Supporting Information

Nanoporous Pd-Cu Thin Films as Highly Active and Durable Catalysts for Oxygen Reduction in Alkaline Media

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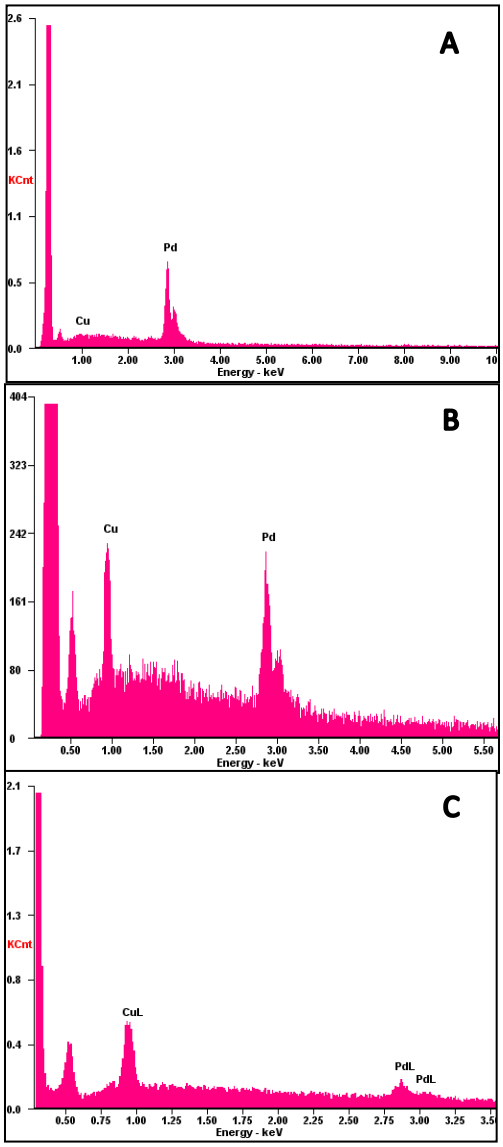

Figure S1. SEM-EDS spectra of precursor alloy films: (A) $Pd_{0.89}Cu_{0.11}$, (B) $Pd_{0.5}Cu_{0.5}$, (C) $Pd_{0.18}Cu_{0.82}$.

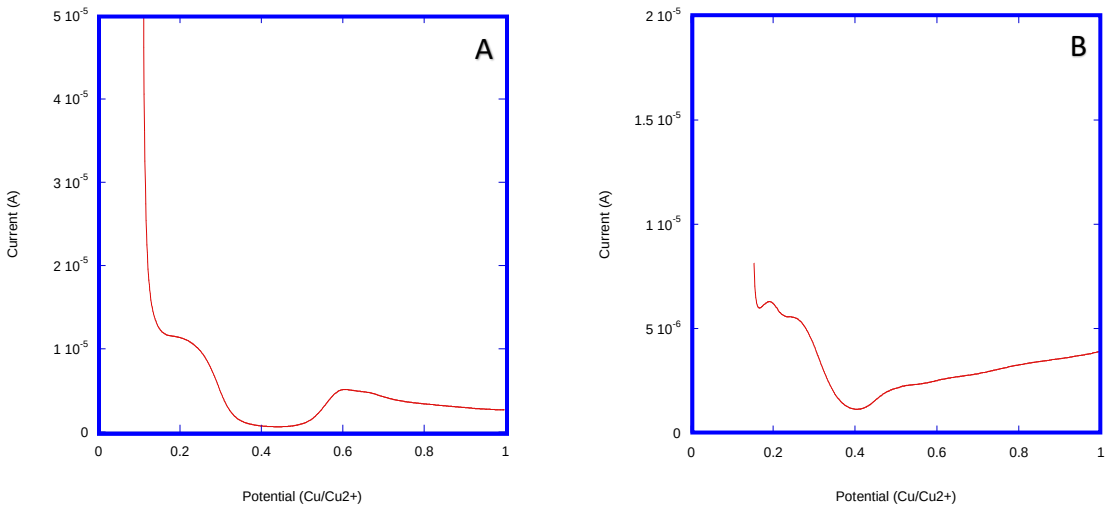

Figure S2. Anodic potential scan of precursor alloys in a 1 mM $CuSO_4$ and 0.1 M $HClO_4$ solution, at a scan rate of 1mV/s: (A) $Pd_{0.18}Cu_{0.82}$ (B) $Pd_{0.50}Cu_{0.50}$

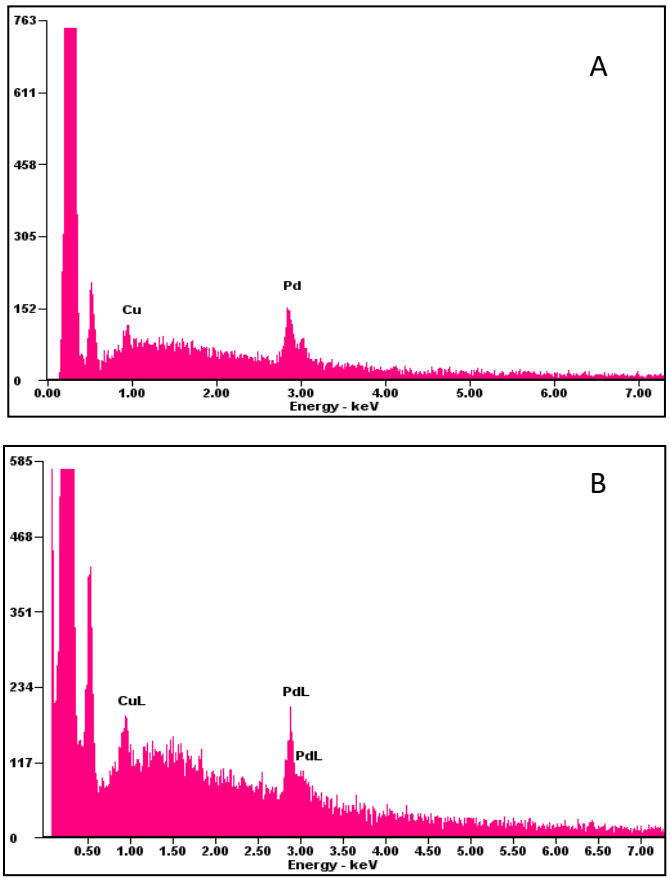

Figure S3. SEM-EDS spectra of (A) np $Pd_{0.37}Cu_{0.63}$ and (B) np $Pd_{0.65}Cu_{0.35}$ alloy catalysts.

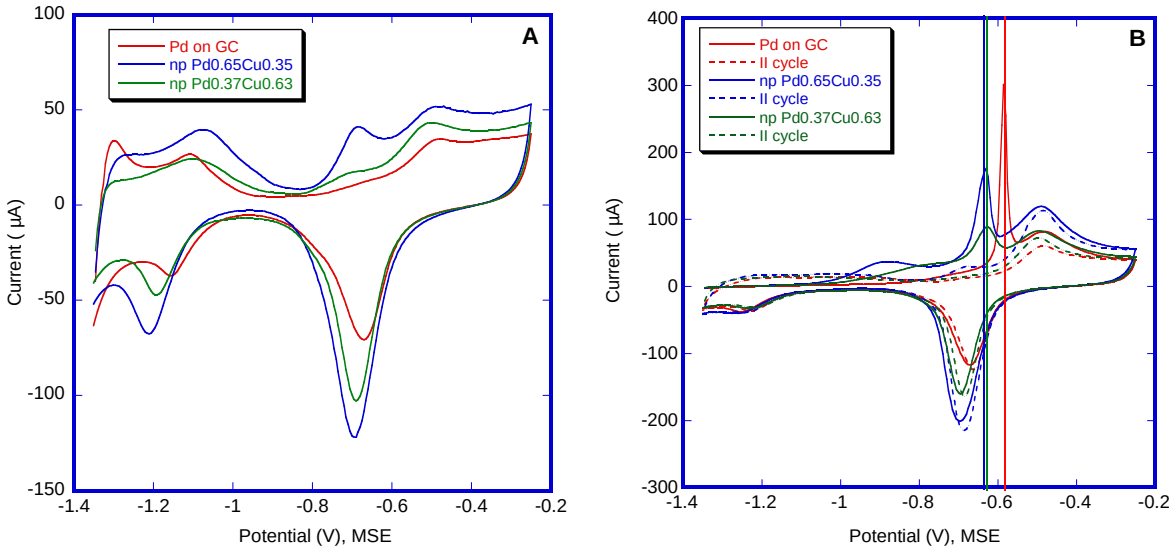

Figure S4. (A) H_{UPD} curves for Pd on GC, np $Pd_{0.65}Cu_{0.35}$ and np $Pd_{0.37}Cu_{0.63}$ catalysts in 0.1 M KOH at 50 mV/s; (B) CO stripping curves for Pd on GC, np $Pd_{0.65}Cu_{0.35}$ and np $Pd_{0.37}Cu_{0.63}$ catalysts in 0.1 M KOH at 50 mV/s.

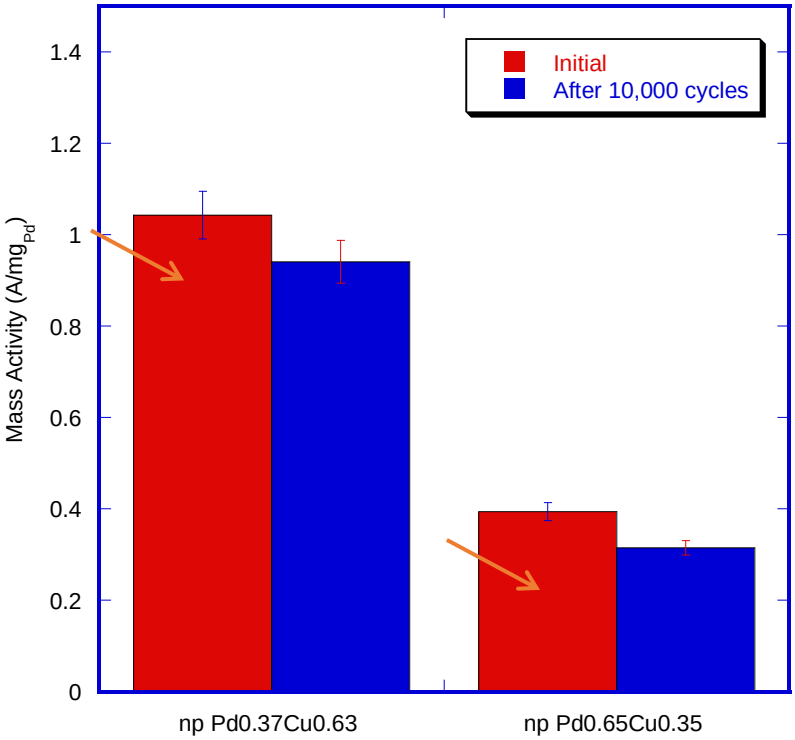

Figure S5. Mass activity change of np $Pd_{0.37}Cu_{0.63}$ and np $Pd_{0.65}Cu_{0.35}$ alloy catalysts after ADT of 10,000 cycles.

Table S1 Comparison of CO stripping peak position at different electrolyte

Electrocatalysts	**Main CO Stripping Peak at Acidic Media (V, RHE)**	**Main CO Stripping Peak at Alkaline Media (V, RHE)**
Pd on GC	**0.92**	**0.83**
np Pd0.65Cu0.35	**0.85**	**0.79**
np Pd0.37Cu0.63	**0.87**	**0.78**

Table S2. Summary of previous studies of Pd-Cu electrocatalysts

Electrocatalysts	**Morphology**	**Half-wave potential (V)**	**Mass Activity (A/mg$_{Pd}$)**	**Reference**
PdCu/C	Hollow nanoparticles	-0.127 vs. Ag/AgCl	0.35 at -0.15 V vs. Ag/AgCl	[1]
Pd-Cu	nanoparticles	0.886 vs. RHE	0.12 at 0.9V (RHE)	[2]
PdCuCo/C	nanoparticles	0.872 vs. RHE	0.12 at 0.9V (RHE)	[3]
PdCu	nanotube	0.825 vs. RHE	N/A	[4]
Pd-Cu	nanoparticles	~0.9V vs. RHE	0.42 at 0.9V (RHE)	[5]
Pd-Cu	***nanoporous***	***0.896 V***	***1.11 at 0.9V (RHE)***	***This work***

References:

[1] L. An, M. Zhu, B. Dai, F. Yu, Hollow palladium–copper bimetallic nanospheres with high oxygen reduction activity, Electrochim Acta, 176 (2015) 222-229.

[2] Y. Yang, G. Chen, R. Zeng, A.M. Villarino, F.J. DiSalvo, R.B. van Dover, H.D. Abruña, Combinatorial Studies of Palladium-Based Oxygen Reduction Electrocatalysts for Alkaline Fuel Cells, Journal of the American Chemical Society, 142 (2020) 3980-3988.

[3] K. Jiang, P. Wang, S. Guo, X. Zhang, X. Shen, G. Lu, D. Su, X. Huang, Ordered PdCu-Based Nanoparticles as Bifunctional Oxygen-Reduction and Ethanol-Oxidation Electrocatalysts, Angewandte Chemie International Edition, 55 (2016) 9030-9035.

[4] D. Wu, D. Cheng, Structure-controlled synthesis of one-dimensional PdCu nanoscatalysts via a seed-mediated approach for oxygen reduction reaction, Applied Surface Science, 493 (2019) 139-145.

[5] G. Bampos, L. Sygellou, S. Bebelis, Oxygen reduction reaction activity of Pd-based bimetallic electrocatalysts in alkaline medium, Catalysis Today, 355 (2020) 685-697.