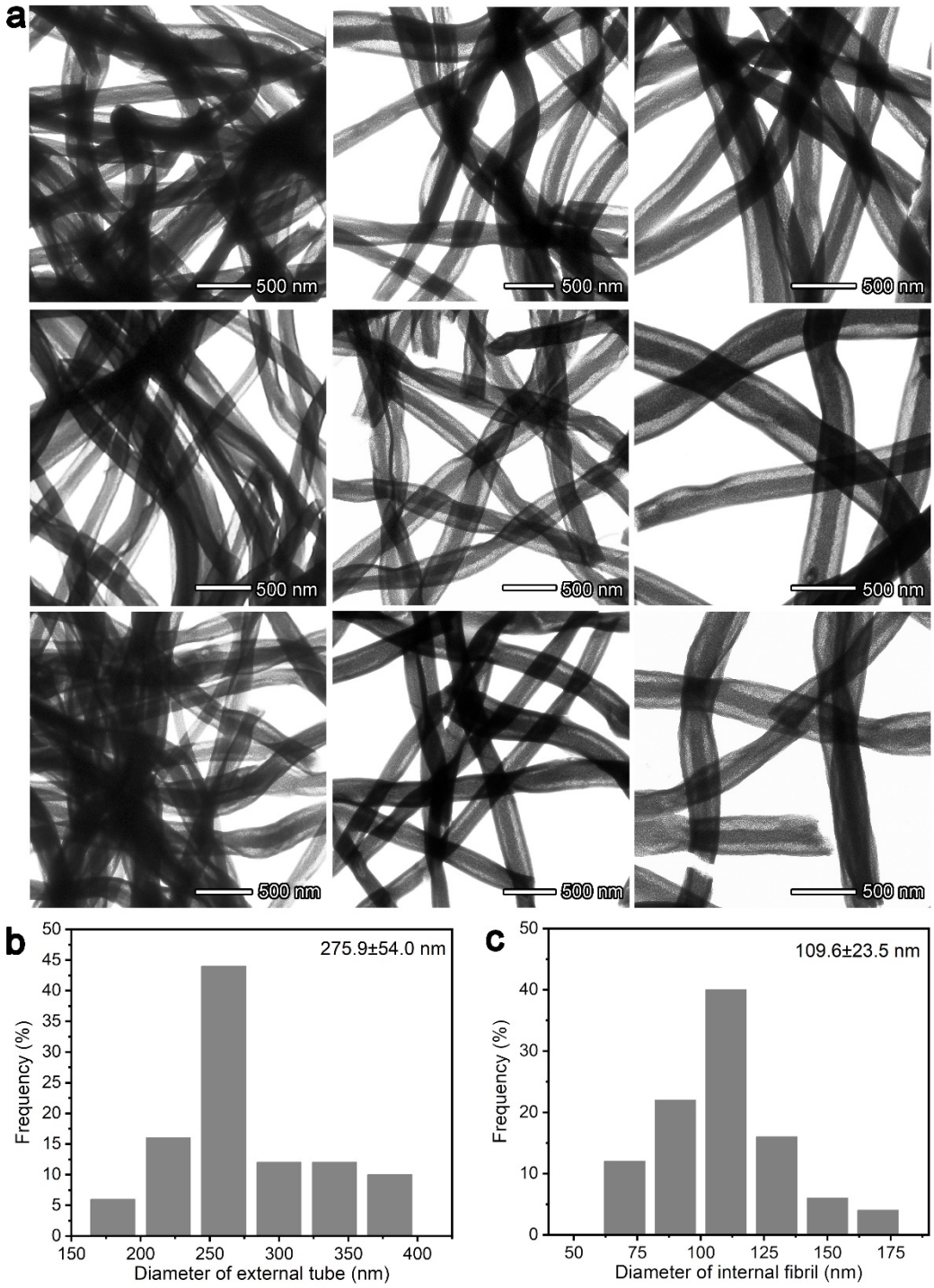

Fig. S1 (a) TEM images of CeO_2/Al_2O_3 fibril-in-tubes at different regions. (b, c) Diameter distribution of the external tube and internal fibril.

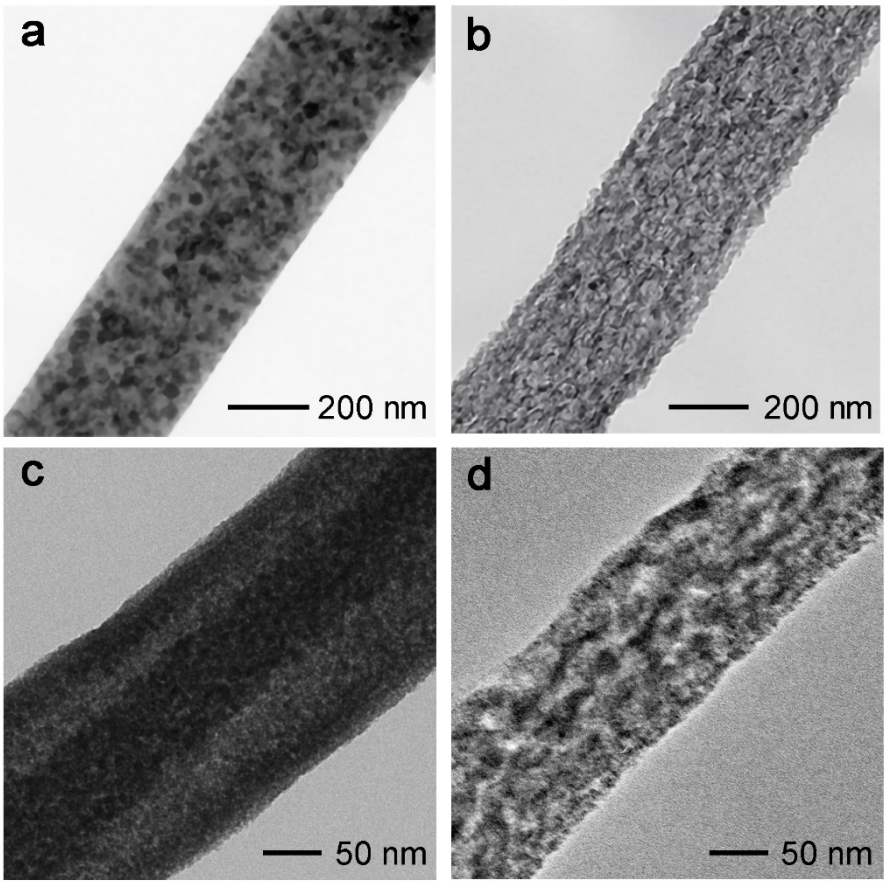

Fig. S2 TEM images of (a) CeO_2, (b) Al_2O_3, (c) CeO_2/Al_2O_3-2.5, and (d) CeO_2/Al_2O_3-0.8 nanofibers.

Note for the fabrication of CeO_2/Al_2O_3-2.5 and CeO_2/Al_2O_3-0.8 nanofibers:

The CeO_2/Al_2O_3-2.5 and CeO_2/Al_2O_3-0.8 nanofibers were prepared by electrospinning a precursor containing 0.087 g (for CeO_2/Al_2O_3-2.5) or 0.267 g (CeO_2/Al_2O_3-0.8) of $Al(acac)_3$, 0.3 g of $Ce(acac)_3$, 0.4 g of PVP ($M_w \approx 1.3 \times 10^6$), and 6 mL of ethanol with a flow rate of 0.5 mL/h, at 15 kV, followed by calcination at 500 °C for 2 h in air with a ramping rate of 4.2 °C/min. Before electrospinning, the precursor was sonicated for 20 min, to achieve better homogeneity.

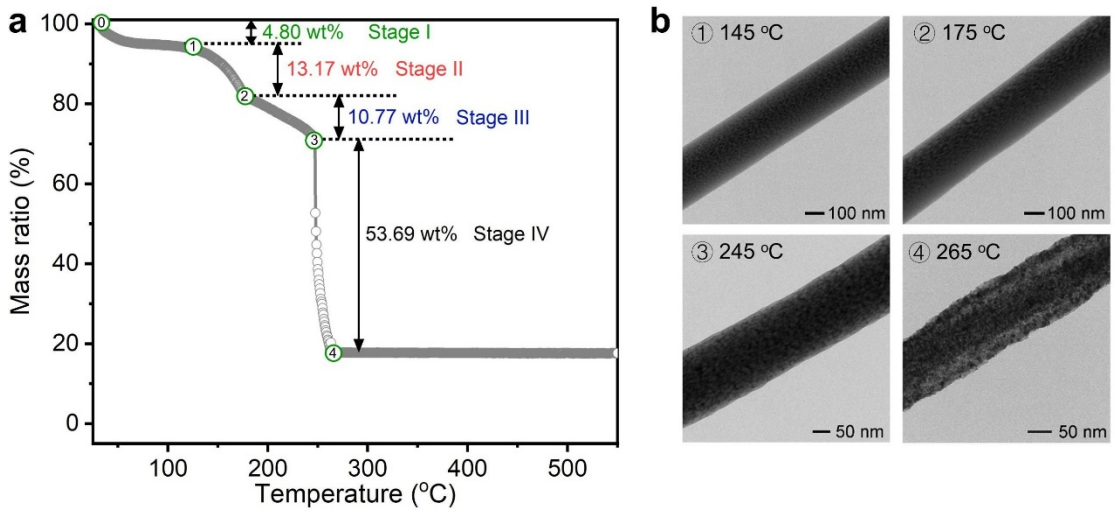

Fig. S3 (a) TG curves of $Ce(acac)_3/Al(acac)_3$/PVP as-spun nanofibers calcined in the air with a raping rate of 4.2 °C/min. (b) TEM images of $Ce(acac)_3/Al(acac)_3$/PVP nanofibers after being calcined in the air at 145, 175, 245, and 265 °C with a raping rate of 4.2 °C/min.

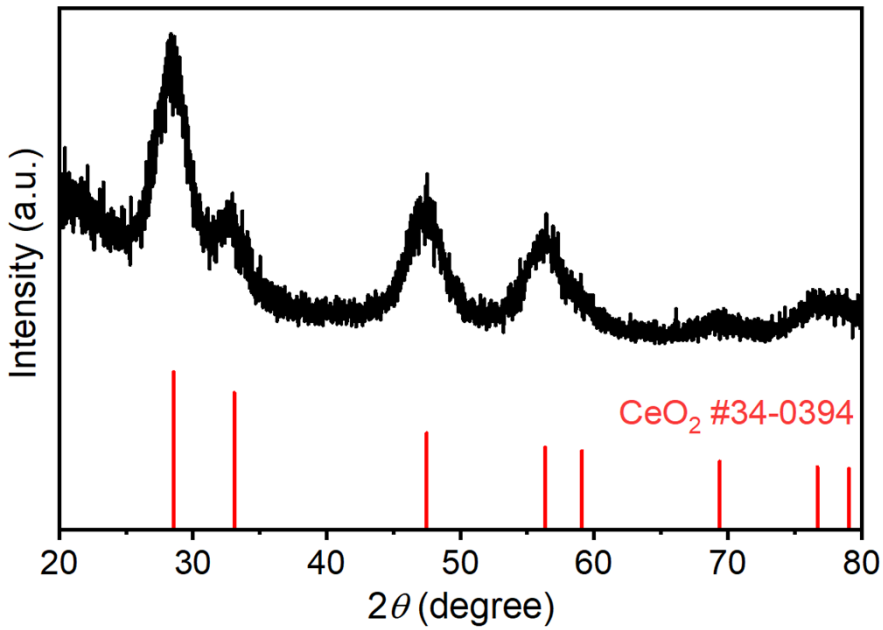

Fig. S4 X-ray diffraction patterns of the CeO_2/Al_2O_3 fibril-in-tubes.

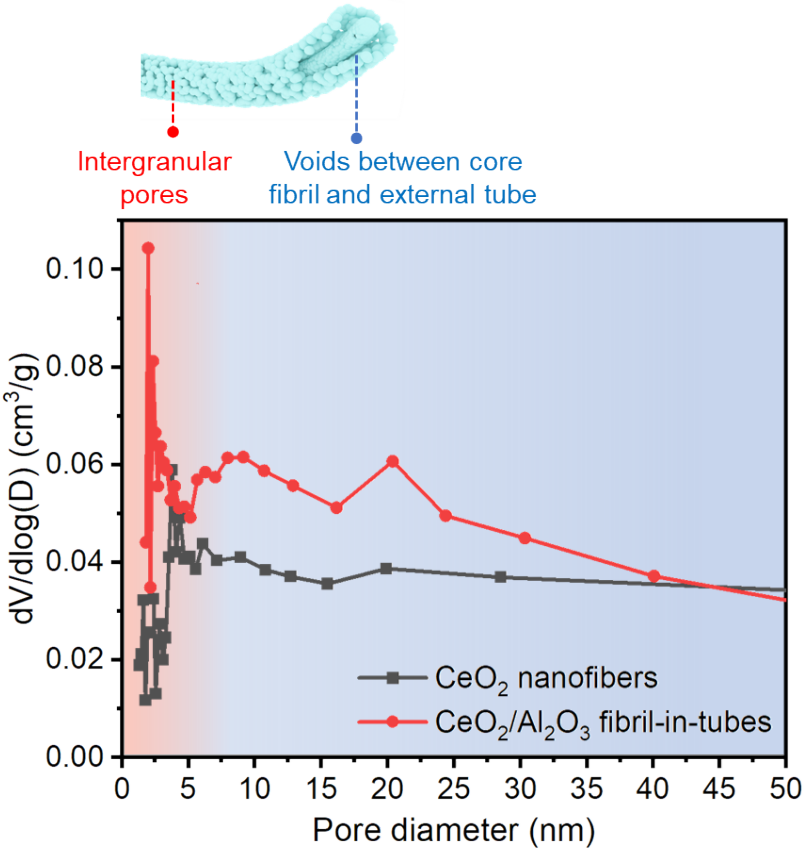

Fig. S5 Barrett−Joynes−Halenda (BJH) pore size distribution curves of CeO_2/Al_2O_3 fibril-in-tubes and pure CeO_2 nanofibers.

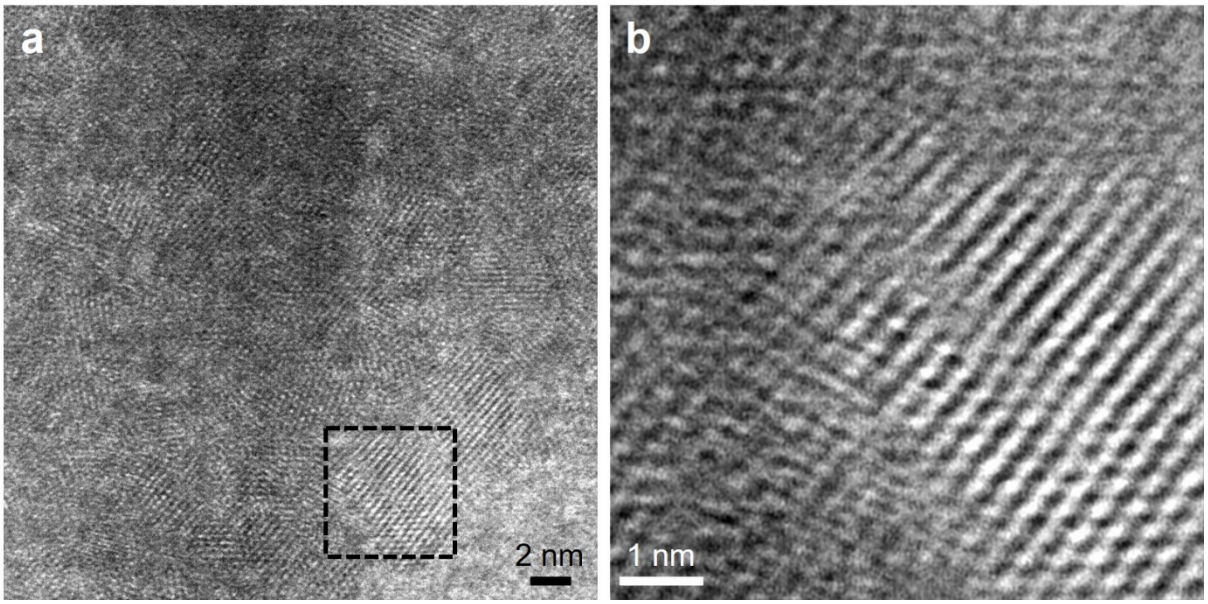

Fig. S6 (a) HRTEM image of the cross-section of CeO_2/Al_2O_3 nanofibers. (b) The corresponding inverse-FFT image of the squared area in a.

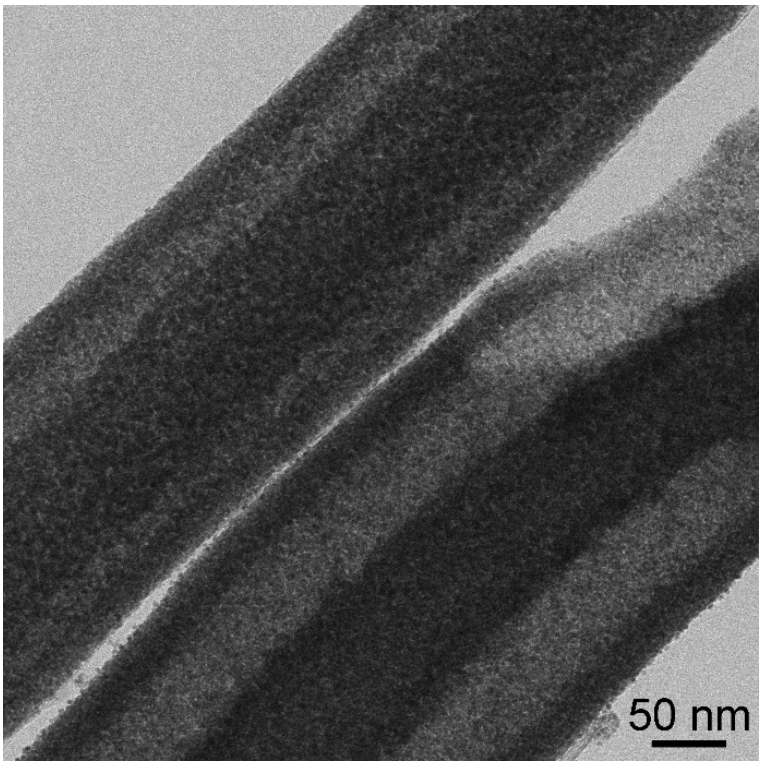

Fig. S7 TEM image of as-prepared Pt@CeO_2/Al_2O_3 fibril-in-tubes.

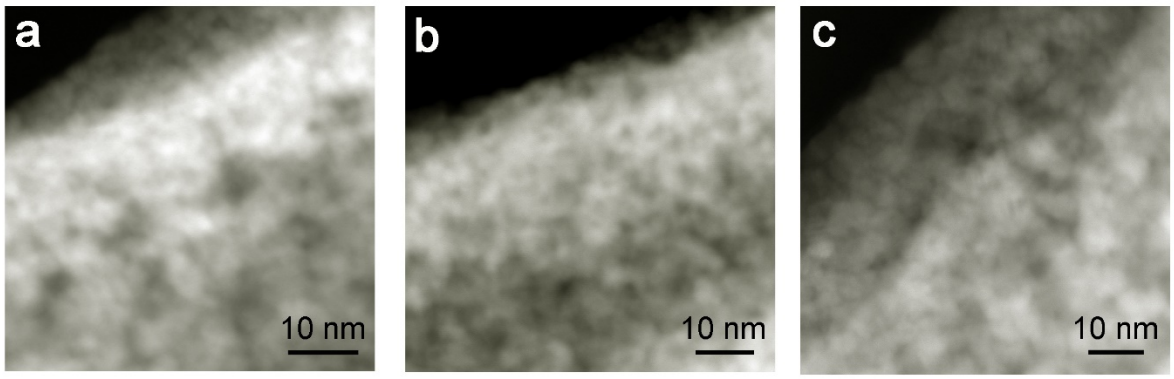

Fig. S8 High-magnification HAADF-STEM images of Pt@CeO_2/Al_2O_3 fibril-in-tubes after being aged (a) in dry air at 700 °C for 2 h, (b) in humid air (10 vol% of water) at 700 °C for 2 h, and (b) in dry air at 750 °C for 10 h. The HAADF-STEM images were colored for a better demonstration.

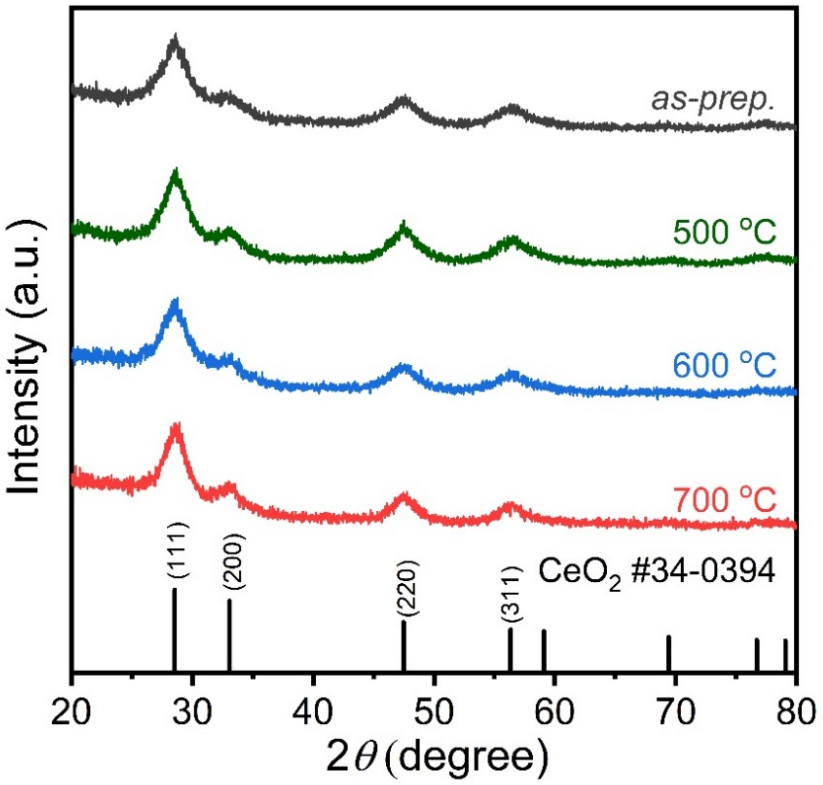

Fig. S9 XRD patterns of Pt@CeO_2/Al_2O_3 before and after aging at 500, 600, and 700 °C for 2 h in air.

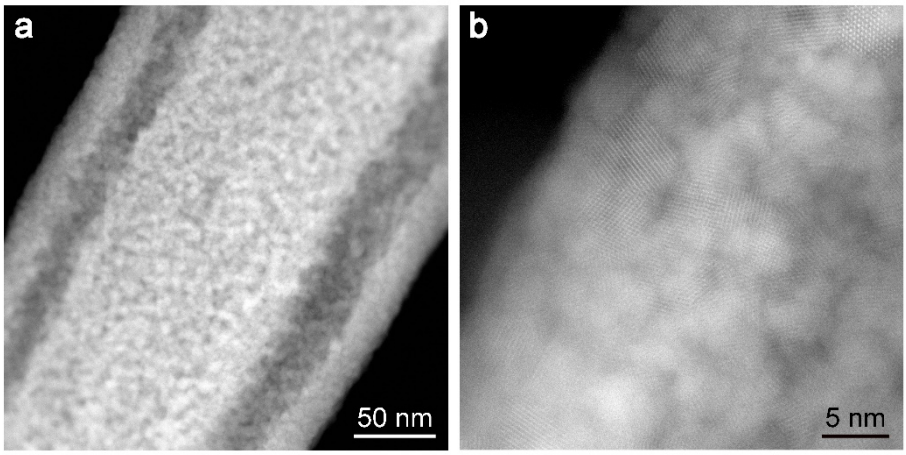

Fig. S10 AC-HAADF-STEM images of Pt@CeO_2/Al_2O_3 after aging at 750 °C for 10 h in air.

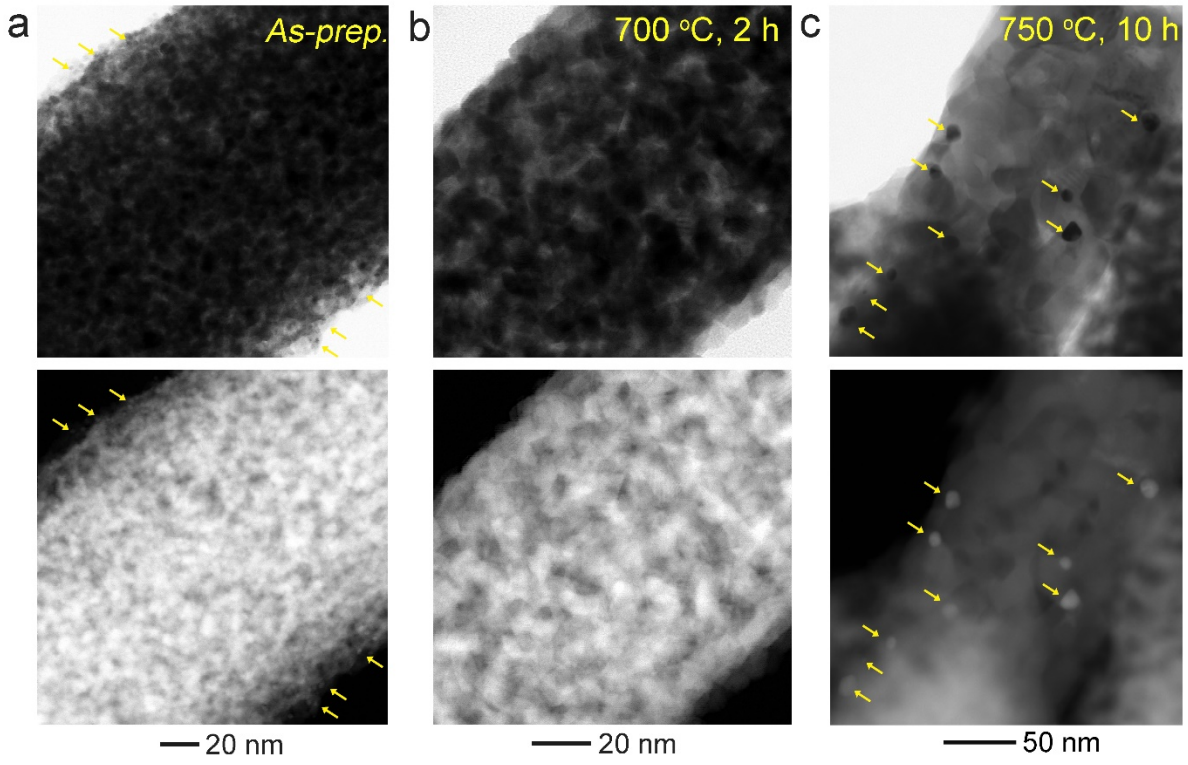

Fig. S11 TEM (top) and HAADF-STEM (bottom) images of $Pt@CeO_2$ nanofibers. (a) As-prepared $Pt@CeO_2$ nanofibers. (b) $Pt@CeO_2$ nanofibers after being aged at 700 °C for 2 h in the air. (c) $Pt@CeO_2$ nanofibers after being aged at 750 °C for 10 h in the air. The yellow arrows in a and c highlight the Pt species.

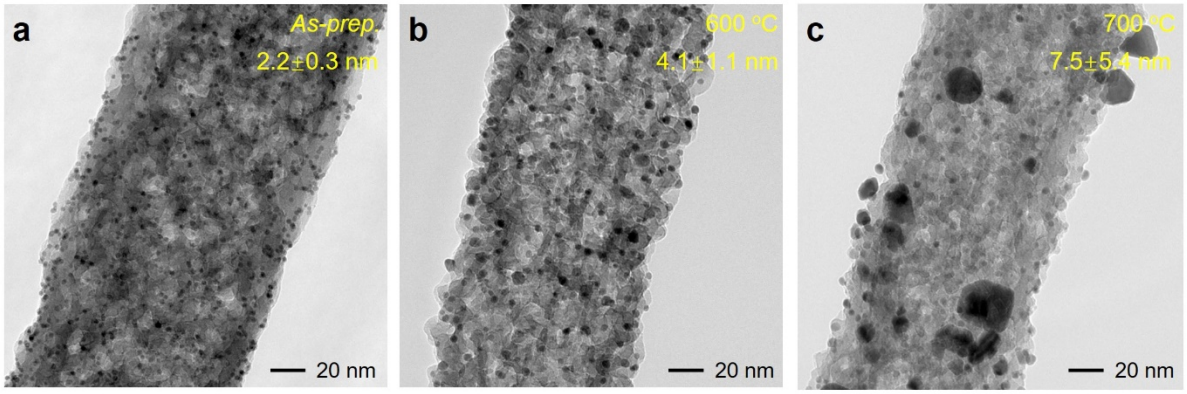

Fig. S12 TEM images of $Pt@Al_2O_3$ nanofibers (a) before and after being aged at (b) 600 °C and (c) 700 °C in the air for 2 h.

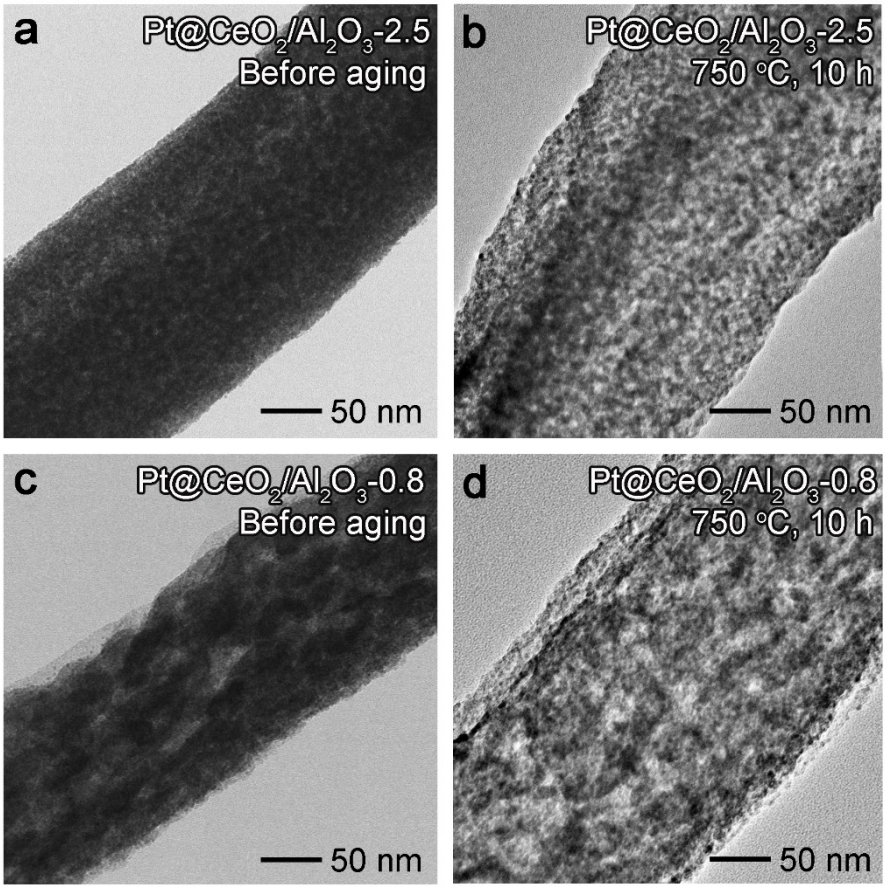

Fig. S13 TEM images of Pt@CeO_2/Al_2O_3-2.5 nanofibers (a) before and (b) after being severely aged at 750 °C in the air for 10 h. TEM images of Pt@CeO_2/Al_2O_3-0.8 nanofibers (c) before and (d) after being severely aged at 750 °C in the air for 10 h.

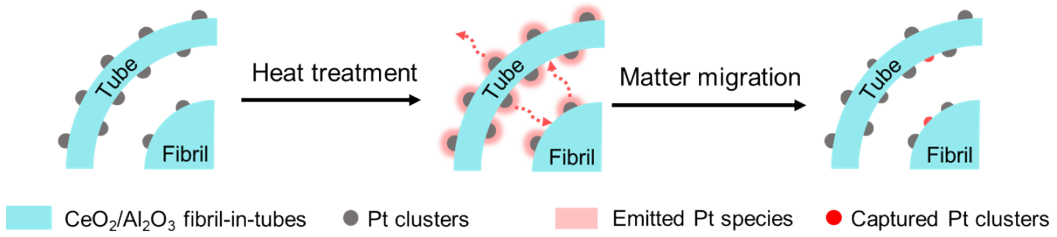

Fig. S14 Schematic illustration of the suppressed leaching on CeO_2/Al_2O_3 fibril-in-tubes.

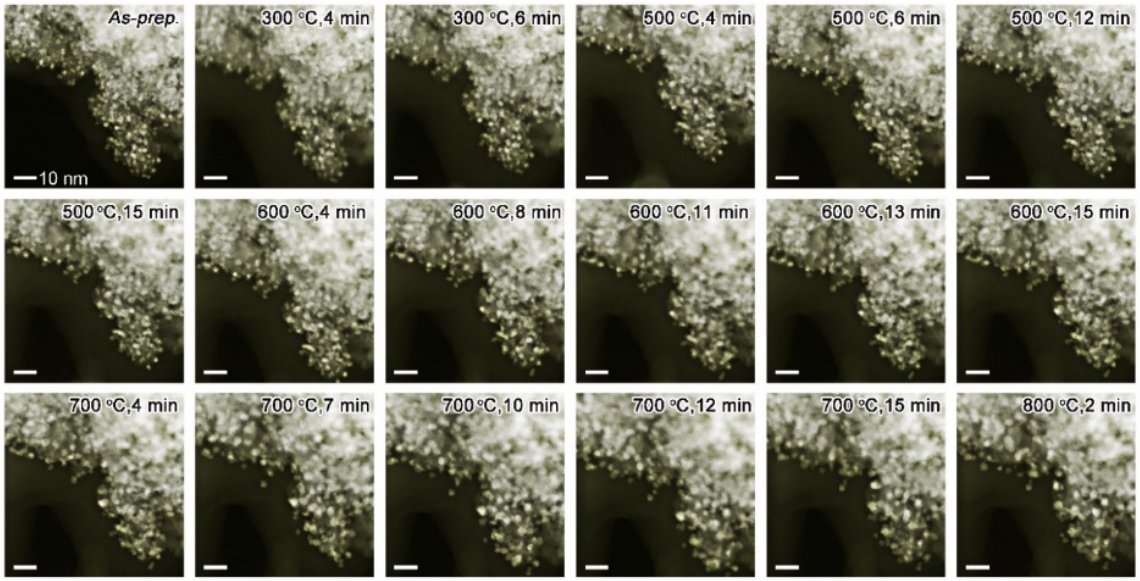

Fig. S15 Zoom-in HAADF-STEM images of the dashed box in Fig. 4a. All the scale bars indicate 10 nm. The HAADF-STEM images were colored for a better demonstration.

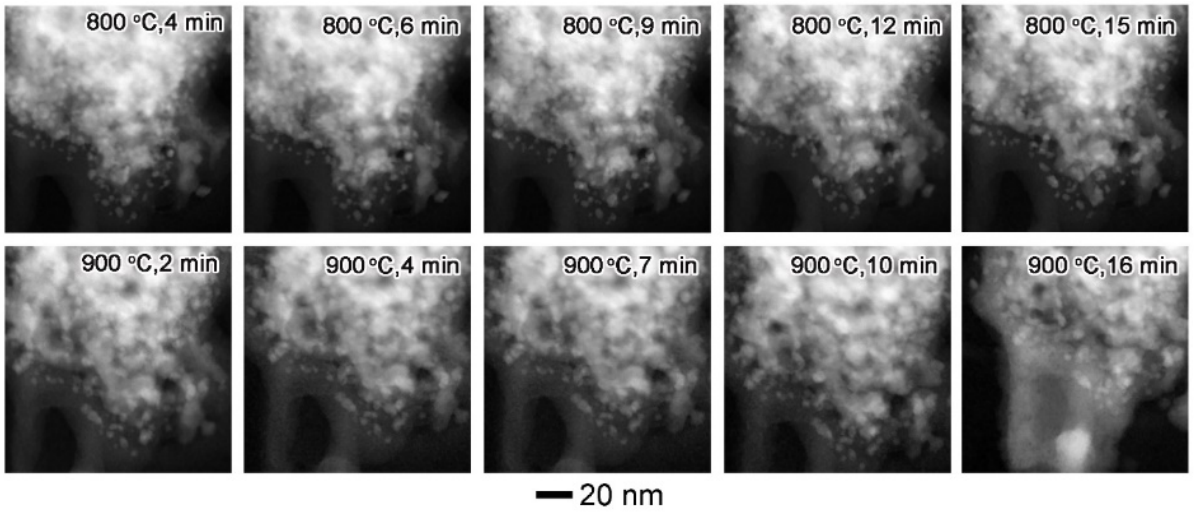

Fig. S16 *In situ* HAADF-STEM observation on Pt@CeO_2/Al_2O_3 fibril-in-tubes at 800 and 900 °C.

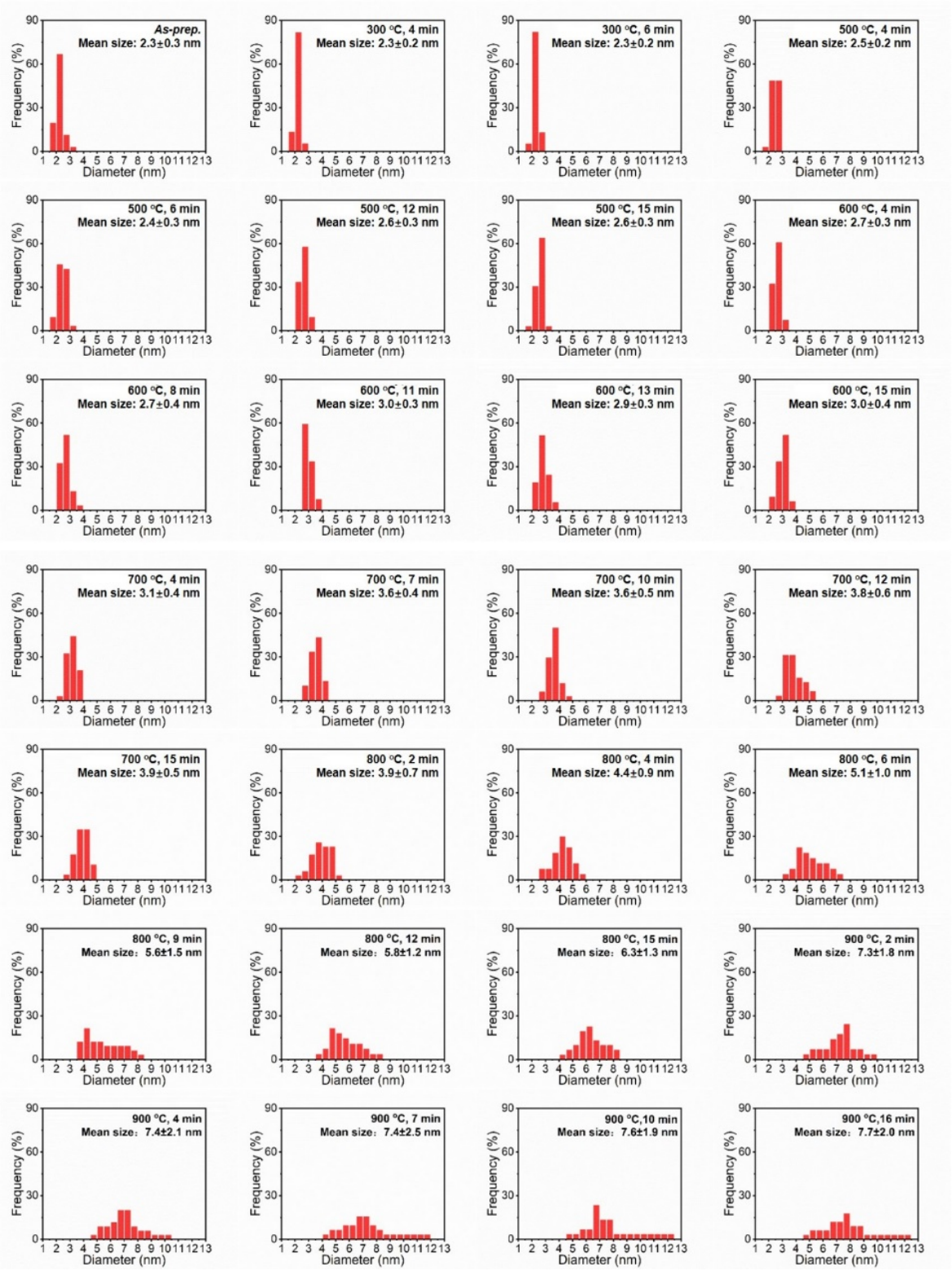

Fig. S17 Pt size distributions based on the corresponding *in situ* HAADF-STEM images.

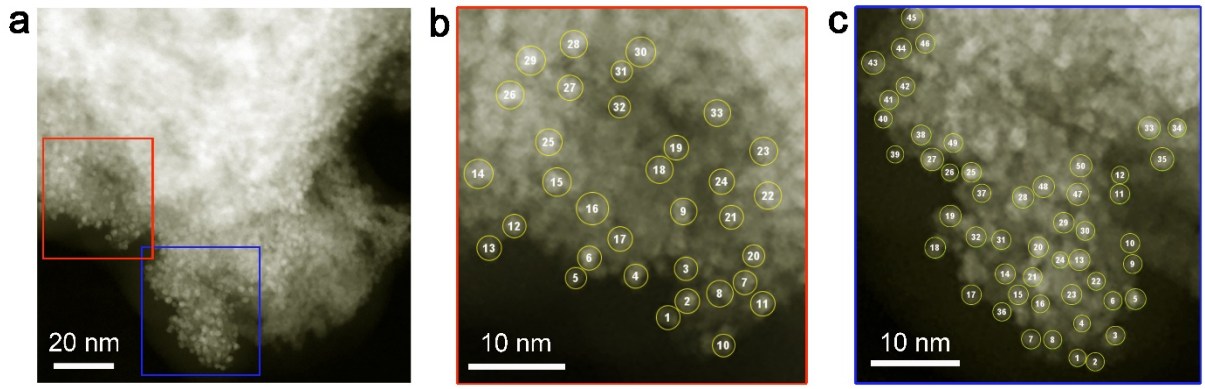

Fig. S18 Labeled Pt clusters with the aid of Image J, to accurately measure the average neighboring distance. In specific, the nearest neighboring distance was obtained by taking the minimum value of the distance between one cluster and any other cluster. The HAADF-STEM images were colored for a better demonstration.

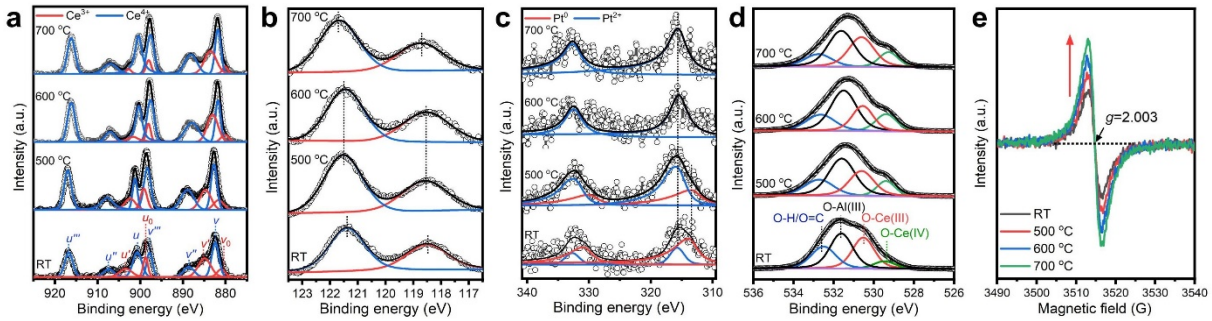

Fig. S19 (a−d) Ce 3*d*, Al 2*s*, Pt 4*d*, and O 1*s* high-resolution XPS spectra of Pt@CeO_2/Al_2O_3. (e) EPR spectra of Pt@CeO_2/Al_2O_3 fibril-in-tubes before and after aging at 500, 600, and 700 °C.

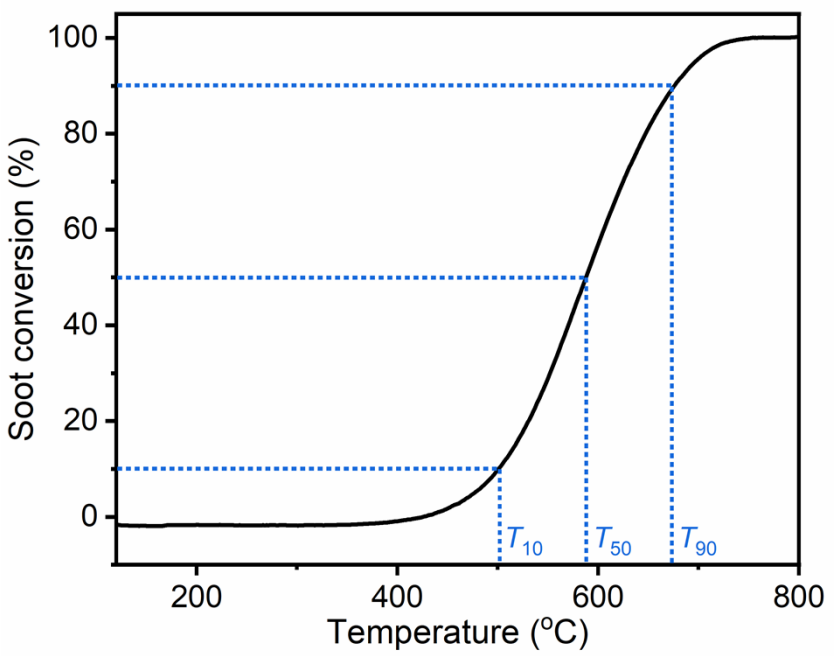

Fig. S20 Soot conversion without catalyst at a ramping rate of 10 °C/min.

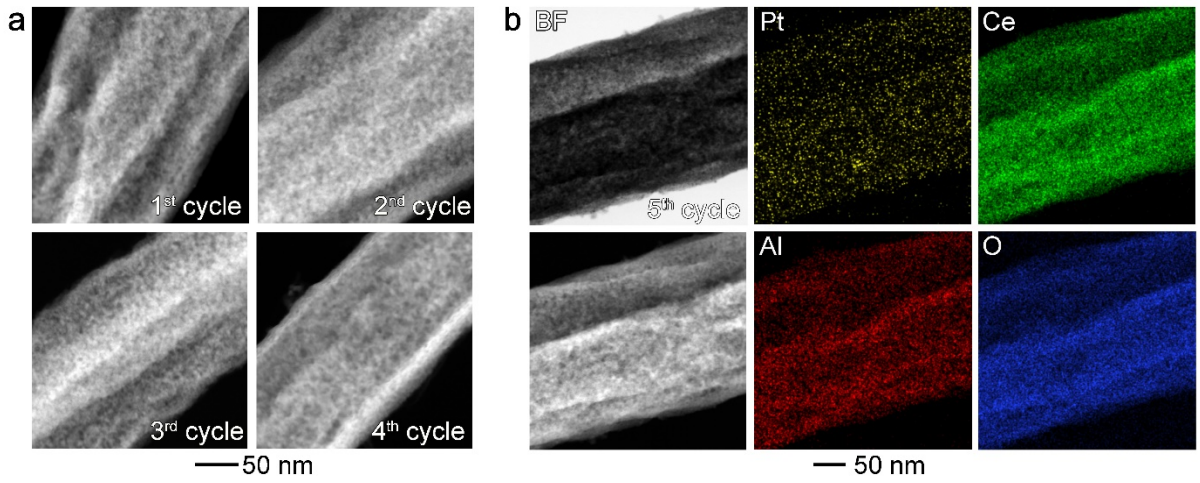

Fig. S21 (a) HAADF-STEM images of Pt@CeO_2/Al_2O_3 after four cycles of soot combustion. (b) TEM, HAADF-STEM, and elemental mappings of Pt@CeO_2/Al_2O_3 after the fifth cycle of soot combustion.

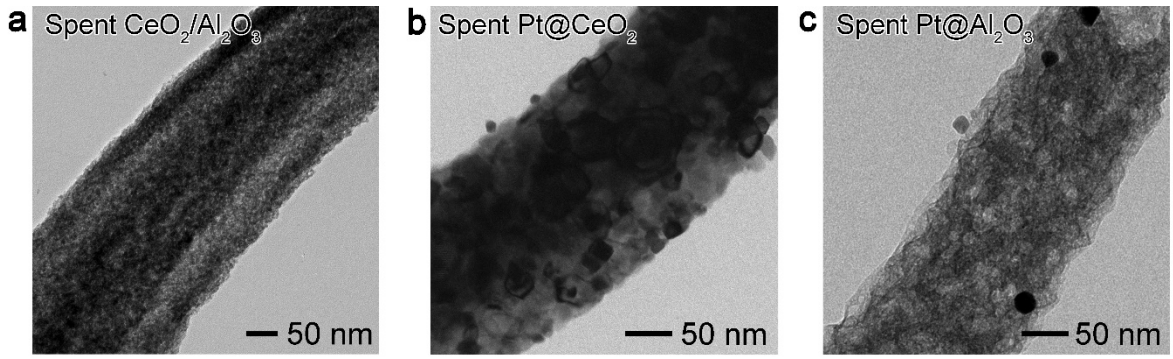

Fig. S22 TEM images of (a) CeO_2/Al_2O_3 fibril-in-tubes, (b) $Pt@CeO_2$ nanofibers, and (c) $Pt@Al_2O_3$ nanofibers after soot combustion for 3 cycles.

Table S1. EDX results of collected at 5 randomly selected positions in $Pt@CeO_2/Al_2O_3$ which was aged at 500 ºC for 2 h.

Position	Element	Family	Atomic fraction (at%)	Mass fraction (wt%)	Fit error (%)	Atomic ratio of Ce/Al
1	O	K	64.77	24.57	1.62	1.24
	Al	K	15.61	9.98	1.06	
	Ce	L	19.43	64.54	0.09	
	Pt	L	0.19	0.90	2.84	
2	O	K	80.39	39.81	1.36	1.71
	Al	K	7.17	5.99	1.30	
	Ce	L	12.28	53.27	0.10	
	Pt	L	0.15	0.92	1.75	
3	O	K	71.26	31.45	1.73	1.08
	Al	K	13.73	10.22	1.02	
	Ce	L	14.84	57.35	0.07	
	Pt	L	0.18	0.98	1.59	
4	O	K	81.99	46.24	0.88	1.00
	Al	K	8.91	8.47	1.07	
	Ce	L	8.92	44.07	0.14	
	Pt	L	0.18	1.22	2.11	
5	O	K	78.66	39.11	0.73	1.30
	Al	K	9.19	7.70	0.37	
	Ce	L	11.98	52.17	0.10	
	Pt	L	0.17	1.01	1.90	

Table S2. The catalytic activity of Pt@CeO_2/Al_2O_3 fibril-in-tubes, Pt@CeO_2, Pt@Al_2O_3, and CeO_2/Al_2O_3 for soot combustion under loose contact, along with the comparison to recently reported catalysts.

Catalyst	T_{10} (°C)	T_{50} (°C)	T_{90} (°C)	Gas flow rate (mL/min)	Catalyst dosage (wt%)	Soot dosage (wt%)	Ramping rate (°C/min)	Reference
CeO_2/Al_2O_3	258	533	607	100	90.0	10.0	10.0	This work
Pt@CeO_2/Al_2O_3	247	480	518	100	90.0	10.0	10.0	This work
Pt@CeO_2	356	520	563	100	90.0	10.0	10.0	This work
Pt@Al_2O_3	153	522	572	100	90.0	10.0	10.0	This work
Soot (Printex-U)	501	587	672	100	0	100	10.0	This work
CeO_2-Ag/P25	~390	~514	~600	60.0	90.9	9.09	5.00	1
$SmMn_2O_5$	471	508	545	150	83.3	16.7	2.00	2
CeO_2	~430	540	~600	100	90.9	9.09	5.00	3
Au/TiO_2	~410	~480	~546	100	83.3	16.7	2.00	4
CoAlO	440	533	NA	150	95.2	4.76	5.00	5
Ag@CoAlO	352	461	NA	150	95.2	4.76	5.00	5

References

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