Supporting information

High durability palladium catalyst applied to oxygen reduction reaction in an alkaline environment

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Half-cell test in acidic condition

The electrochemical activity and durability of the catalysts were investigated with a three-electrode system. A Glassy Carbon Electrode (GCE, 0.196 cm^2, Autolab) served as a working electrode, with a Ag/AgCl (3.5 M KCl) used as a reference electrode, and a graphite rod as a counter electrode. The catalyst ink slurry was prepared by dispersing 5 mg of Pd@CS/CNF600, 800, 900, and Pd@An/CNF in a mixture of the 30 μL of nafion solution (5 wt%, Dupont) and, 1200 μL of ethanol (EtOH). The ink slurry was applied to the GCE to achieve a catalyst loading of 15 $\mu g_{Pd}/cm^2$. For comparison purpose, commercial Pd/C (10 wt%, sigma-aldrich) was also tested with the loading amount of 20 $\mu g_{Pd}/cm^2$. Cyclic Voltammetry (CV) test was performed from 0.05 to 1.2 V at a scan rate of 100 mV/s in an N_2-saturated 0.1 M $HClO_4$. ORR polarization curves were obtained in an O_2-saturated 0.1 M $HClO_4$ at 1,600 rpm with a scan rate of 20 mV/s over a potential range of 0.05-1.05 V. The stability test to confirm the durability of the catalyst was conducted for 1,000 cycles under same conditions in the in the N_2-saturated 0.1 M $HClO_4$. The electrochemically active surface areas (ECSAs) of the catalyst were determined by H_{upd} from CV at acid media. All potential was converted to the reversible hydrogen electrode (RHE). Electrochemical impedance spectroscopy (EIS) measurements were taken at 0.8 V (vs. RHE) across a frequency range of 100 kHz to 0.1 Hz with an amplitude of 10 mV. The solution resistances (R_s) and charge transfer resistance (R_{ct}) derived from EIS were used for iR-correction of the voltammograms obtained from the ORR curves.

PEMFC test

Catalyst coated membrane (CCM) method was used for preparing the membrane electrode assembly (MEA) having an active area of 5 cm^2. The catalyst ink slurry for cathode consisted of 6.25 mg of Pd@CS/CNF, 625 μL NPA (1-Propanol, Sigma-aldrich), and 30 μL nafion

ionomer (5 wt%, Dupont). Commercial Pt/C (40wt%, HiSPEC 4000 Johnson Matthey Co.) ink slurry for anode was composed of 6.25 mg Pt/C, 625 μL isopropyl alcohol, 45 μL FAA-3-10 ionomer. The catalyst ink slurry was coated onto both sides nafion212 membrane. The loading of metal was controlled at 0.025 mg_{metal} /cm^2 of Pt/C on the anode electrode. On the other hand, 0.1 mg_{metal}/cm^2 of Pd@CS/CNF or Pd/C was sprayed on the cathode. After spraying the catalysts, the membrane was placed between two GDL (39BB) and pressed with 8.5 N ·m torque. The unit cell test was conducted at 80ºC using a PEMFC test station (CNL-SPPS, CNL Energy). During the evaluation, fully humidified H_2 gas (300 ccm) and O_2 gas (800 ccm) were fed to anode and cathode side, respectively, without any back pressure. EIS measurements were obtained at 0.6 V (Vs. RHE) in the frequency range of 100 MHz–0.1 Hz with an amplitude of 10 mV.

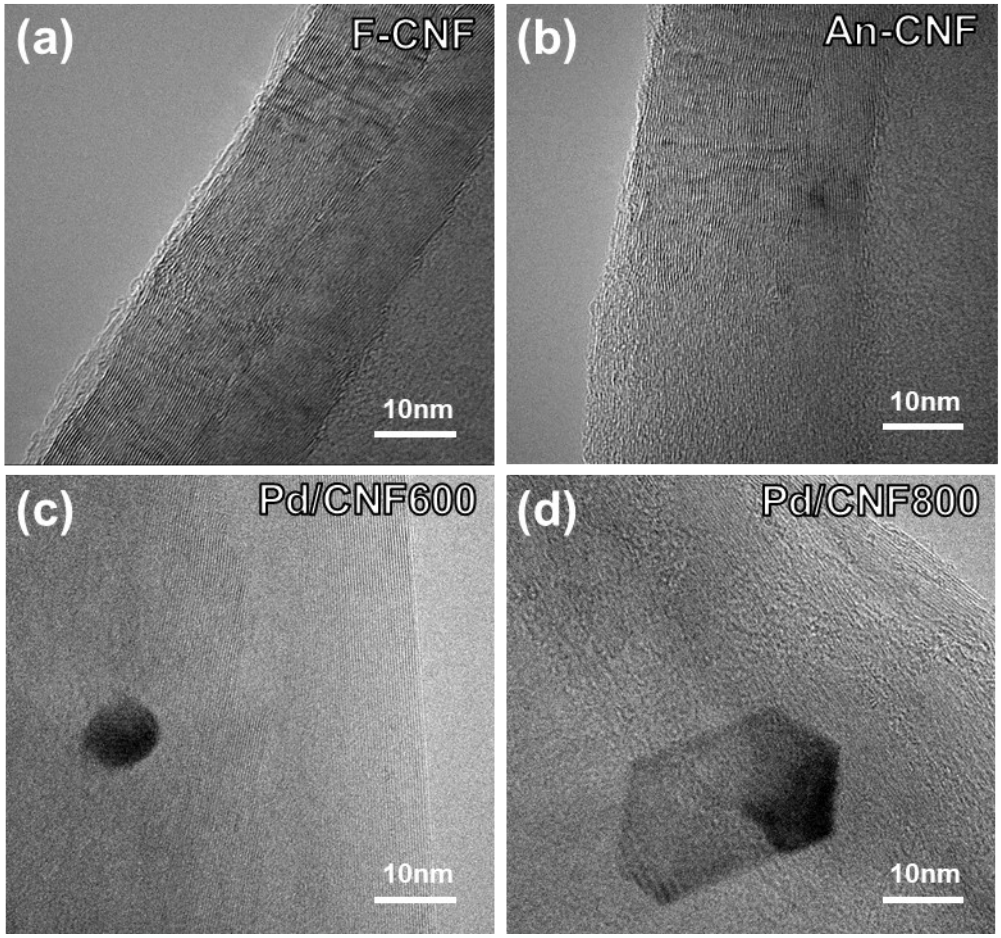

Figure S1. TEM image of (a) F-CNF, (b) An-CNF, (c) Pd/CNF600, and (d) Pd/CNF800.

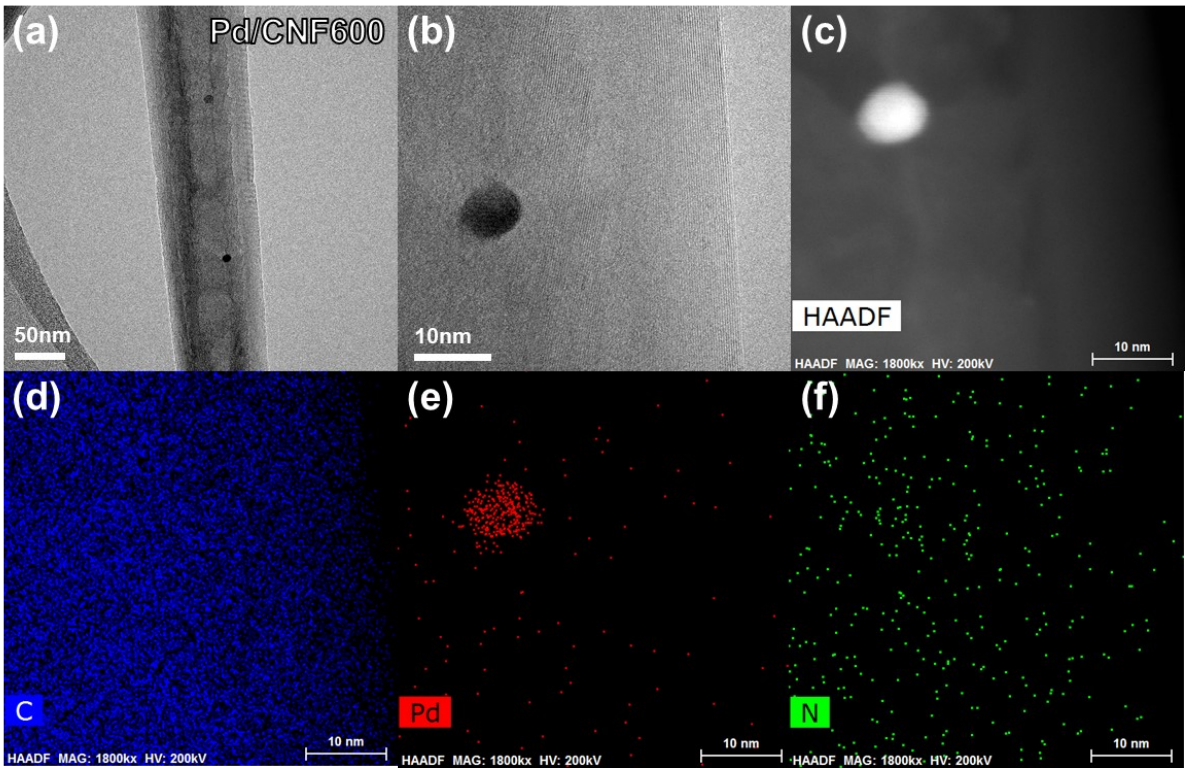

Figure S2. (a) TEM image, (b) enlarged image of (a), (c) HAADF-STEM image, and corresponding EDS mapping of (d) C, (e) Pd, and (f) N of the Pd/CNF600.

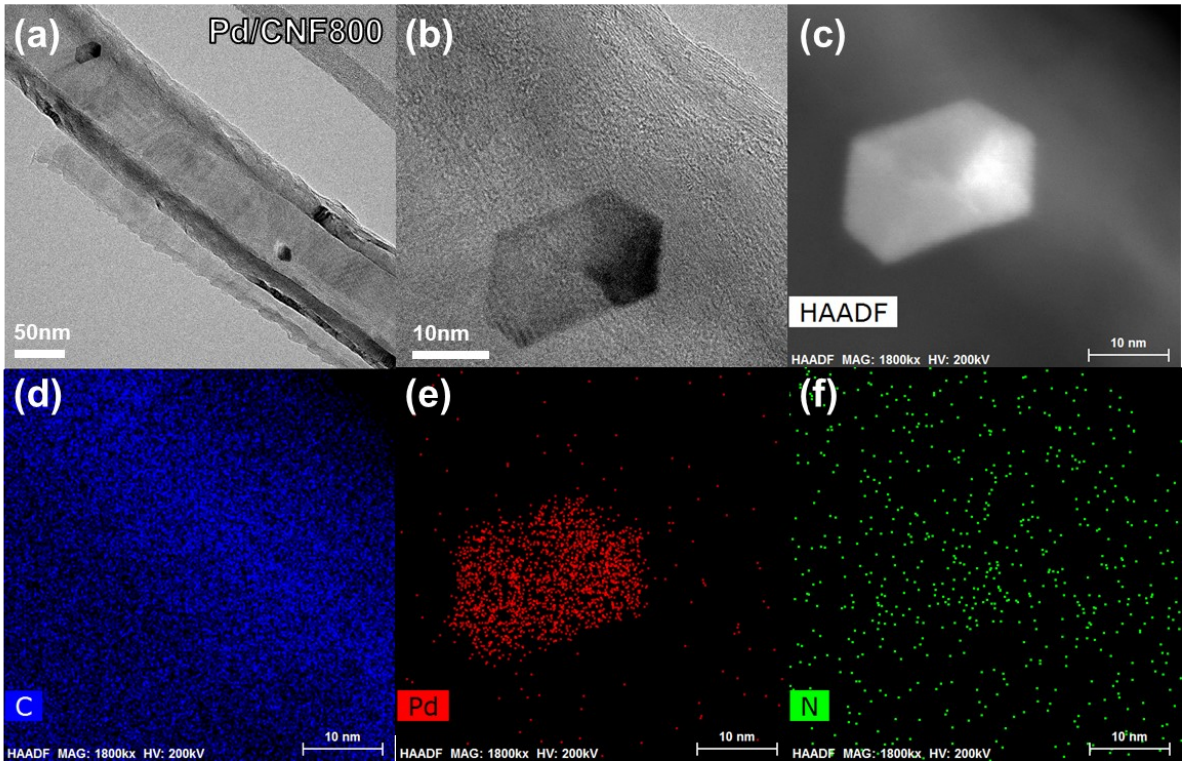

Figure S3. (a) TEM images, (b) enlarged image of (a), (c) HAADF-STEM image, and corresponding EDS mapping of (d) C, (e) Pd, and (f) N of the Pd/CNF800.

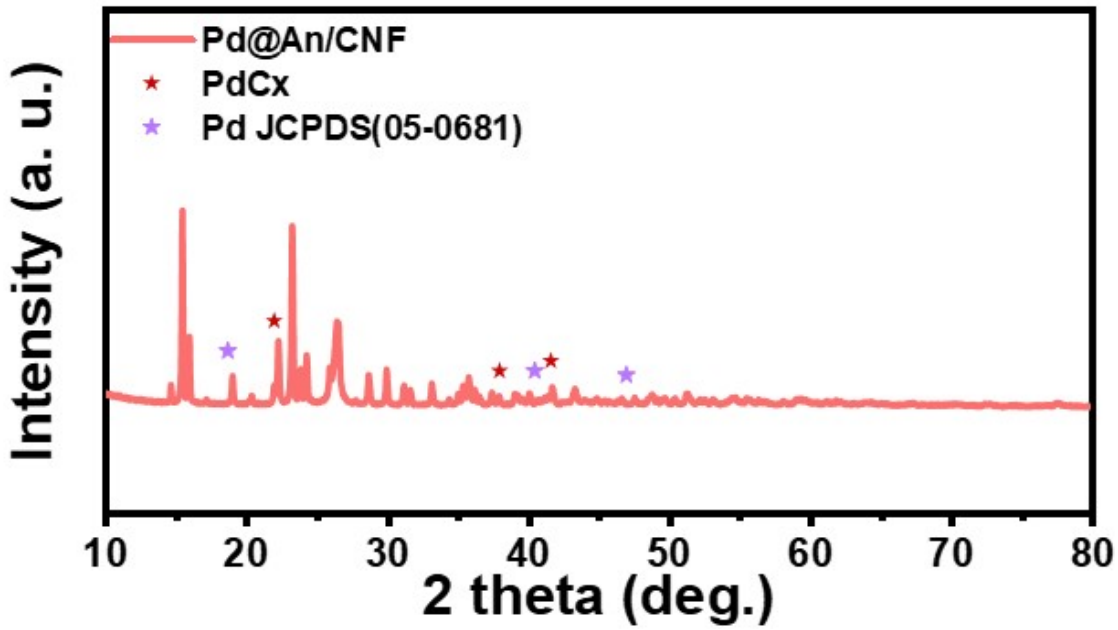

Figure S4. XRD spectrum of Pd@An/CNF observed in the extended 2 theta range.

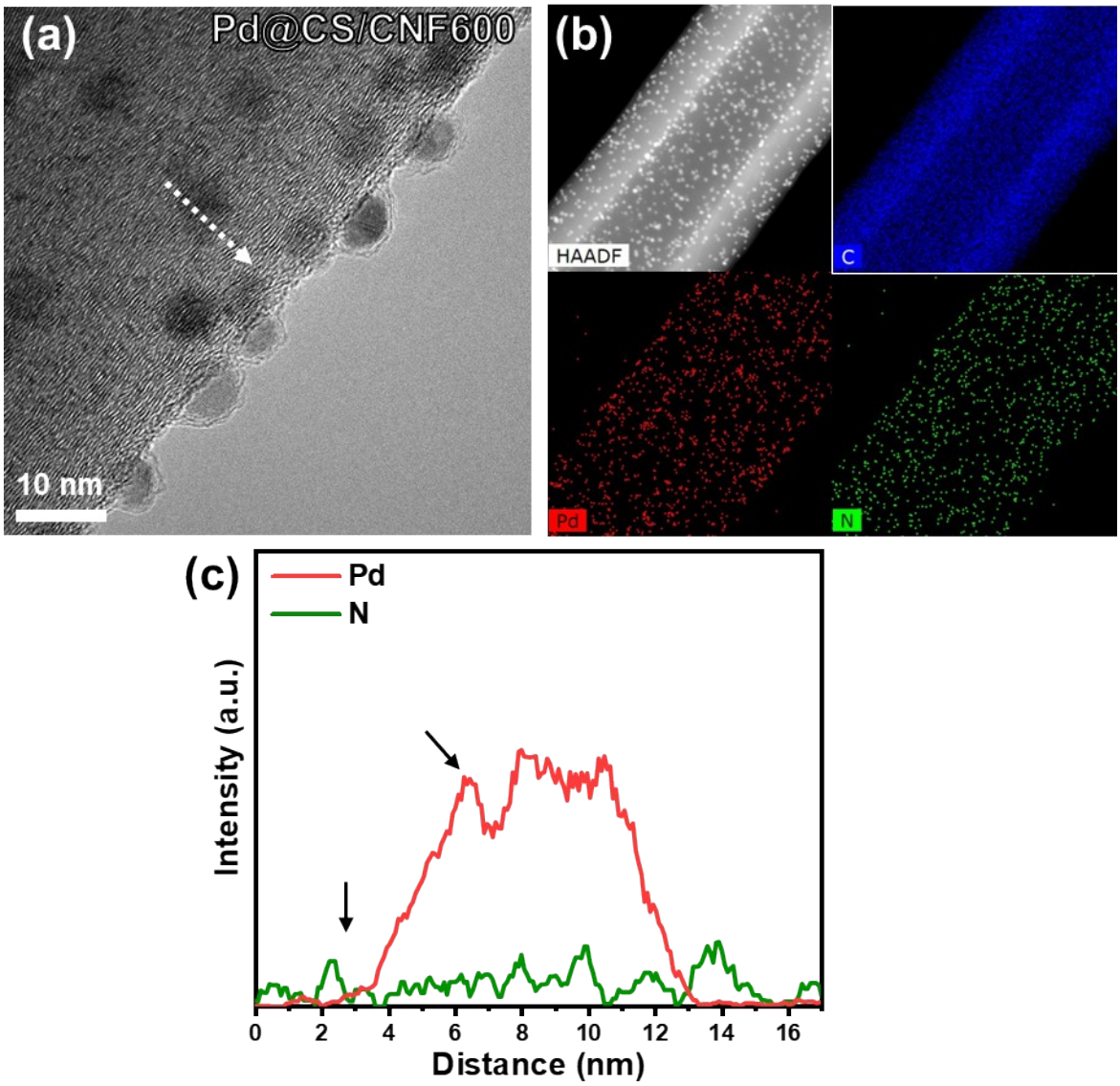

Figure S5. (a) TEM Image, and (b) HAADH-STEM image along with its corresponding elemental mappings of Pd@CS/CNF600. (c) EDS line scan across the Pd@CS/CNF600 as indicated by the dashed line in (a).

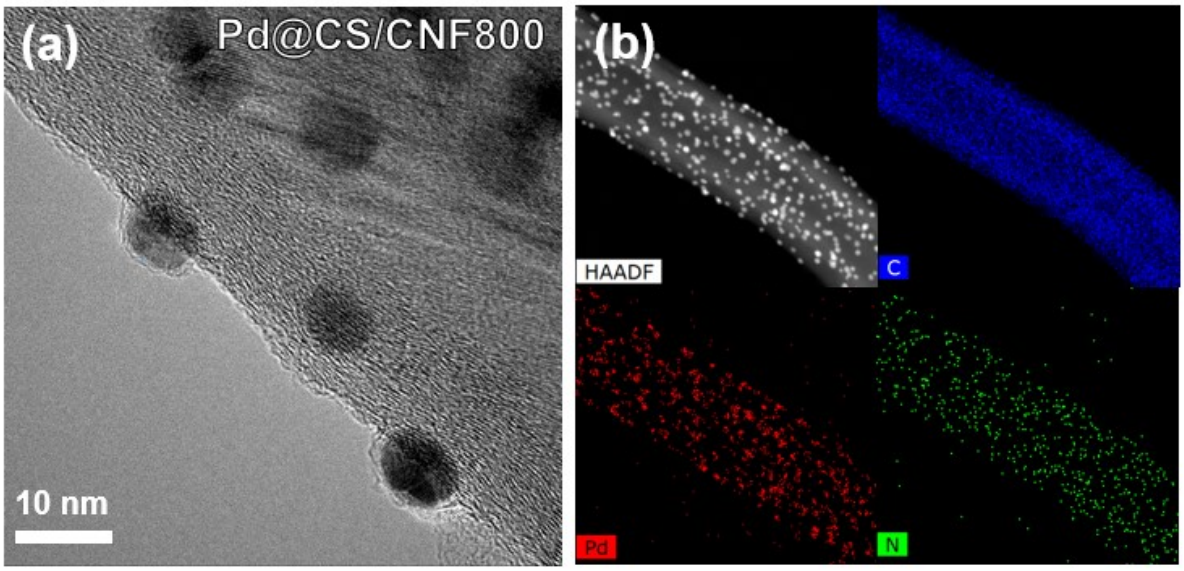

Figure S6. (a) TEM Image, and (b) HAADH-STEM image along with its corresponding elemental mappings of Pd@CS/CNF800.

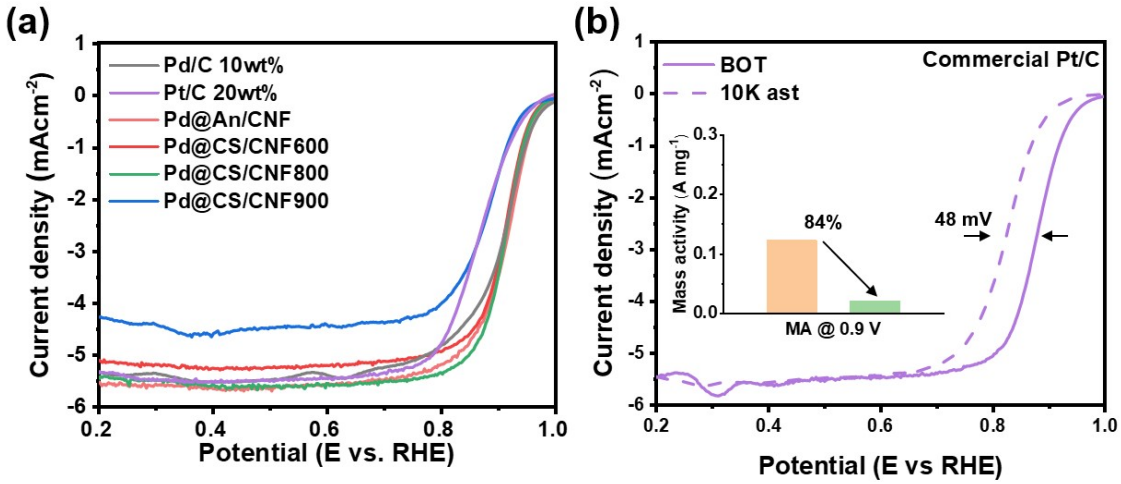

Figure S7. (a) ORR curves of commercial Pd/C, commercial Pt/C, Pd@An/CNF, Pd@CS/CNF600, Pd@CS/CNF800, and Pd@CS/CNF900. (b) ORR curves of the Commercial Pt/C before and after durability test (10,000cycles) in O_2-saturated 0.1 M KOH at a scan rate of 100 mV/s from 0.6 to 1.0 V (vs. RHE).

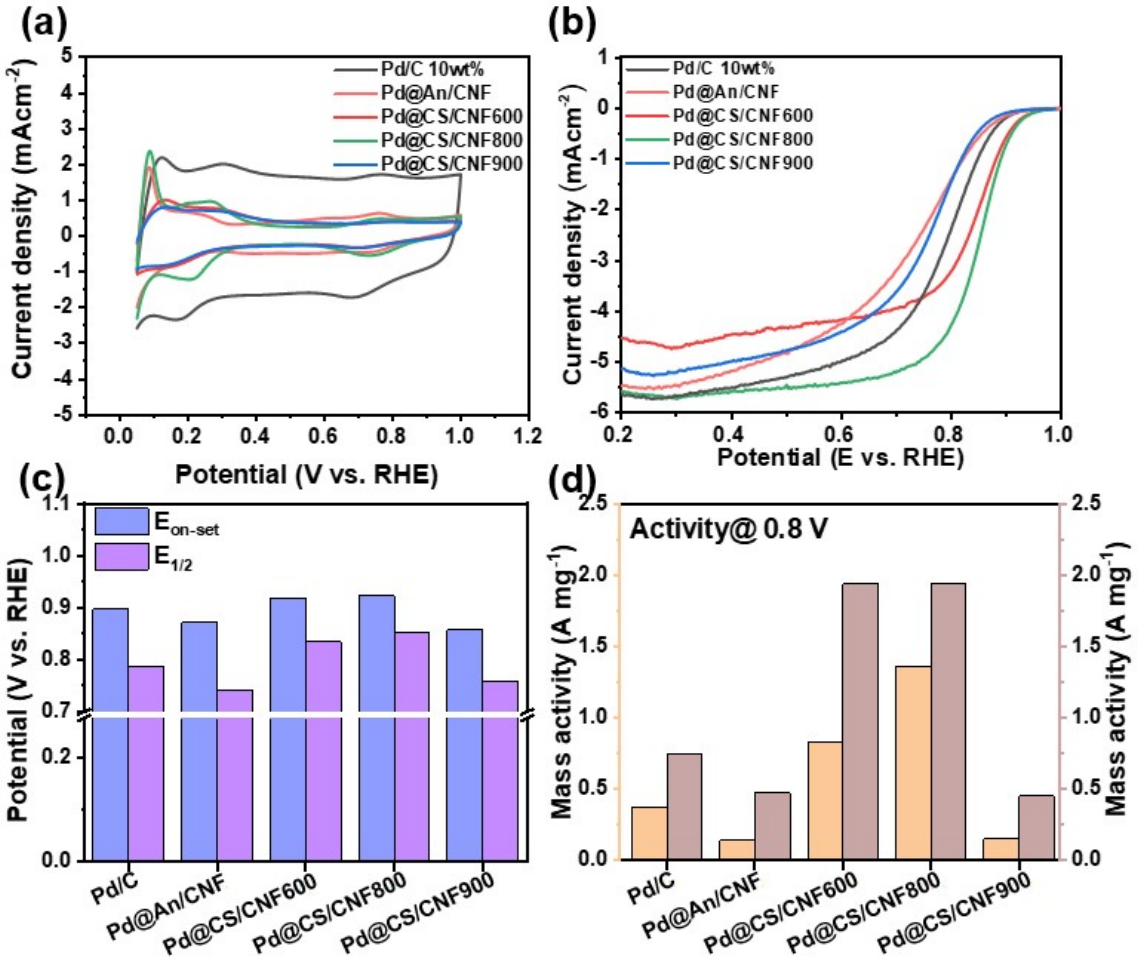

Figure S8. (a) CV curves and (b) ORR polarization curves of Pd/C, Pd@An/CNF, Pd@CS/CNF600, Pd@CS/CNF800, and Pd@CS/CNF900 obtained in N_2-saturated and O_2-saturated 0.1 M $HClO_4$, respectively. (c) on-set potential and half-wave potential and (d) mass activities and specific activities at 0.8 V.

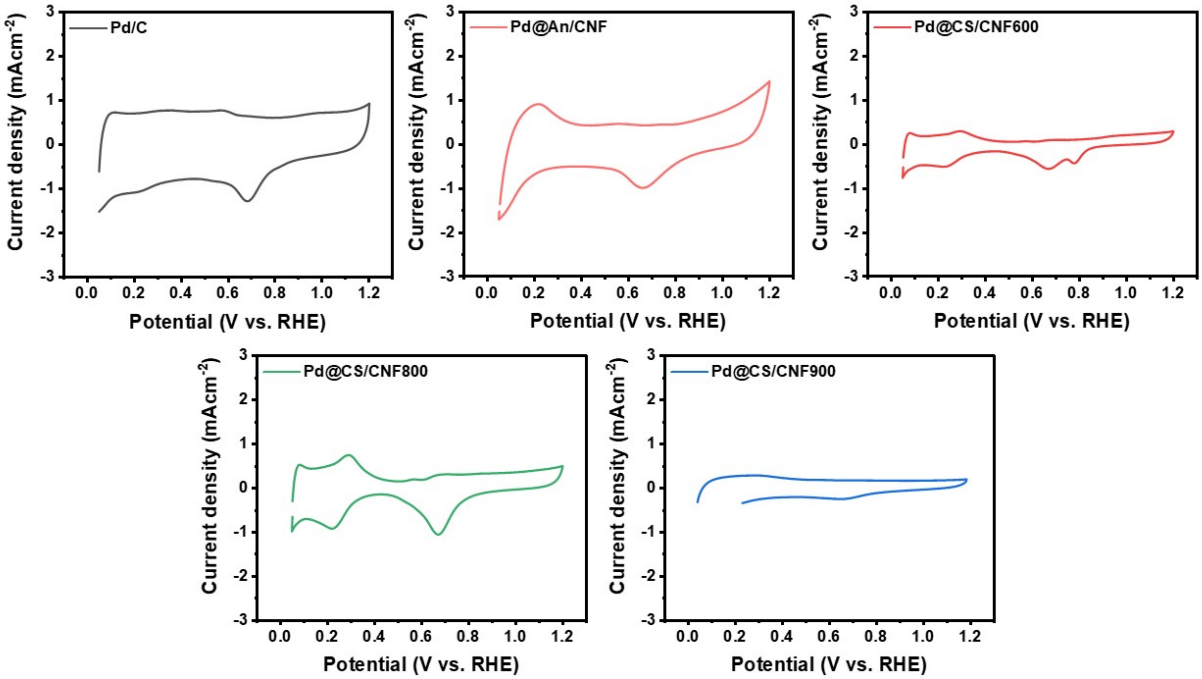

Figure S9. CV curves for Pd oxide peaks of Pd/C, Pd@An/CNF, Pd@CS/CNF600, Pd@CS/CNF800, and Pd@CS/CNF900 obtained in 0.1 M KOH at scan rate 50 mV/s.

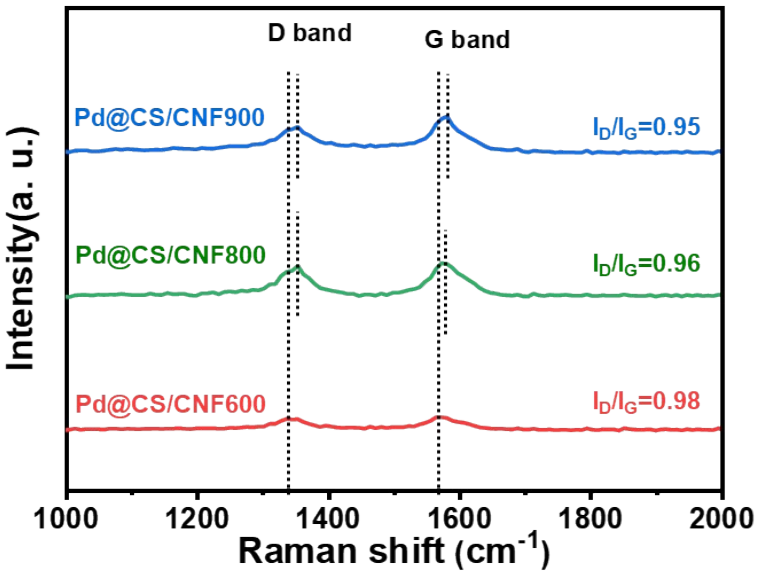

Figure S10. Raman spectra of Pd@CS/CNF600, Pd@CS/CNF800, Pd@CS/CNF900.

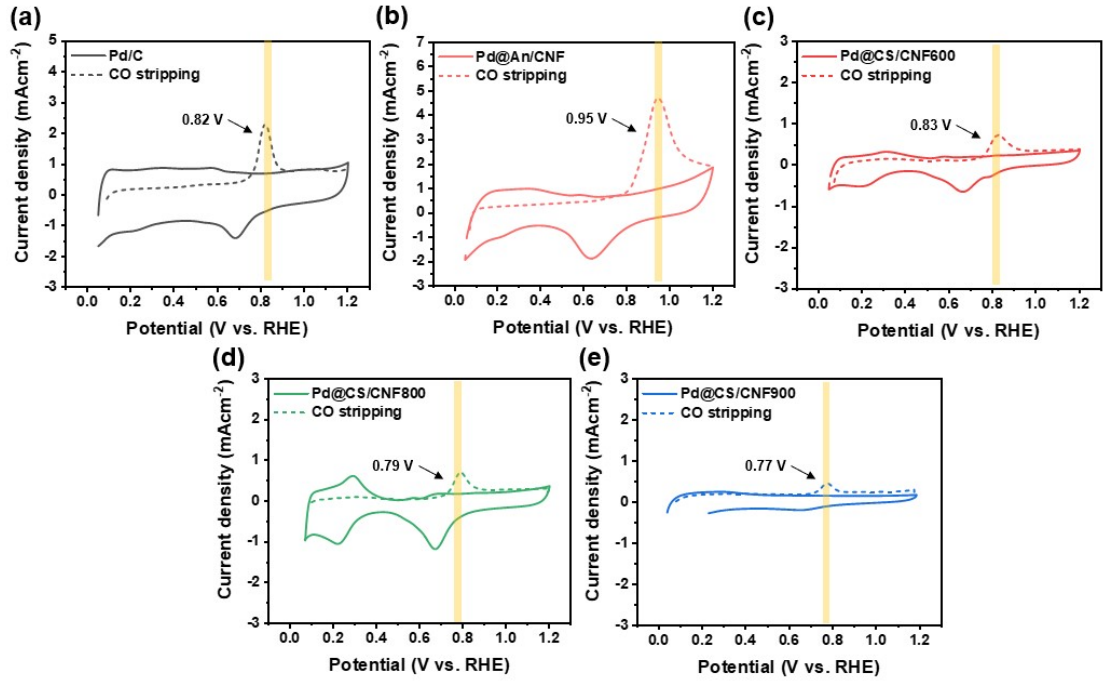

Figure S11. CO stripping curves of (a) Pd/C, (b) Pd@An/CNF, (c) Pd@CS/CNF600, (d) Pd@CS/CNF800, and (e) Pd@CS/CNF900 in 0.1 M KOH at scan rate 50 mV/s.

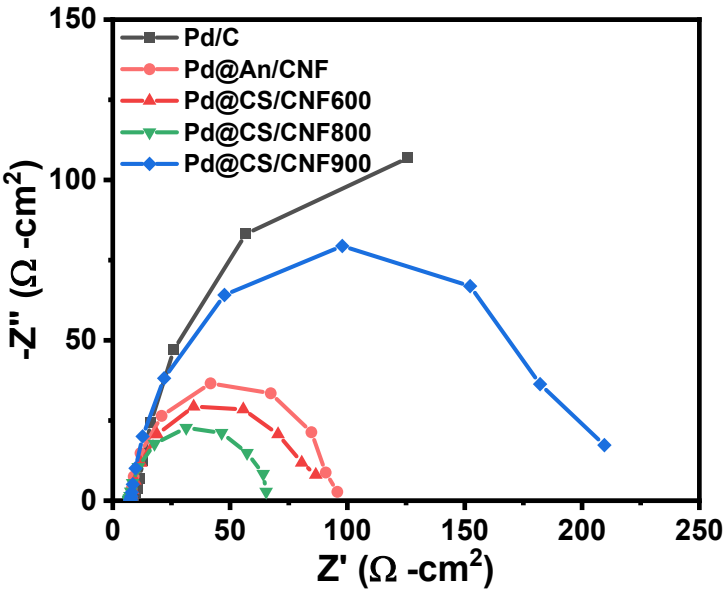

Figure S12. The EIS plot obtained at 0.9 V for commercial Pd/C, Pd@An/CNF, Pd@CS/CNF600, 800, and 900 in an O_2-saturated 0.1 M KOH.

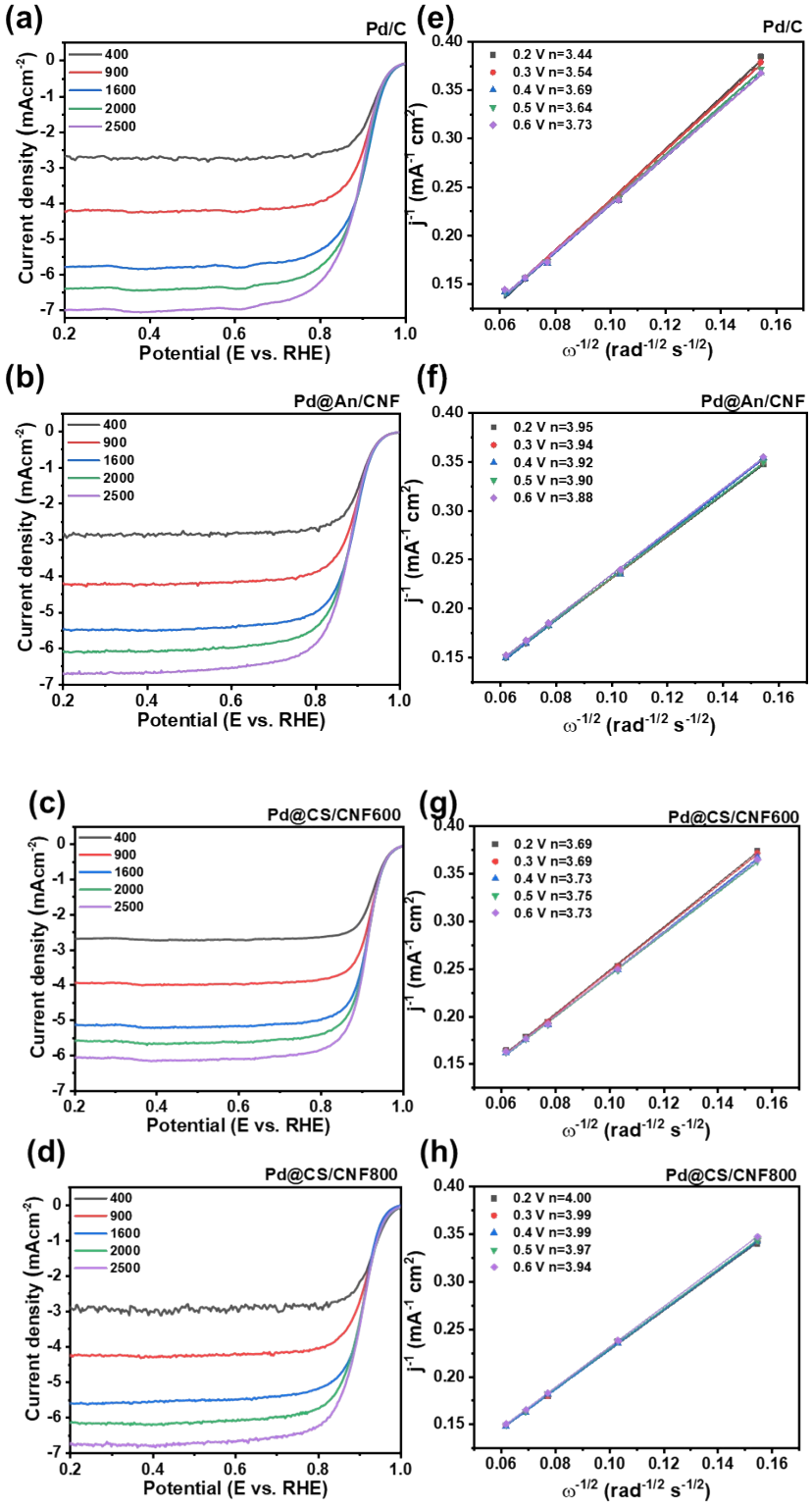

Figure S13. ORR curves of (a) Pd/C, (b) Pd@An/CNF, (c) Pd@CS/CNF600, and (d) Pd@CS/CNF800 in O_2-saturated 0.1 M KOH with different rotating speed at scan rate of 20 mV/s. The K-L plot and the electron transfer numbers of (e) Pd/C, (f) Pd@An/CNF, (g) Pd@CS/CNF600, and (h) Pd@CS/CNF800.

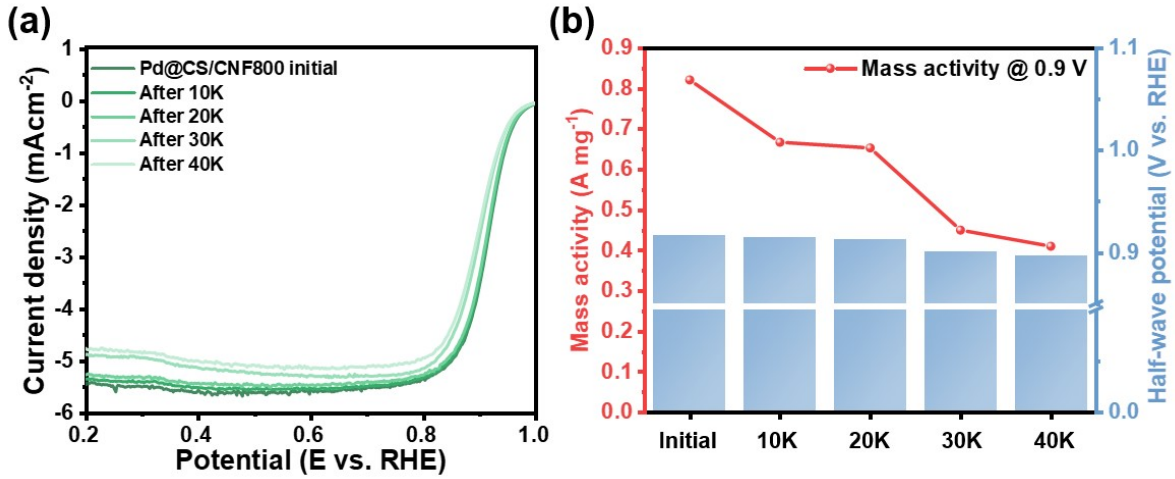

Figure S14. (a) ORR curves of the Pd@CS/CNF800 before and after the durability test (extended cycles up to 40,000cycles) in O_2-saturated 0.1 M KOH at a scan rate of 100 mV/s from 0.6 to 1.0 V (vs. RHE), (b) variation of mass activity and half-wave potential respect to the number of AST cycles.

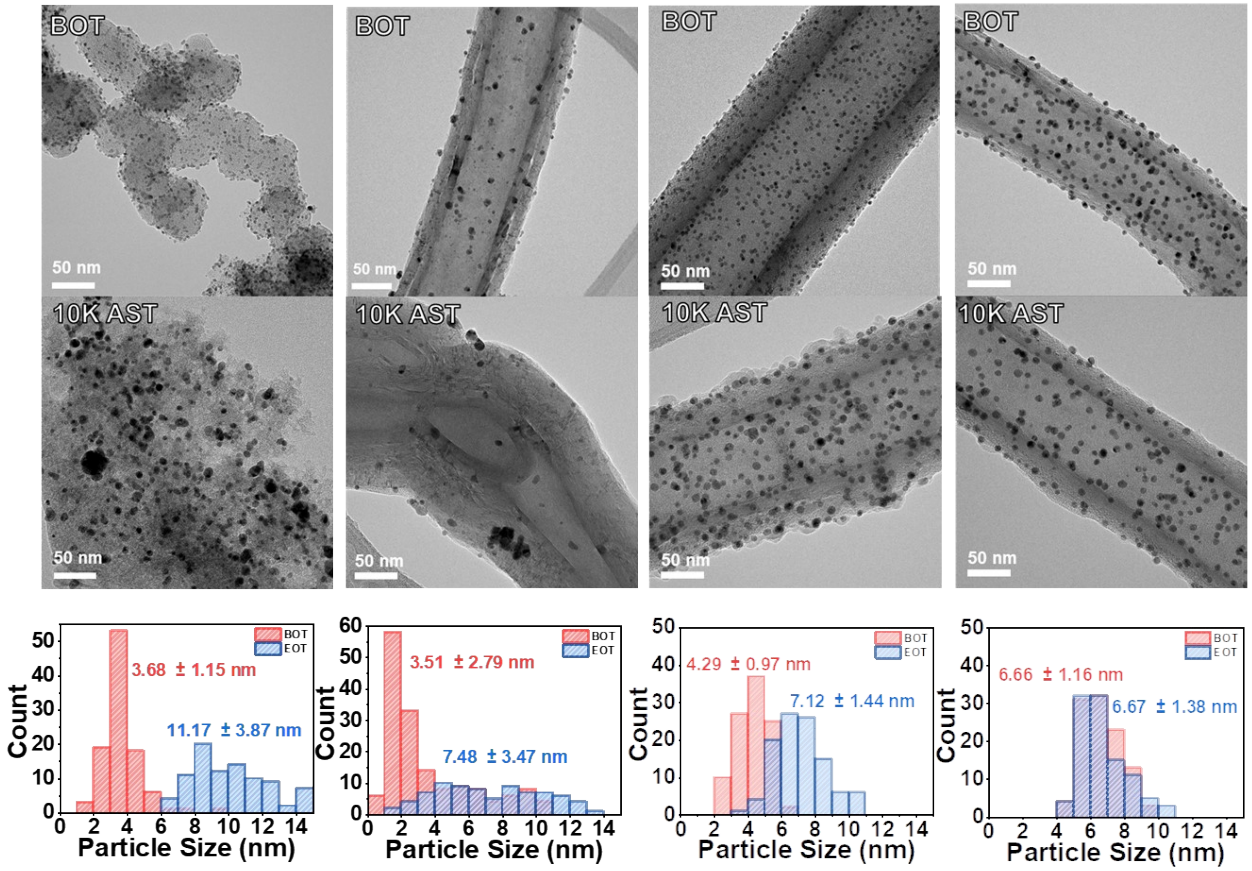

Figure S15. TEM images and particle size distribution of commercial Pd/C, Pd@An/CNF, Pd@CS/CNF600, and Pd@CS/CNF800 before and after AST in the order from the left to right.

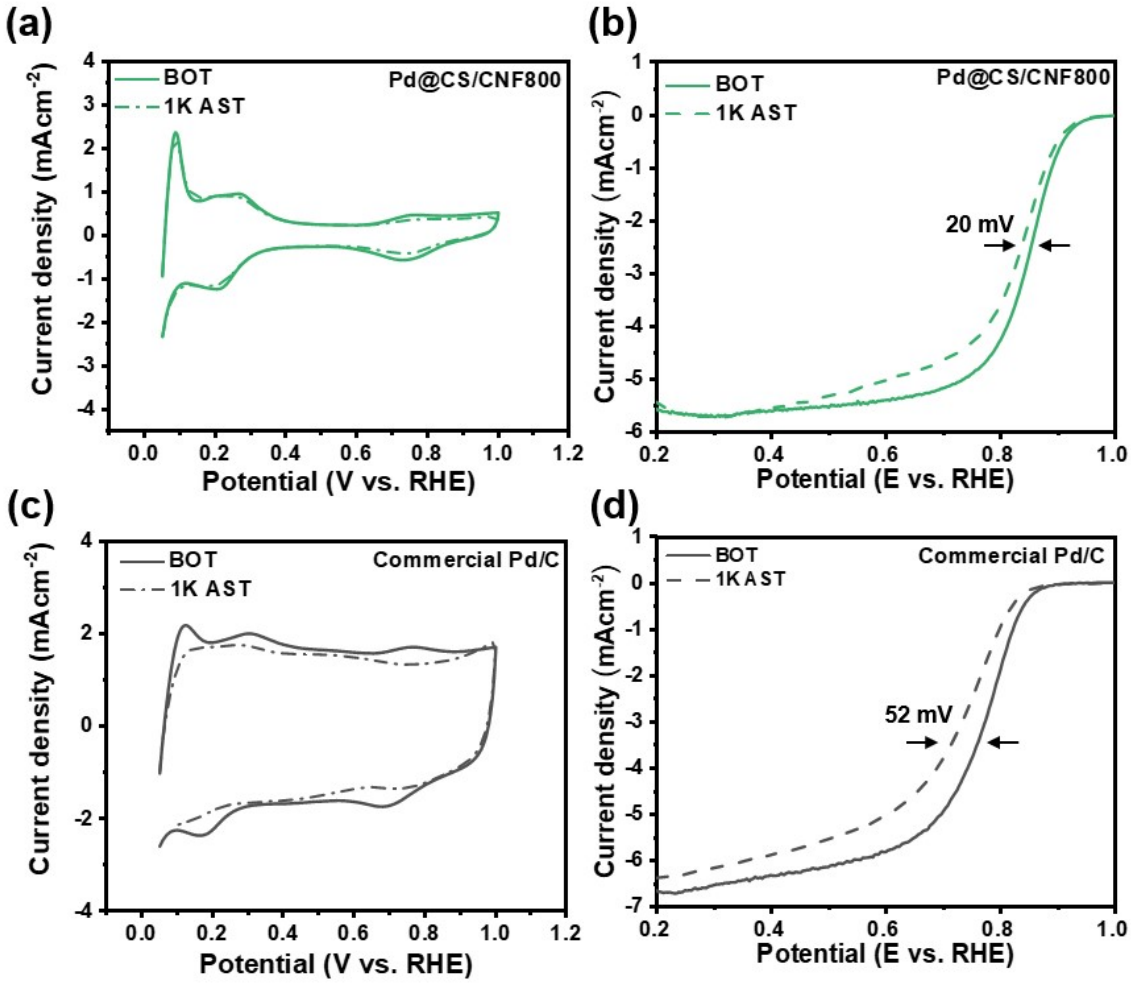

Figure S16. CV curves of (a) Pd@CS/CNF800 and (c) commercial Pd/C. LSV curves for ORR of the (b) Pd@CS/CNF800, (d) commercial Pd/C before and after durability test (1,000 cycles) in N_2-saturated 0.1 M $HClO_4$ at a scan rate of 100 mV/s from 0.6 to 1.0 V (vs. RHE).

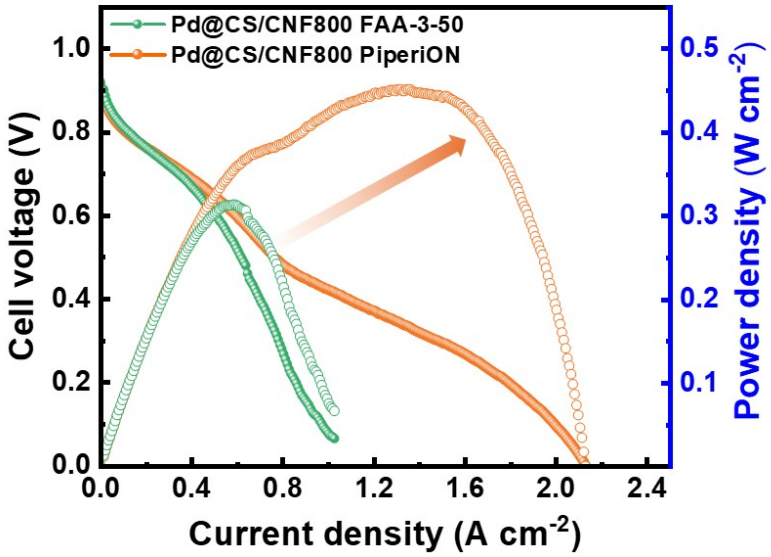

Figure S17. I-V polarization curves of AEMFC obtained with commercial Pt/C 40 wt% (0.4 mg/cm^2) as the anode side and Pd@CS/CNF800 (0.25 mg/cm^2) as the cathode side under H_2-O_2 (500 ccm-600 ccm) and RH 100% conditions at 60 ℃, FAA-3-50 of Fumasep (green line) and PiperION of Versogen (orange line)

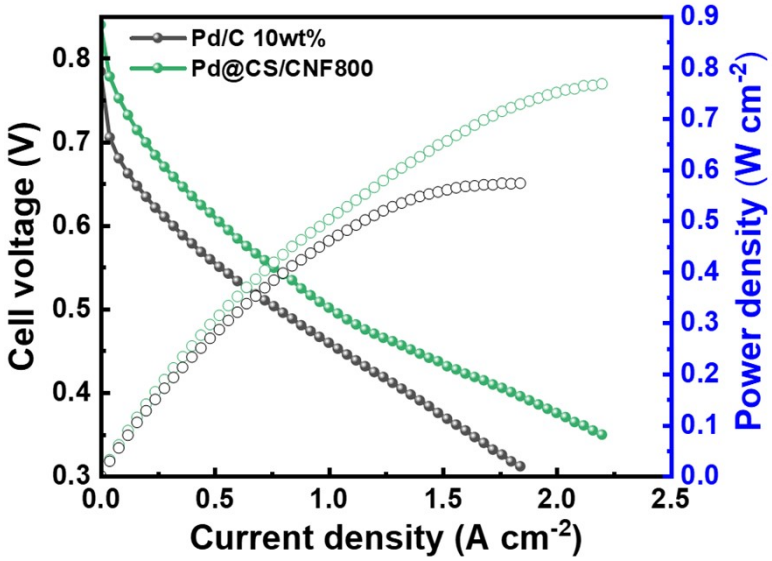

Figure S18. I-V polarization curves of the PEMFC of Commercial Pd/C 10 wt% and Pd@CS/CNF800 as cathode side (0.1 mg/cm^2), Pt/C 40 wt% as the anode side (0.05 mg/cm^2) under H_2-O_2 and RH 100% conditions wo back pressure.

Table S1. wt% of Pd metal form ICP-OES of the Pd/C and Pd@An/CNF, Pd@CS/CNF600, and 900.

Materials	Pd wt%
Pd/C 10wt%	9.4
Pd@An/CNF	14.3
Pd@CS/CNF600	22.6
Pd@CS/CNF800	23.1
Pd@CS/CNF900	23.8

Table. S2 Particles size and peak shift at Pd (111) on XRD Patterns.

Materials	size of Pd (111) (nm)	Shift of (111) peak (º)
Pd JCPDS	N/A	40.5 º
Pd@CS/CNF600	3.7	40.2 º
Pd@CS/CNF800	7.0	40.0 º
Pd@CS/CNF900	8.4	40.4 º

Table S3. Atomic concentration of Pd/C, Pd@An/CNF, Pd@CS/CNF600, and Pd@CS/CNF800 from XPS spectra.

Materials	Pd3d	N1s	C1s	O1s
Pd/C	2.98	N/A	2.98	16.58
Pd@An/CNF	2.51	4.21	78.39	14.89
Pd@CS/CNF600	6.01	3.02	77.17	13.80
Pd@CS/CNF800	5.37	2.48	79.37	12.78
Pd@CS/CNF900	5.50	2.02	85.24	9.94

Table S4 The summary table of Pd@CS/CNF's ORR performance, in comparison with other reported catalysts in alkaline media.

Materials	Mass activity (A/mg_{PGM}) @0.9 V	Specific activity (mA/cm) @0.9 V	$E_{1/2}$ (V vs. RHE)	Ref.
Pd@CS/CNF800	0.83	1.14	0.917	Our study
Pd/C	0.569	0.725	0.911	Our study
Pd metallene	0.43	1.01	0.97	[15]
Pd/p-BNO-2	0.25	0.41	0.89	[17]
Pd-HCS-700	0.06	N/A	0.802	[46]
Fe-Pd UPM	0.736	0.225	0.914	[47]
Pd/F, N-doping G	0.074	N/A	0.87	[48]
Pd_3Pb UPINs/C	0.59	1.18	0.908	[49]
PdCu nanoplate	0.522	0.245	0.900	[50]
Pd-Net	0.62	1.88	1.01	[51]
Pd@PANI metallene	1.79	2.96	0.925	[52]
$Pd/Ti_3C_2T_X$-CNT	0.11	0.2	0.883	[53]
Pd-B/C	0.055	0.17	0.93	[54]
Pd/Co_3O_4-N-C-300	0.07	0.54	0.93	[55]
Pd-B/Pd	0.82	1.2	0.98	[56]
Pd@PEI-EDA	0.73	1.3	0.968	[57]
$PdNFe_3$@Pd/C	1.14	1.95	0.91	[58]

Table S5. Performance comparison to previous studies.

Catalyst (mg/cm²)		OCV (V)	Current density @0.6 V (A/cm²)	P_{max} (W/cm)	Specific power density (W/g_{total})	Conditions	Reference
Anode	**Cathode**						
Pt/C 40wt% (0.4 mg_{Pt}/cm^2)	Pd@CS/CNF800 (0.25 mg_{Pd}/cm^2)	0.919	0.504	0.313	2.40	FAA-3-50/FAA-3-10 SOLUT 500/800 wo bp 60°C	Our study
Pt/C 40wt% (0.4 mg_{Pt}/cm^2)	Pd@CS/CNF800 (0.25 mg_{Pd}/cm^2)	0.911	0.614	0.451	3.47	PiperION/FAA-3-10 SOLUT 500/800 wo bp 60°C	Our study
Pt/C 40wt% (0.4 mg_{Pt}/cm^2)	Pd/C 10wt% (0.4 mg_{Pd}/cm^2)	0.873	0.249	0.170	1.06	FAA-3-50/FAA-3-10 SOLUT 500/800 wo bp 60°C	Our study
Pt/C 50wt% (0.3 mg_{Pt}/cm^2)	Pd-N/3D-GNS-L90 (0.3 mg_{Pd}/cm^2)	-	0.280	0.220	1.83	TokuyamaA201/AS 4/-/- 200/250 2.3bar_{abs}	[30]
Pt/C 40wt% (0.4 mg_{Pt}/cm^2)	Pd/$Ti_3C_2T_X$-CNT (0.4 mg_{Pd}/cm^2)	0.990	0.070	0.048	0.3	-/150/150 60°C	[53]
Pt/C 40wt% (0.5 mg_{Pt}/cm^2)	$PdNFe_3$@Pd/C (0.5 mg_{Pd}/cm^2)	-	0.399	0.270	1.35	1000/1000 2bar_{abs}60°C	[58]
Pt/C 40wt% (0.8 mg_{Pt}/cm^2)	rGO-PdPSe/C (1.4 mg_{Pd}/cm^2)	1.030	0.300	0.200	0.45	FAA-3-50/FAA-3-10 SOLUT	[65]
PtRu/C (0.61g_{PtRu}/cm^2)	Ag_0Pd_{100} (0.08 mg_{Pd}/cm^2)	1.040	0.543	0.420	3.0	FAA-3-50-RF (ePTFE) wo binder 500/500 wo bp 60°C	[66]
Pt/C	Ag-Pd NRT/C	0.967	0.060	0.041	-	FAA-3-50/FAA-3-10 SOLUT	[67]
Pt/C 50wt% (0.6 mg_{Pt}/cm^2)	Pd-N/3D-GNS (0.3 mg_{Pd}/cm^2)	-	0.308	0.250	1.38	TokuyamaA201/AS 4/-/- 2.3bar_{abs}	[68]
Pt/C 60wt%	AL-Pd/Mo_2C	-	0.450	0.490	-	Alkymer 400/400 2bar_{abs} 80°C	[69]

PtRu/C 50wt% 25wt% (0.8g_{PtRu}/cm^2)	Pd40/ECS-003604 (0.4 mg_{Pd}/cm^2)	-	0.290	0.250	1.04	-/HMT-PMBI 500/800 3bar_{abs}60°C	[70]