Dual confinement strategy for Pt–Co intermetallic electrocatalyst with superior durability in proton exchange membrane fuel cells

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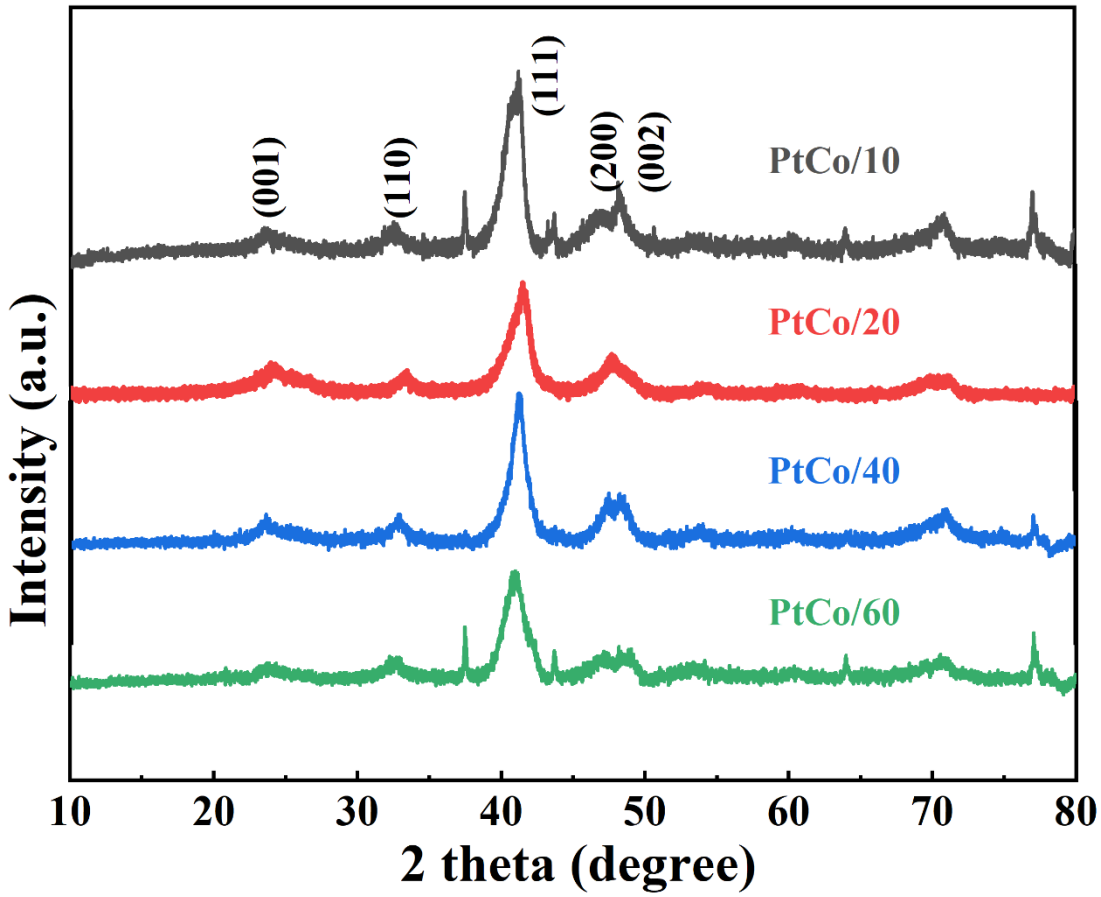

Figure S1. X-ray diffraction (XRD) patterns of PtCo NPs treated with different amount of dopamine.

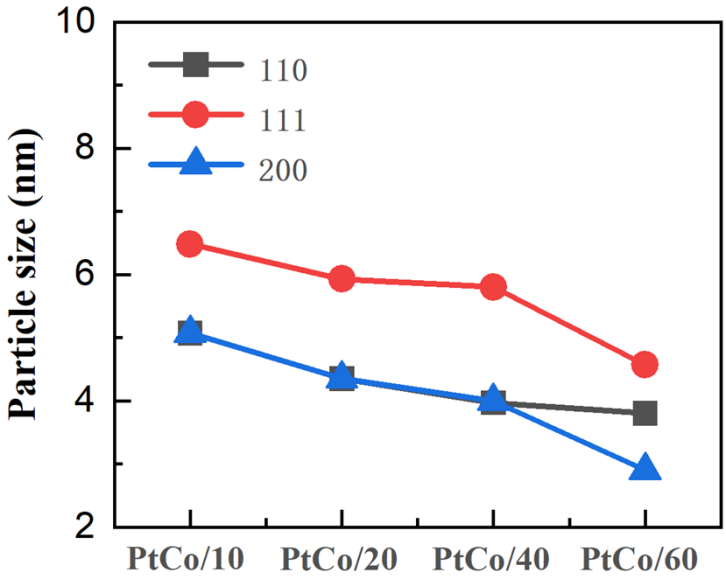

Figure S2. Particle size calculated by XRD patterns of PtCo NPs treated with different amount of dopamine.

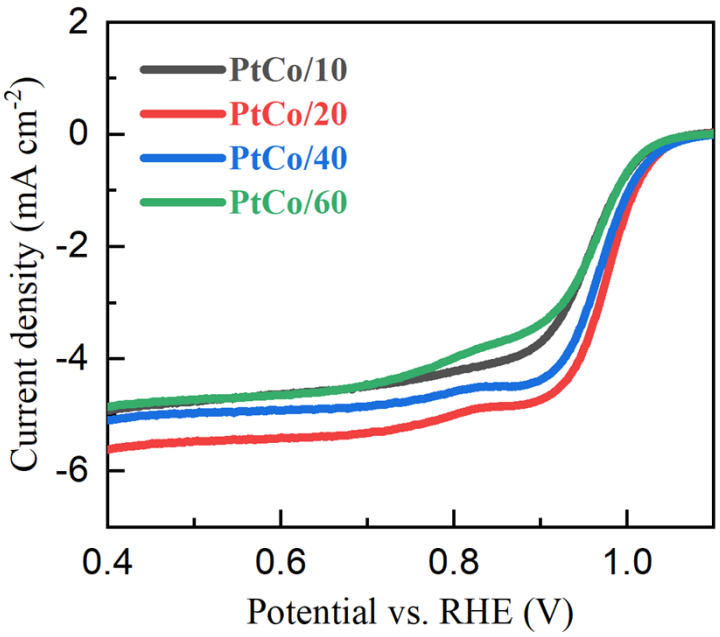

Figure S3. Oxygen reduction reaction (ORR) performance of PtCo NPs treated with different amount of dopamine.

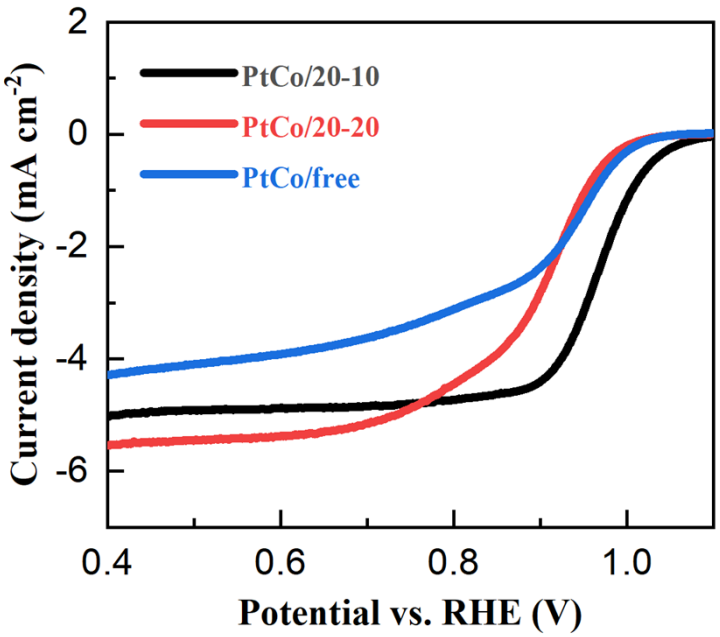

Figure S4. ORR performance of PtsCo NPs treated with different amount and sequence of dopamine.

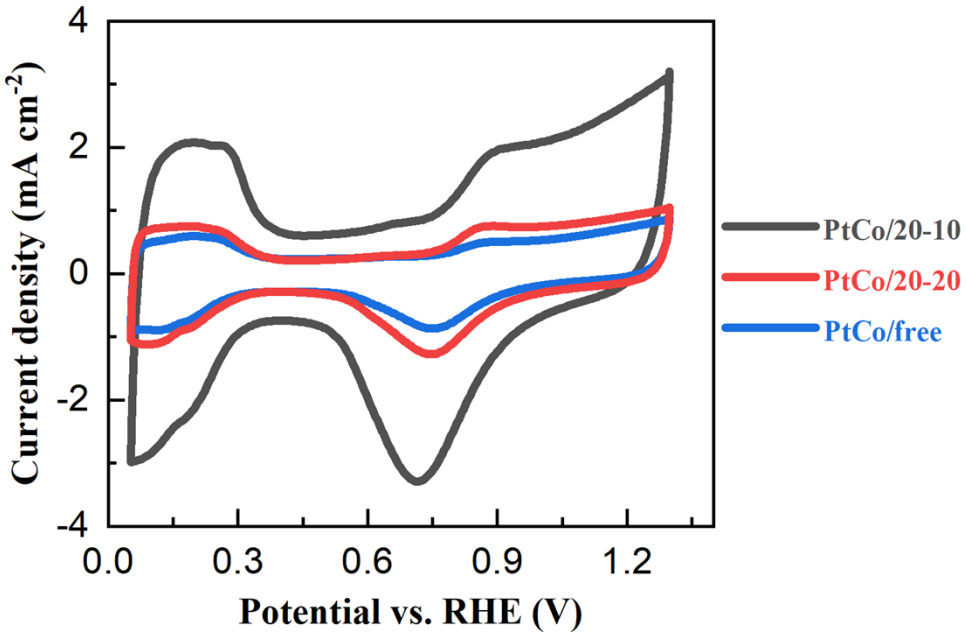

Figure S5. The electrochemical active surface area (ECSA) of PtCo NPs treated with different amount and sequence of dopamine.

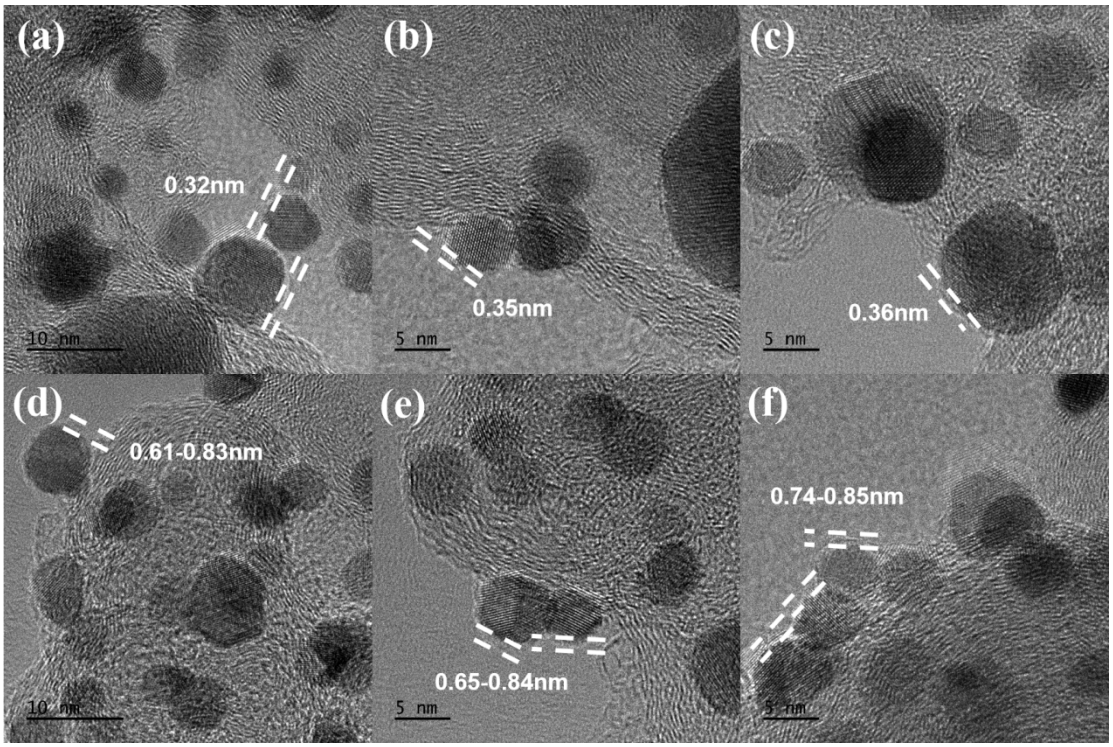

Figure S6 More transmission electron microscope images of the PtCo/20 (a-c) and PtCo/20-10 (d-f) , respectively.

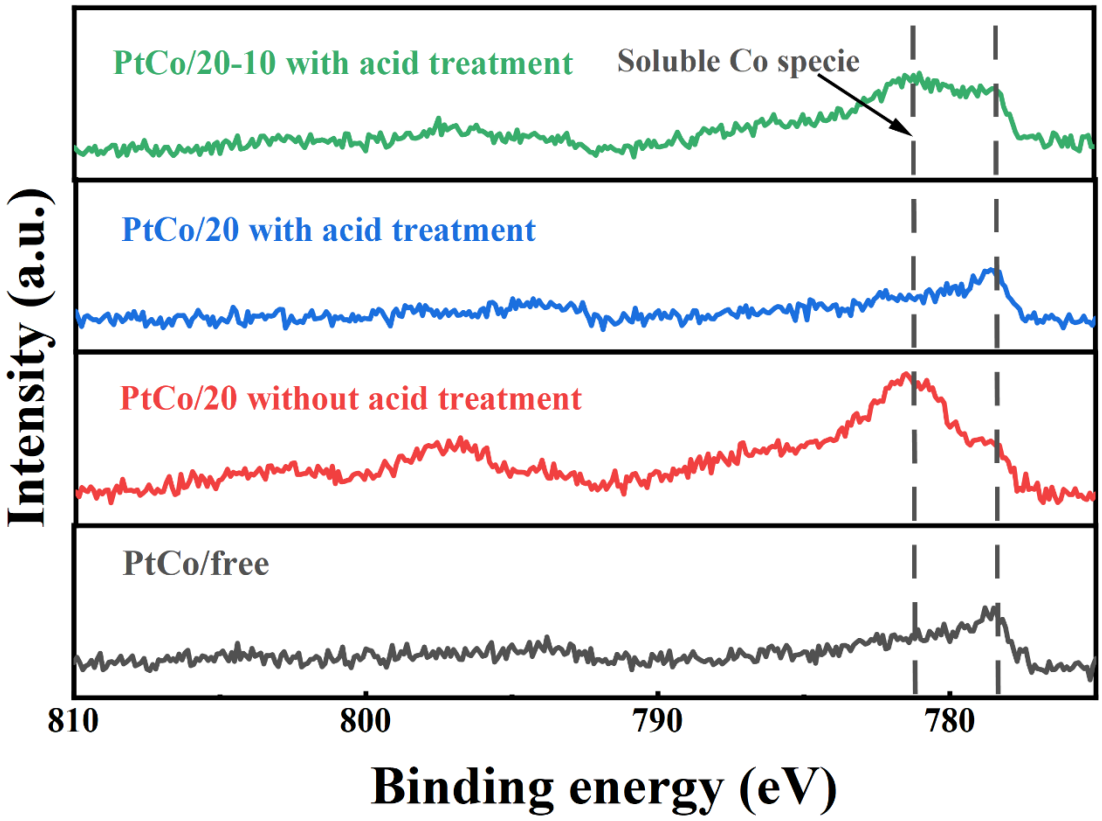

Fig S7. X-ray photoelectron spectroscopy (XPS) of Pt–Co/C-DA-free, Pt–Co/C-DA-20 with and without heat treatment and Pt–Co/C-DA-20-DA-10.

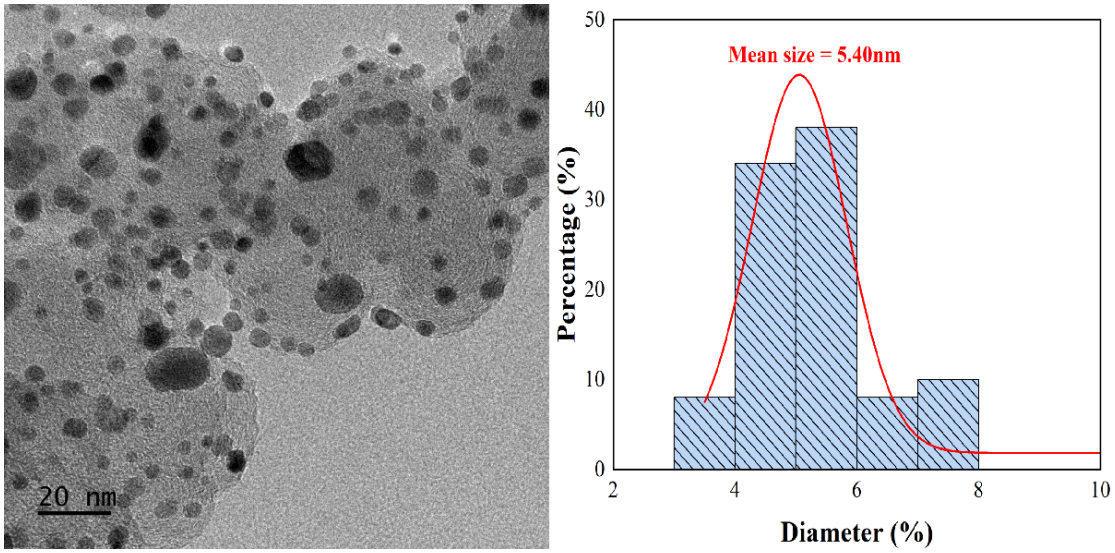

Figure S8. TEM images of PtCo/20 with secondary heat treatment. The corresponding

images on the right show the particle size histogram.

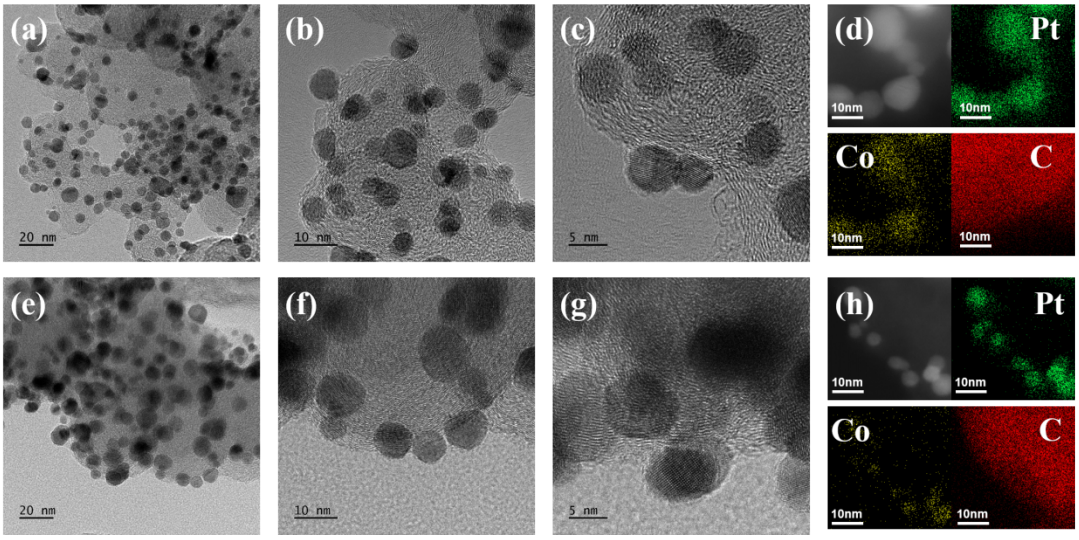

Figure S9. Transmission electron microscope images images of PtCo/20-10 and PtCo/20 catalysts after cycling (a-d) PtCo/20-10 and PtCo/20 (e-h) , respectively.

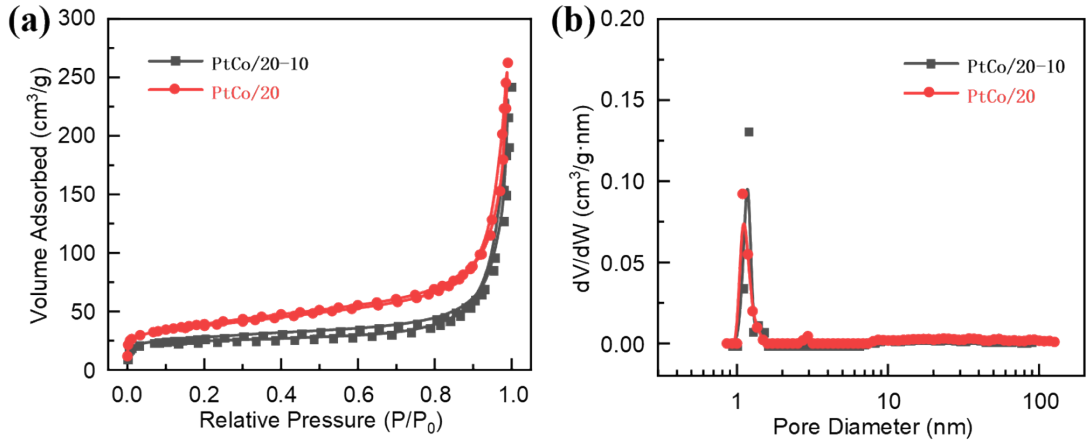

Figure S10. (a) N_2 adsorption–desorption isotherms and corresponding (b) pore size distributions of PtCo/20-10 and PtCo/20.

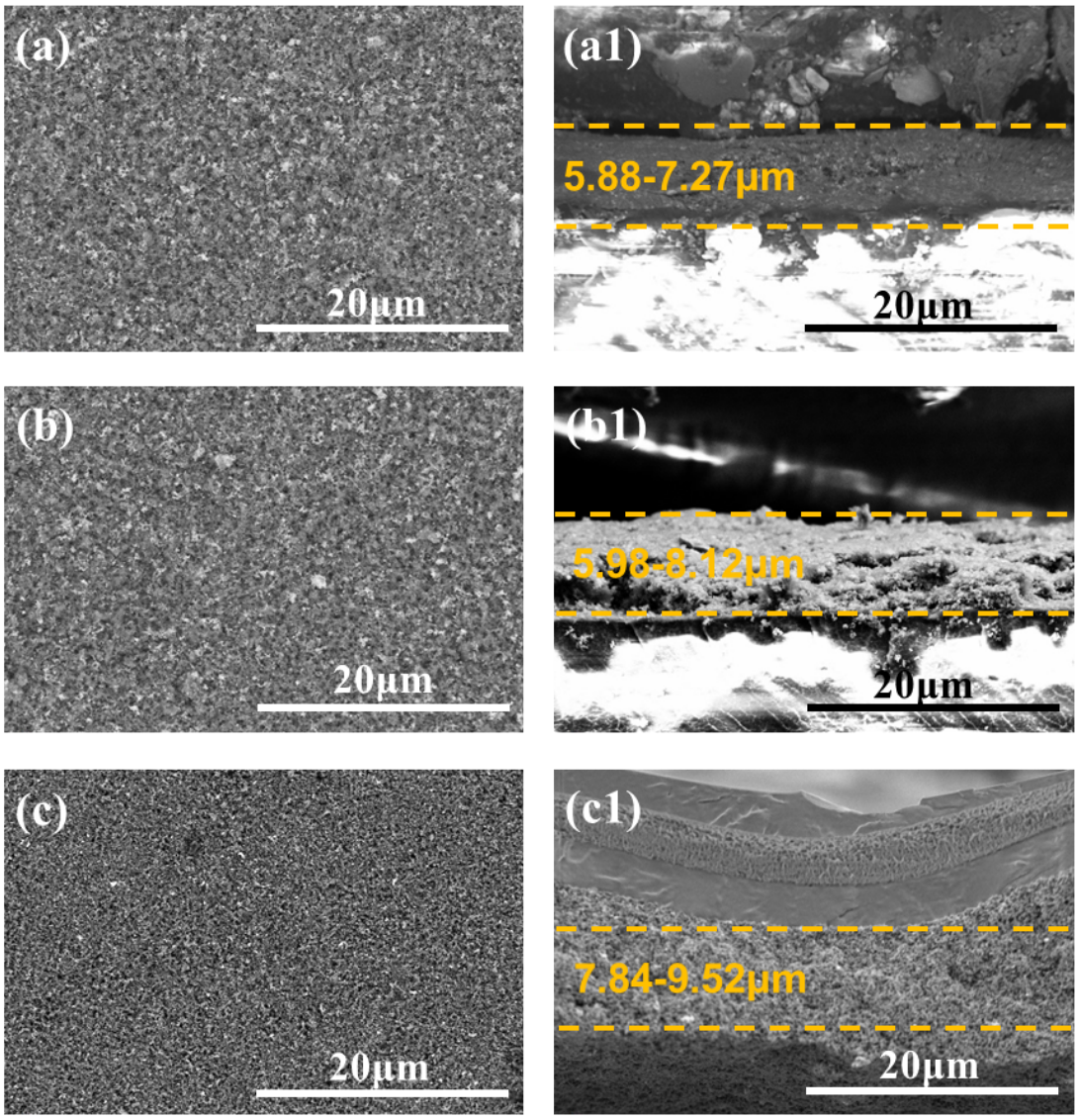

Figure S11 The SEM images of the three cathode electrodes. Planar (a) and cross-sectional (a1) images of PtCo/20-10-based cathode electrode; Planar (b) and cross-sectional (b1) images of PtCo/20-based cathode electrode; Planar (c) and cross-sectional (c1) images of PtCo/free-based cathode electrode.

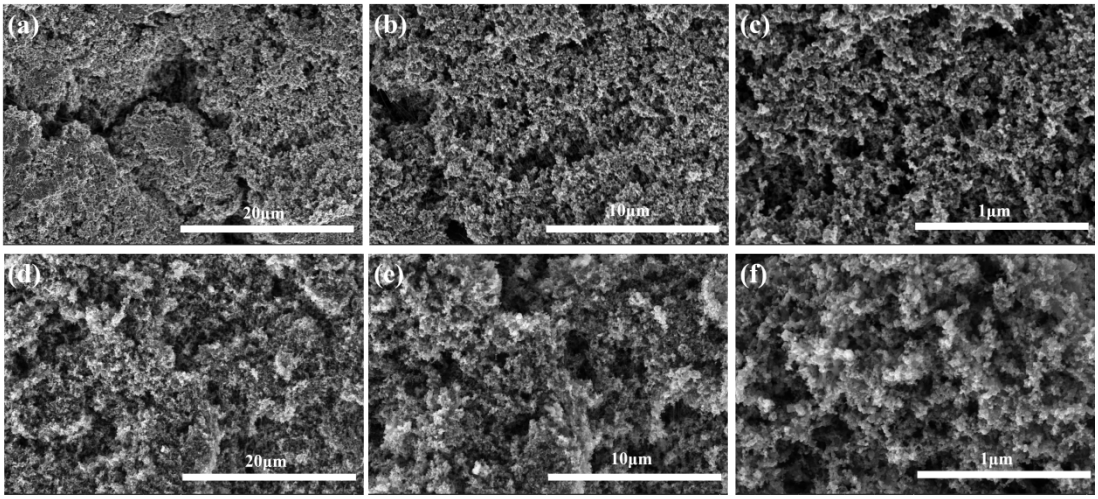

Figure S12 Morphological characterizations of the cathode electrodes based on PtCo/20 and PtCo/20-10 catalysts after 30,000 accelerated durability test (ADT) cycles. (a–c) PtCo/20 catalyst-based cathode electrode; (d–f) PtCo/20-10 catalyst-based cathode electrode.

Table S1. ICP-MS measurement for PtCo NPs.

Sample	Pt/Co atomic ratio	Pt loading (wt%)
PtCo/20-10	0.93	19.04
PtCo/20	0.94	19.14

Table S2. EXAFS fitting parameters at the Pt L3 –edge for samples

Sample	Shell	CN[a]	R(Å)[b]	σ^2(Å^2)[c]	R factor
Pt foil	Pt-Pt	12*	2.76±0.00	0.0044±0.00021	0.0022
PtO_2	Pt-O	6*	2.00±0.01	0.0025±0.0011	0.0077
Pt sample	Pt-O	1.0±0.2	1.97±0.01	0.0029±0.0021	0.001
	Pt-Co	2.7±0.5	2.65±0.00	0.0055±0.0011	
	Pt-Pt	6.1±0.8	2.71±0.01	0.0065±0.00069	

(a) CN, coordination number; (b) R, distance between absorber and backscatter atoms; (c) σ2, Debye-Waller factor to account for both thermal and structural disorders; R factor indicates the goodness of the fit

Table S3. EXAFS fitting parameters at the Co K –edge for samples

Sample	Shell	CN[a]	R(Å)[b]	σ^2(Å^2)[c]	R factor
Co foil	Co-Co	12*	2.49±0.00	0.0063±0.00025	0.00052
CoO	Co-O	6*	2.11±0.01	0.011±0.0028	0.011
	Co-Co	12*	3.01±0.01	0.0089±0.0011	
Co_3O_4	Co-O	4*	1.92±0.01	0.0021±0.0017	0.0094
Co sample	Co-Pt	11.9±1.3	2.67±0.02	0.0143	0.019
	Co-Co	8.4±1.6	2.93±0.01	0.012	

(a) CN, coordination number; (b) R, distance between absorber and backscatter atoms; (c) σ2, Debye-Waller factor to account for both thermal and structural disorders; R factor indicates the goodness of the fit

Table S4 Comparison of recently published Pt-Co catalyst in PEMFC.

ORR catalyst	Chang of mass activity or ECSA in RDE	Durability of PEMFC	Ref.
O-PtCo@GCoNC	**Mass activity: 13.2%** loss for 30000 cycles	**Voltage loss** at 0.8A cm^{-2} : **28mV** for 30000 cycles	1
PtCo/$P_{2.73}O_x$−KB	**Mass activity: 24.3%** loss for 30000 cycles **ECSA: 13.4%** loss for 30000 cycles	**Voltage loss** at 1.5A cm^{-2} : **10mV** for 30000 cycles	2
PtCo/CoNC	**Mass activity: 38.8%** loss for 30000 cycles	/	3
STG-assisted PtCo	/	**Voltage loss** at 0.8A cm^{-2} : **21mV** for 30000 cycles	4
$L1_0$-N-PtCo-H@Pt/C	**ECSA: 9%** loss for 30000 cycles	**Voltage loss** at 0.8A cm^{-2} : **22mV** for 30000 cycles	5
$Ga_{0.1}$-PtCo	/	**Voltage loss** at 0.8A cm^{-2} : **27mV** for 30000 cycles	6
MSA-PtCo/C	/	**Voltage loss** at 0.8A cm^{-2} : **28mV** for 30000 cycles	7
DS-PtFe $_{0.6}$ Ti $_{0.4}$	**Mass activity: 13.5%** loss for **30000** cycles	**Voltage loss** at 0.8A cm^{-2}: **14mV** for 30000 cycles	8
Pt−Co/C-DA-20-DA-10	**Mass activity: 4.9%** loss for **40000** cycles **ECSA: 3.7%** loss for 30000 cycles	**Voltage loss** at 0.8A cm^{-2}: **10mV**for 30000 cycles	This work

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