Supporting Information

Nano-engineering of a 3D-ordered membrane electrode assembly with ultrathin Pt skin on open-walled PdCo nanotube arrays for fuel cells

Yachao Zeng, [a, b, †] Hongjie Zhang, [a, b, †] Zhiqiang Wang, [a, b] Jia Jia, [a, b] Shu Miao, [c] Wei Song, [a] Hongmei Yu, [a, *] Zhigang Shao, [a, **] Baolian Yi [a]

a. Fuel Cell System and Engineering Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, Liaoning 116023, China.

b. University of Chinese Academy of Sciences, Beijing 100049, China.

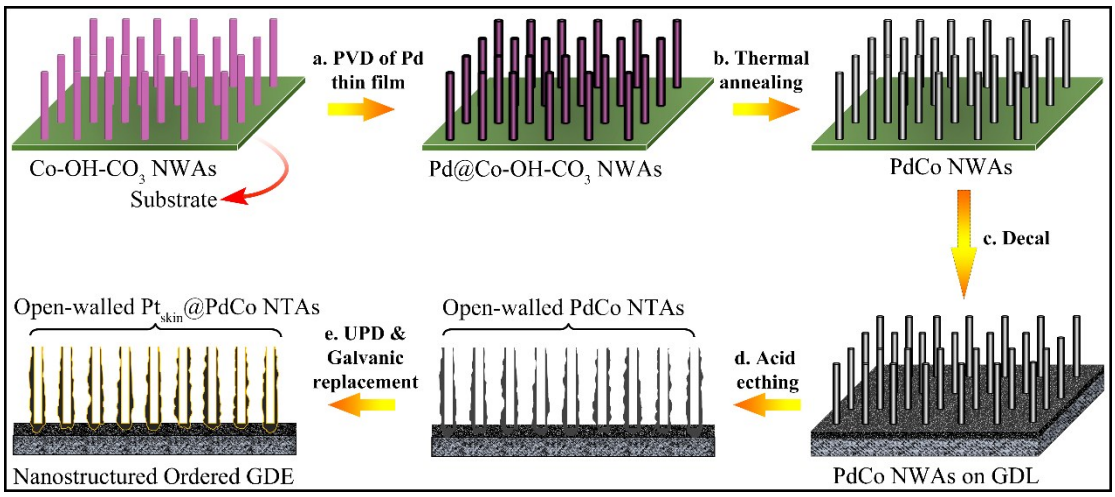
c. Advanced Electron Microscopy Research Group, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, Liaoning 116023, China.

†. *The authors contributed equally and can been considered as co-first authors.*

**Corresponding Authors:*

Email: hmyu@dicp.ac.cn, zhgshao@dicp.ac.cn.

Fax: *+86-84379518;* *Tel:* *+86-84379153.*



Scheme S1. Schematic illustration of the fabrication process of the 3D-ordered GDE based on open walled Pt_{skin}@PdCo NTAs.

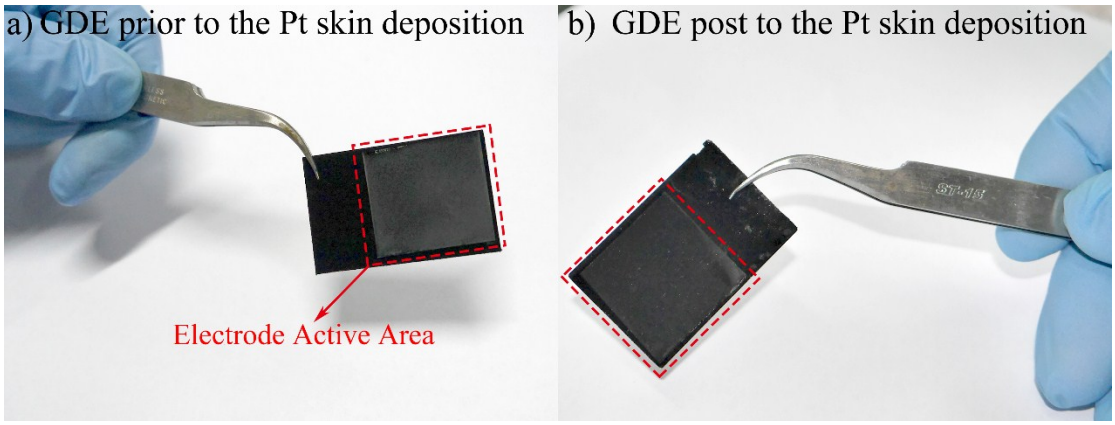


Figure S1. Optical images of the nanostructured GDEs based on PdCo NTAs-400 a) prior to and b) post to the Pt skin deposition.

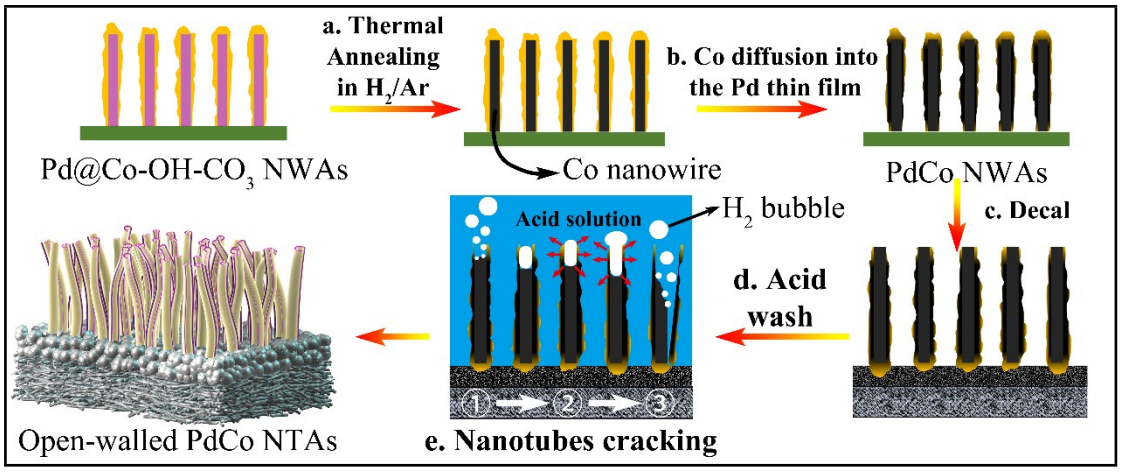


Figure S2. A schematic illustration of the formation process of the open-walled PdCo NTAs.

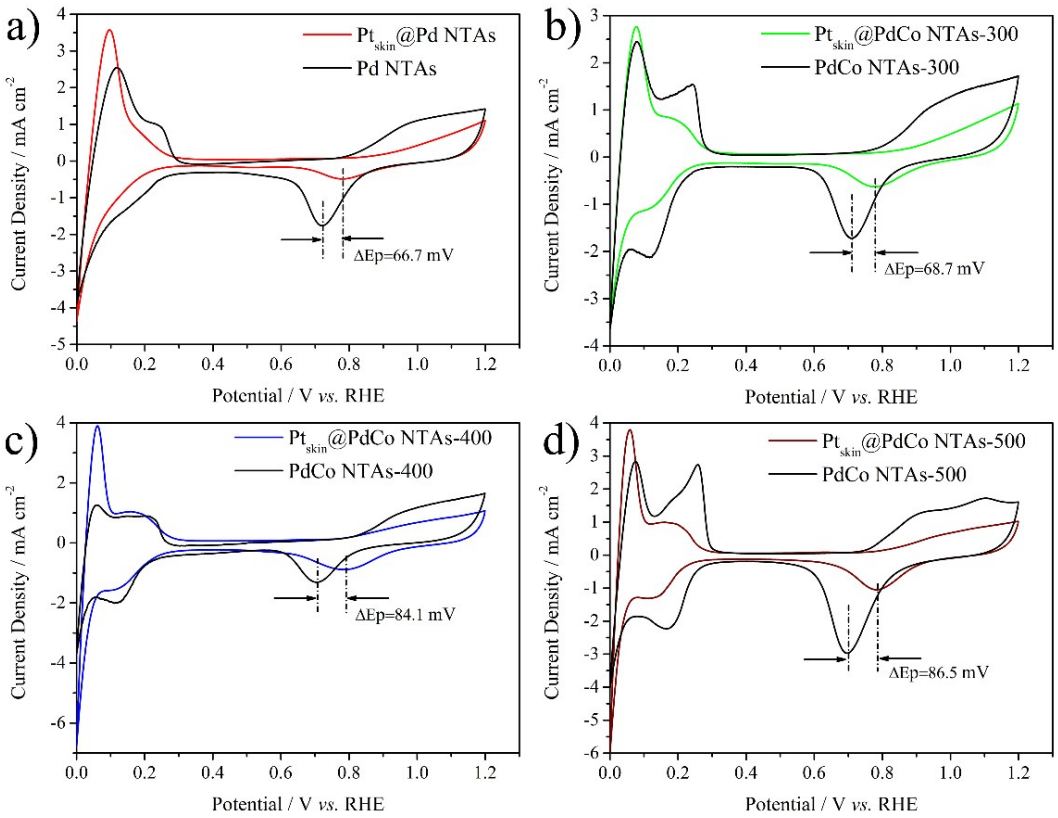


Figure S 3. Cyclic voltammograms of a) Pd NTAs-based, b) PdCo NTAs-300-based, c) PdCo NTAs-400-based and d) PdCo NTAs-500-based GDEs prior and post to the UPD and Galvanic displacement of Cu ML with Pt.

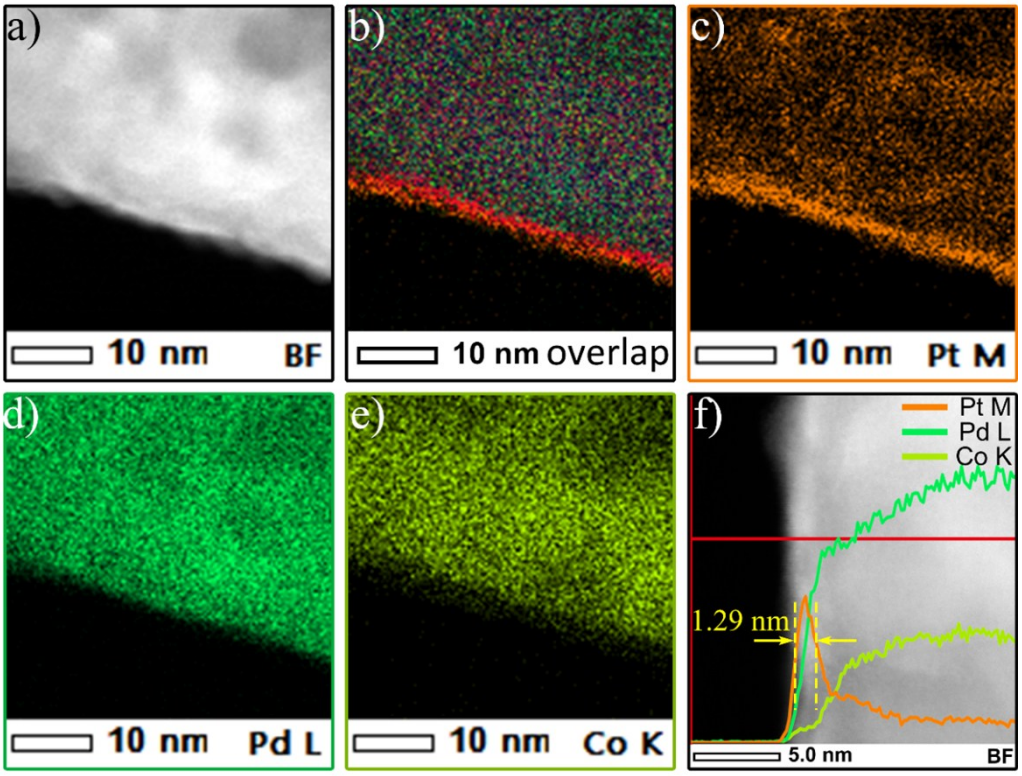


Figure S 4. a) ACSTEM image of Pt$_{skin}$@PdCo NTAs-400 and EDS elemental maps of c) Pt, d) Pd and e) Co. b) EDS map overlapping of Pt, Pd and Co. f) Distribution of elements in a Pt$_{skin}$@PdCo NTAs-400 obtained by a linear scan analysis EDS.

Table S1. A summary of crystal parameters derived from (220) panel of the prepared GDEs.

GDEs	2θ@(220) / degree	d-spacing / Å	Lattice parameters / Å
Pt/C (40 wt. %, JM)	67.60	1.38814	3.926
Pt_{skin}@Pd NTAs	67.61	1.38451	3.916
Pt_{skin}@PdCo NTAs-300	68.32	1.37179	3.880
Pt_{skin}@PdCo NTAs-400	68.79	1.36359	3.857
Pt_{skin}@PdCo NTAs-500	68.84	1.3669	3.866

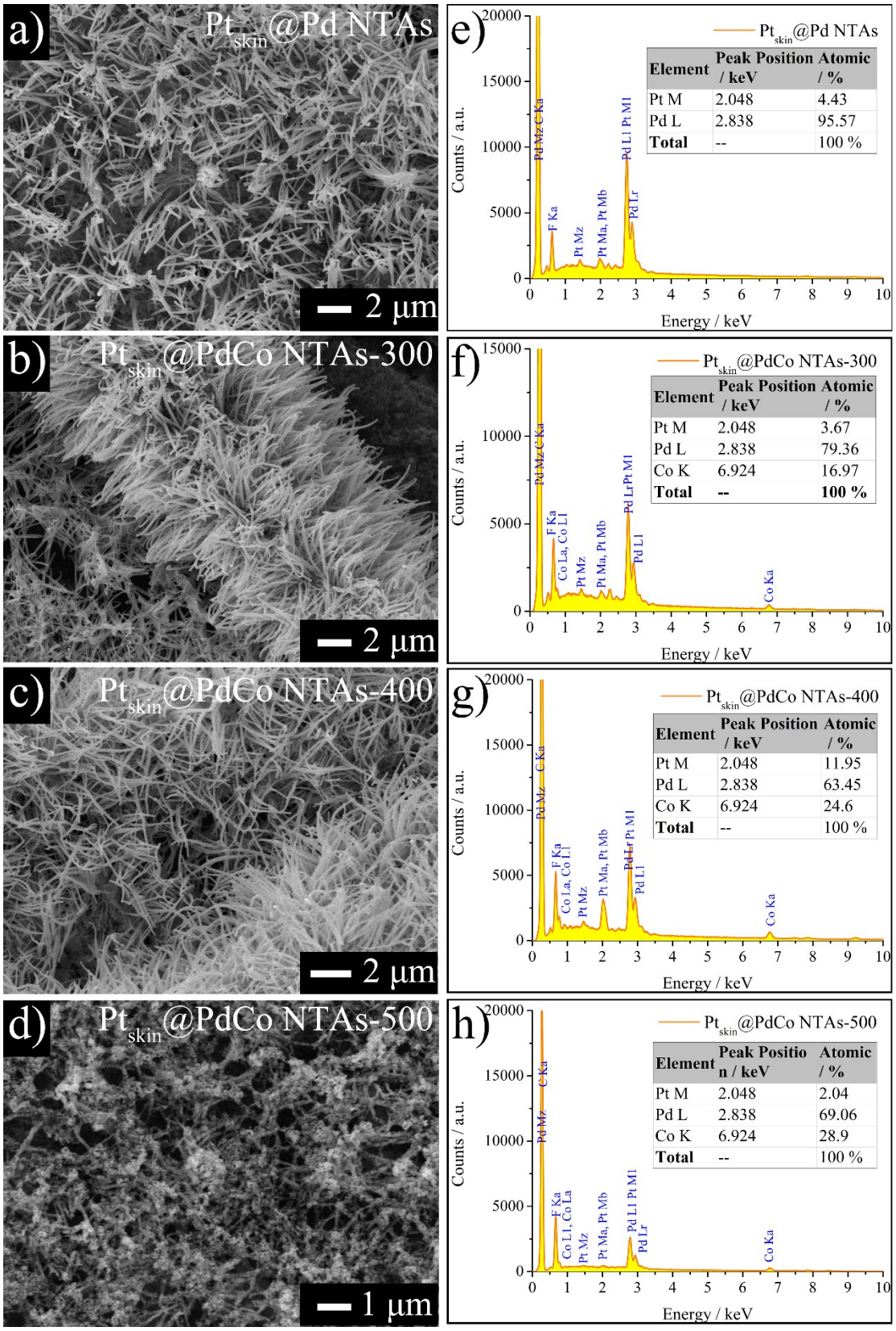


Figure S5. a-d) The in panel SEM images of the prepared nanostructured GDEs. e-h) The corresponding EDS spectra of the nanostructured GDEs.

Table S2. The atomic ratio of Pd : Co in Pd-based NTAs induced from thermal annealing.

GDEs	Atomic ratio of Pd to Co
Pt_{skin}@Pd NTAs	-
Pt_{skin}@PdCo NTAs-300	4.7:1
Pt_{skin}@PdCo NTAs-400	2.6:1
Pt_{skin}@PdCo NTAs-500	2.4:1

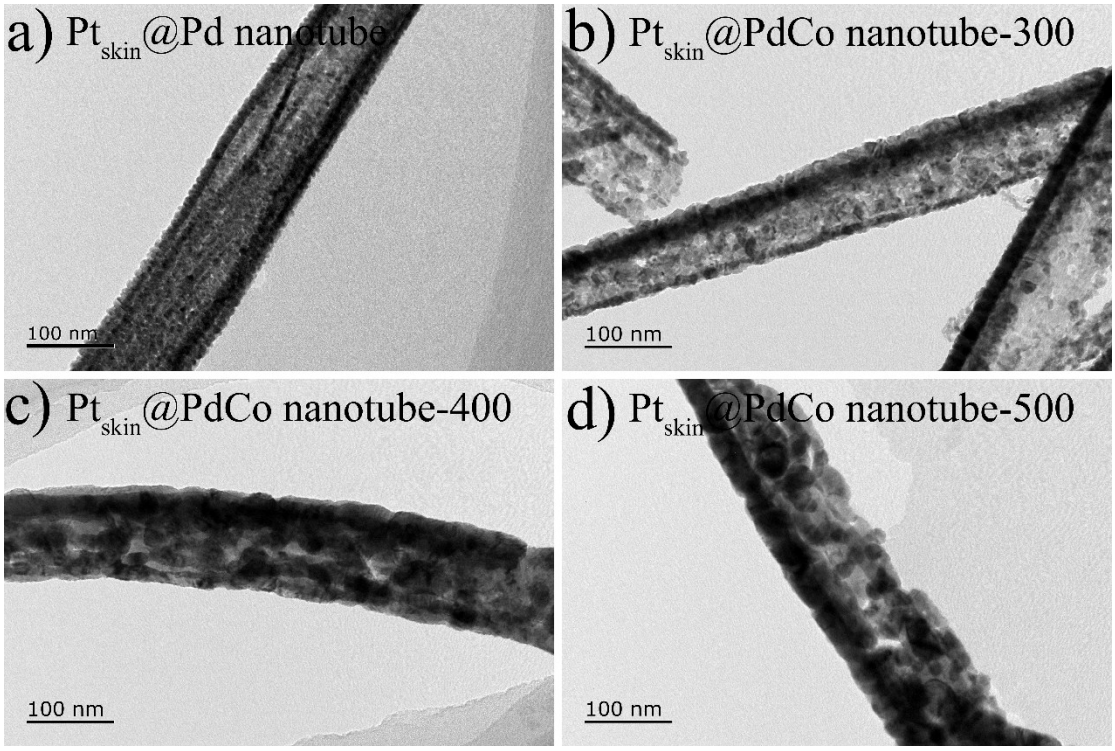


Figure S6. TEM images of a) Pt_{skin}@Pd nanotube, b) Pt_{skin}@PdCo nanotube-300, c) Pt_{skin}@PdCo nanotube-400 and d) Pt_{skin}@PdCo nanotube-500.

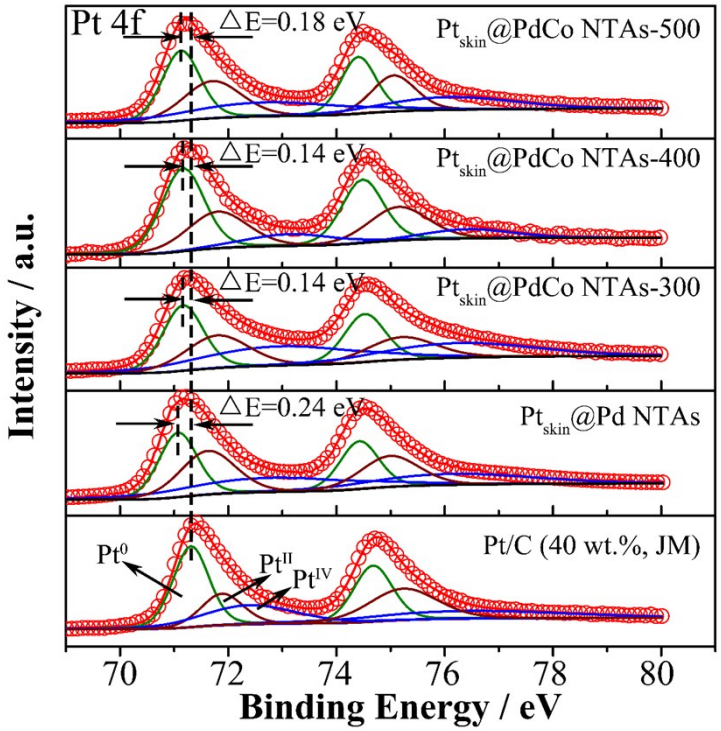


Figure S7. Pt 4f XPS spectra of the nanostructured GDEs and conventional GDE.

Table S 3. The Pt4f XPS data of the conventional and nanostructured GDEs.

	Pt/C (40 wt.%, JM)		**Pt_{skin}@Pd NTAs**		**Pt_{skin}@PdCo NTAs-300**		**Pt_{skin}@PdCo NTAs-400**		**Pt_{skin}@PdCo NTAs-500**	
	B. E. / eV	Ratio / %	B. E. / eV	Ratio / %	B. E. / eV	Ratio / %	B. E. / eV	Ratio / %	B. E. / eV	Ratio / %
Pt^0	71.31	48.29	71.07	33.84	71.17	34.14	71.17	51.70	71.13	37.64
Pt^{II}	71.89	21.96	71.63	32.88	71.80	26.62	71.81	32.29	71.71	30.63
Pt^{IV}	72.38	29.76	72.78	33.28	72.96	39.25	73.15	16.01	72.7	31.74

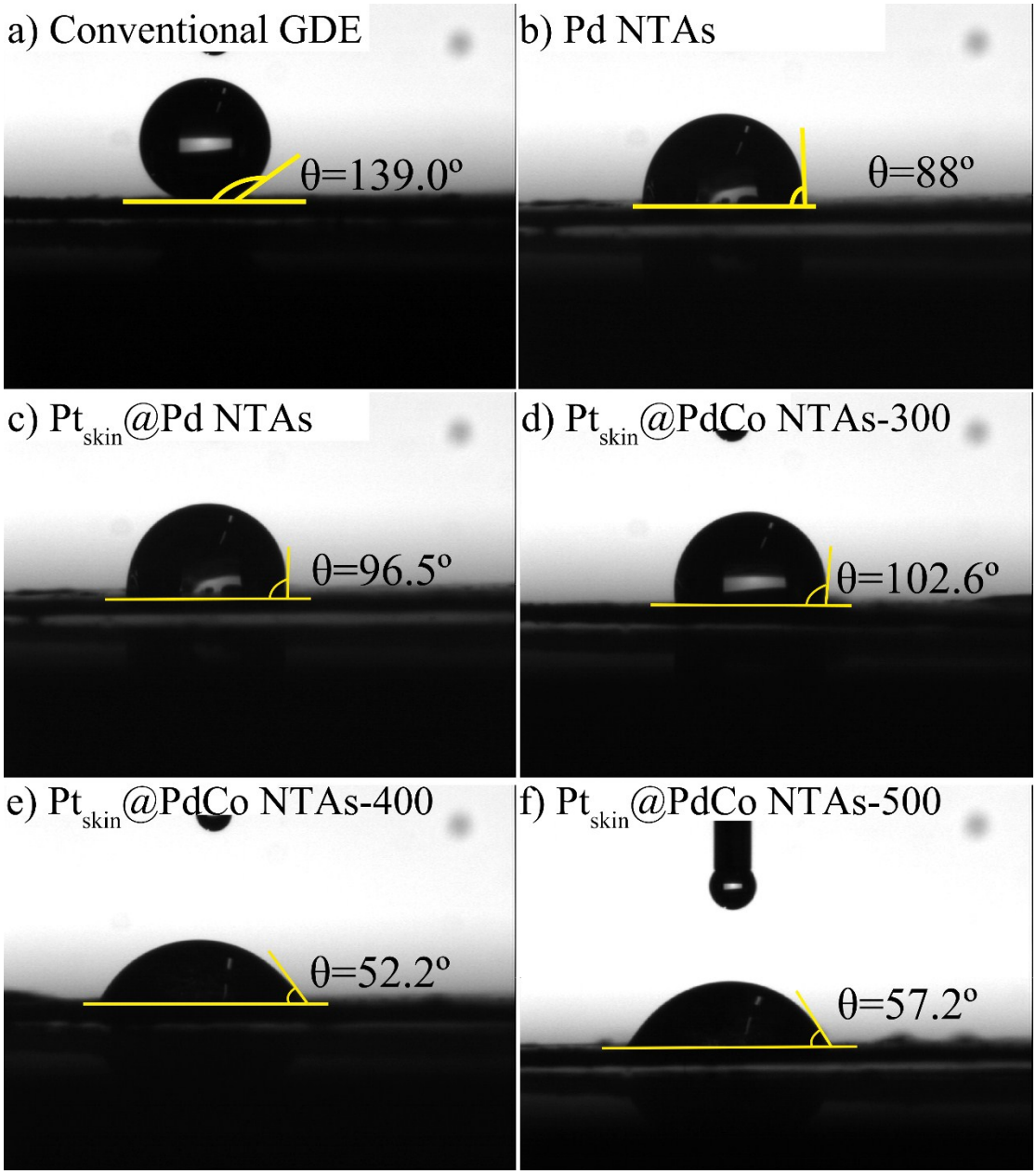


Figure S8. Contact angles of a) conventional Pt/C, b) Pd NTAs, c) Pt_{skin}@Pd NTAs, d) Pt_{skin}@PdCo NTAs-300, e) Pt_{skin}@PdCo NTAs-400 and f) Pt_{skin}@PdCo NTAs-500 based GDEs.

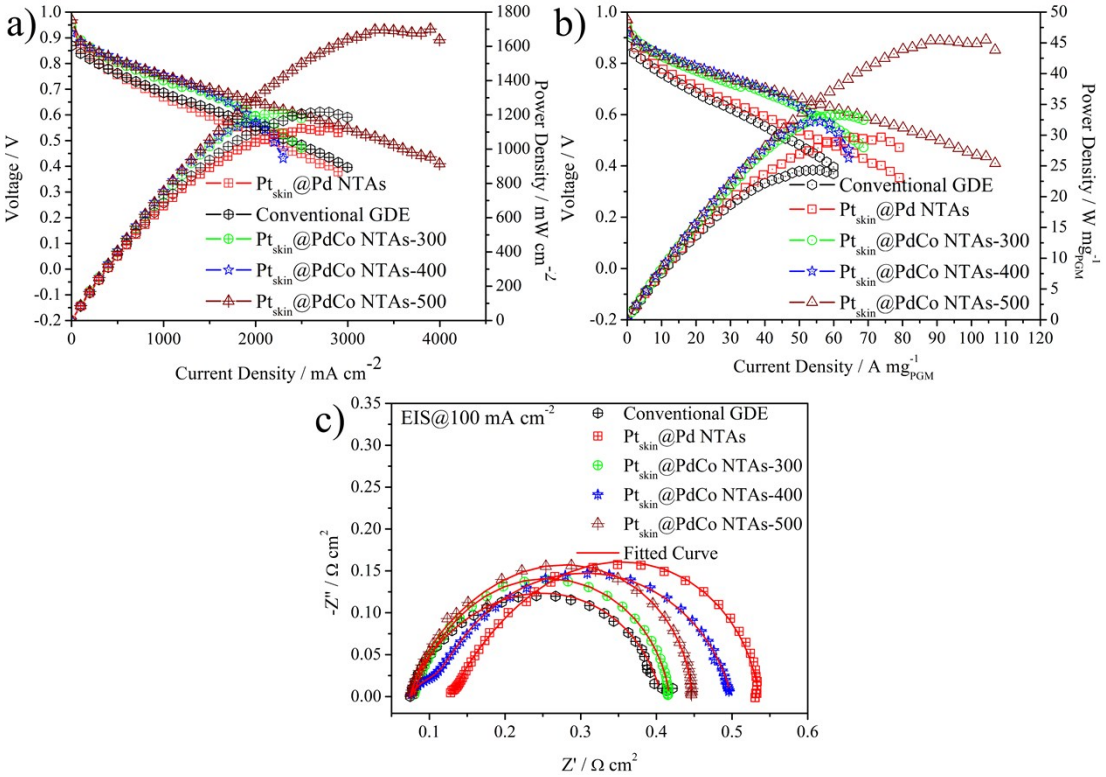


Figure S9. a) Electrode geometric specific and b) mass specific performances of the GDEs based on Pt/C, Pt_{skin}@ Pd NTAs, Pt_{skin}@ PdCo NTAs-300, Pt_{skin}@ PdCo NTAs-400 and Pt_{skin}@ PdCo NTAs-500 serving as anodes, testing conditions: active area: 2.56 cm^2, 80 °C, gas flow rate of H_2/O_2 was 100/200 mL min^{-1}, the gas humidity was 80 %. c) EIS recorded at a current density of 100 mA cm^{-2}.

Table S4. A summary of characteristic parameters of single cell performance with the prepared GDEs serving as anode.

Anodes	Power Density			R_0 / mΩ cm^2	R_{ct} / mΩ cm^2
	mW cm^{-2}	kW g_{Pt}^{-1}	kW g_{PGM}^{-1}		
Conventional GDE	1218.7	24.4	24.4	59.9	82.8
Pt_{skin}@Pd NTAs	1122.0	198.9	29.6	129.7	128.5
Pt_{skin}@PdCo NTAs-300	1210.0	295.1	33.3	75.8	48.6
Pt_{skin}@PdCo NTAs-400	1151.6	323.0	32.2	76.4	29.3
Pt_{skin}@PdCo NTAs-500	1698.1	330.4	45.4	75.5	98.8

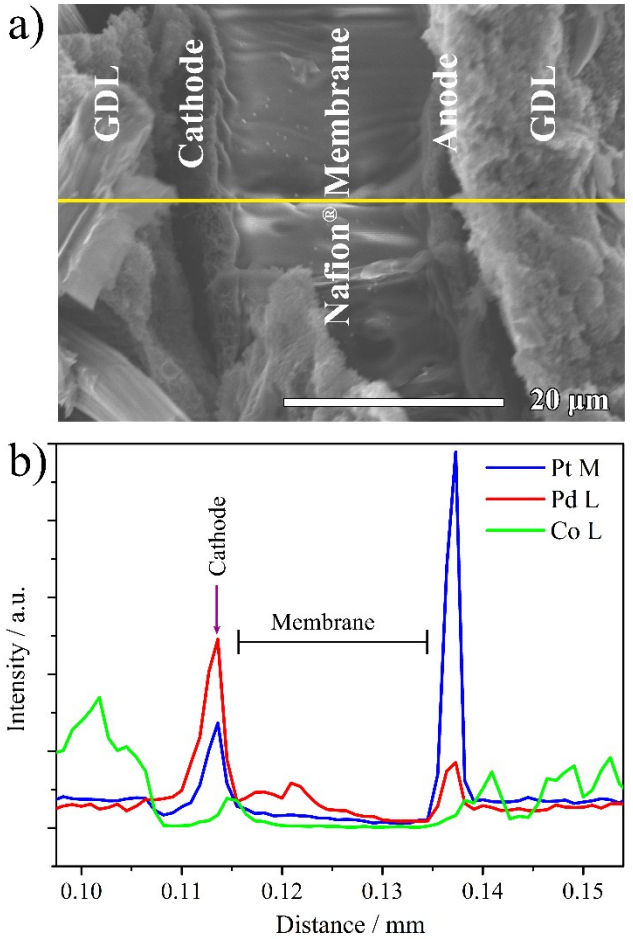


Figure S10. a) Cross sectional image of the Pt_{skin}@PdCo NTAs-400-based MEA after 5000 ADT cycles, in which the yellow line labels the EDS analysis line. b) Elemental distributions in the aged Pt_{skin}@PdCo NTAs-400-based MEA.