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Supporting Information

3D-2D Heterostructure of PdRu/NiZn Oxyphosphides with Improved Durability for Electrocatalytic Methanol and Ethanol Oxidation

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Figures and Tables

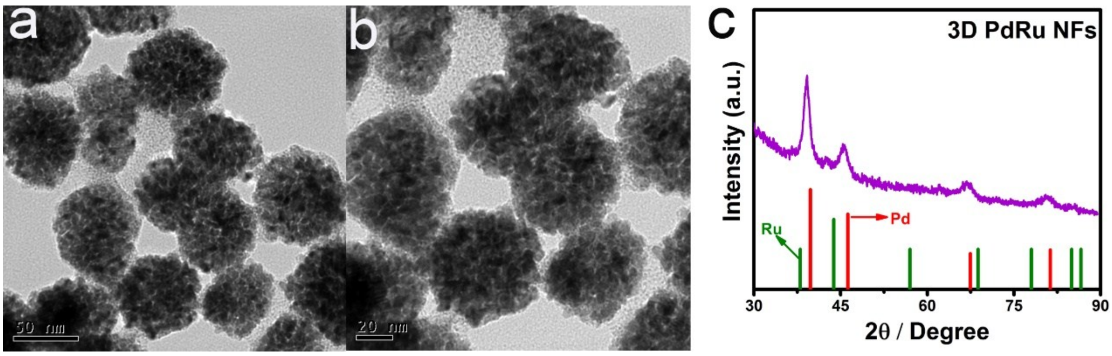

Figure S1 (a and b) Representative TEM images of 3D PdRu NFs with different magnifications and its (c) XRD patterns.

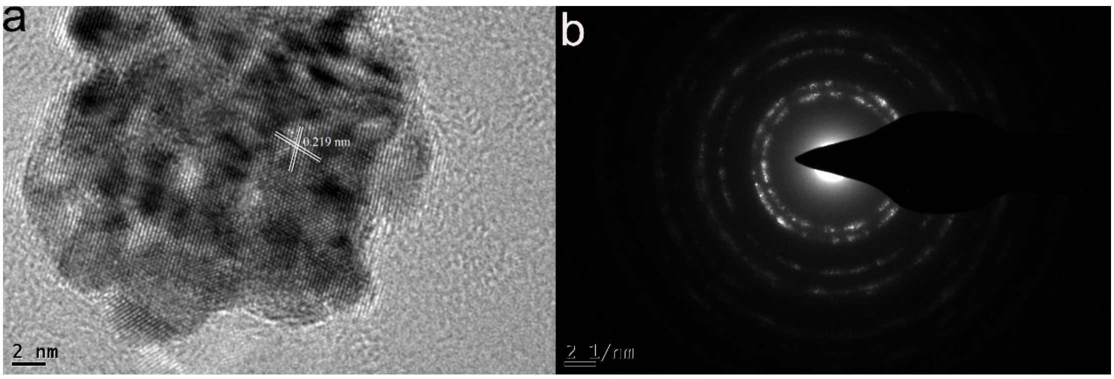

Figure S2 Representative (a) HRTEM images and (b) SAED patterns of 3D PdRu NFs.

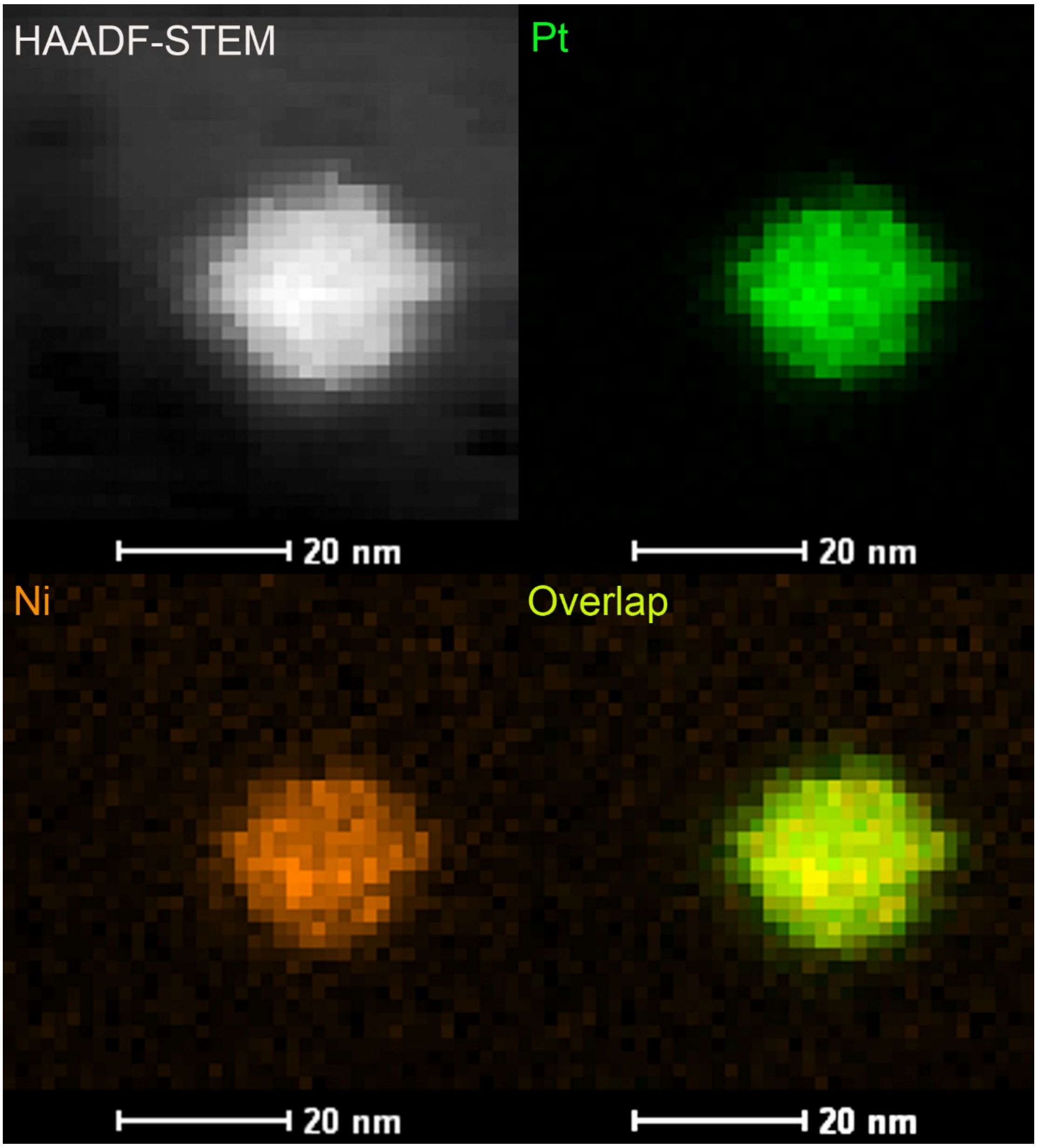

Figure S3 HAADF-STEM image and element mapping patterns of a single PdRu nanoflower.

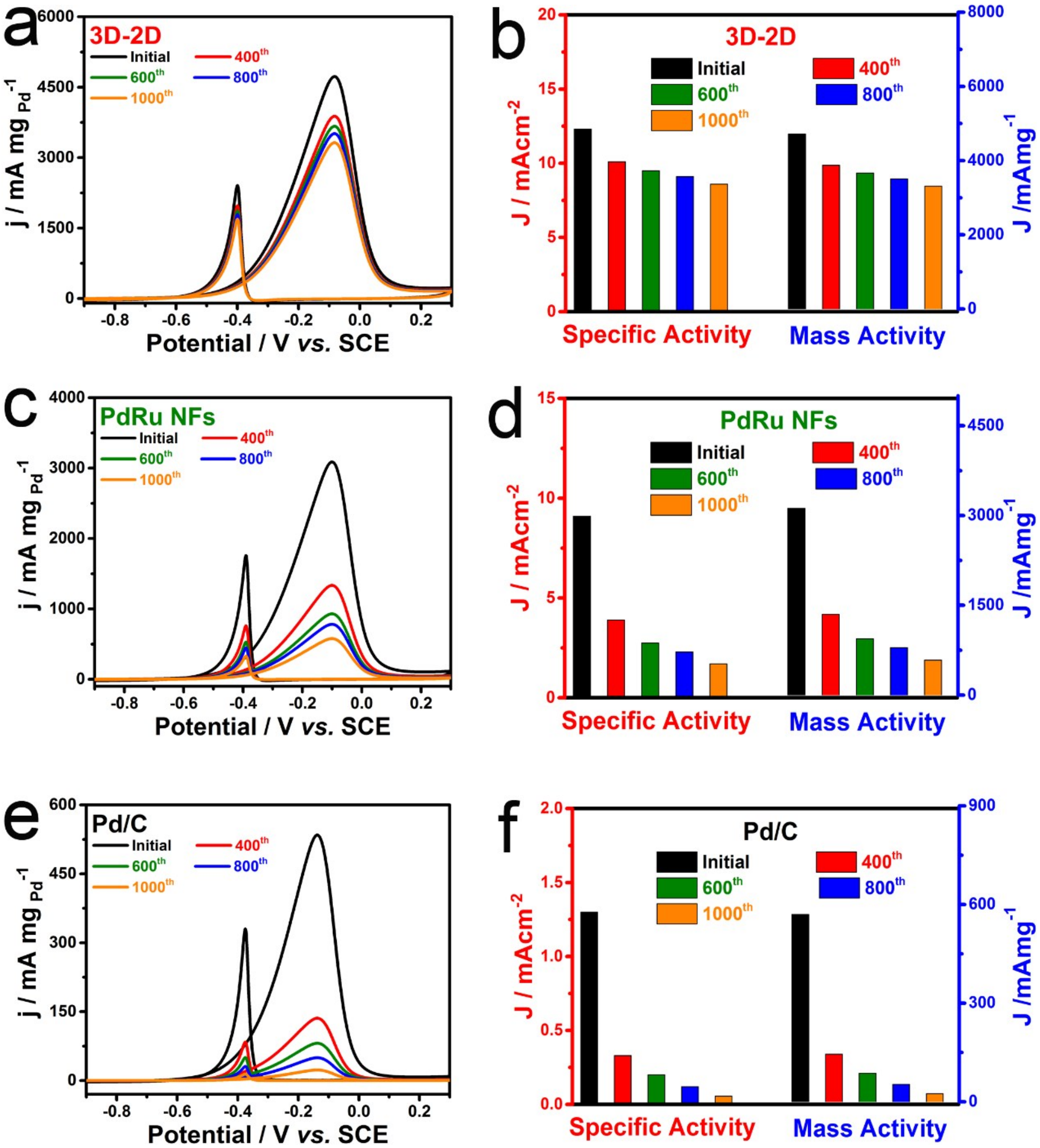

Figure S4 CV (1st, 400th, 600th, 800th, and 1000th cycle) of (a) 3D-2D nanohybrids, (b) 3D PdRu NFs, and (c) commercial Pd/C for EOR at 50 mV s^{-1} in 1.0 M KOH + 1.0 M CH_3CH_2OH, respectively. Corresponding histograms for retained specific and mass activities of (d) 3D-2D nanohybrids, (e) 3D PdRu NFs, and (f) commercial Pd/C for EOR durability test.

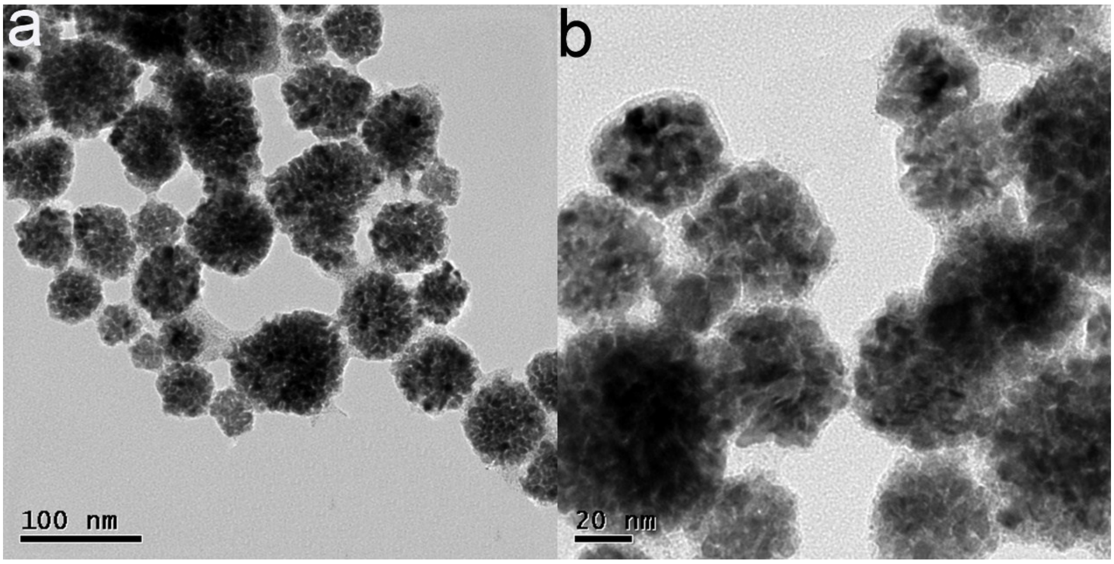

Figure S5 Representative TEM images of 3D PdRu NFs with different magnifications after long-term stability tests.

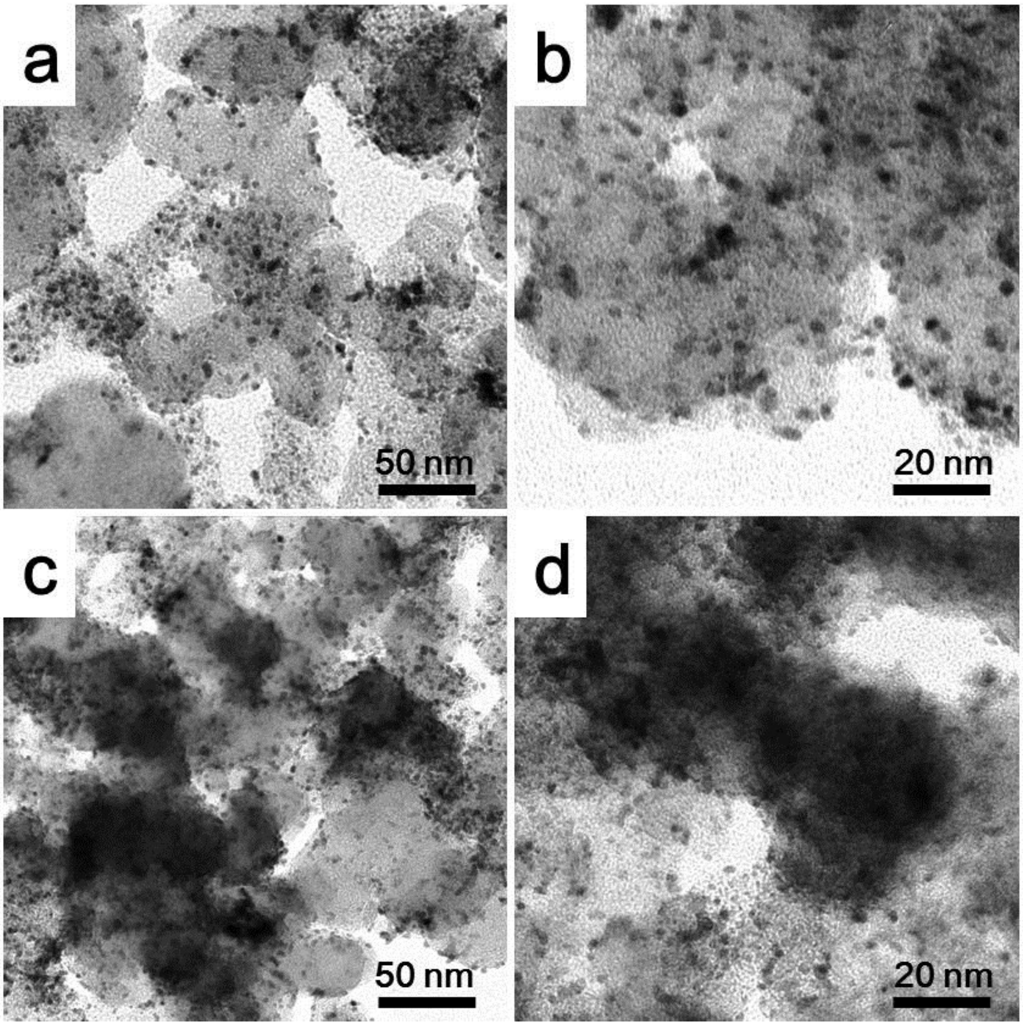

Figure S6 Typical TEM images of commercial Pd/C catalysts (a and b) before and (c and d) after long-term stability tests.

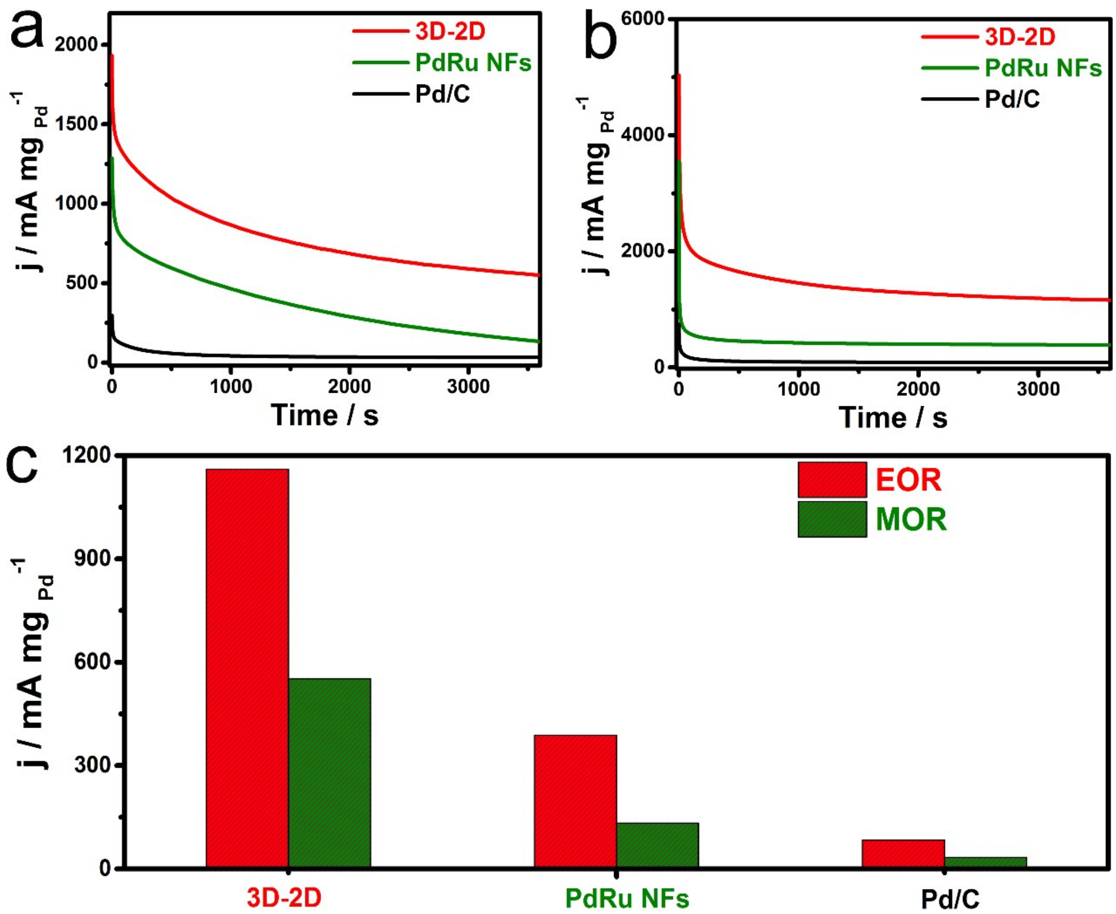

Figure S7 CA curves of 3D-2D nanohybrids, 3D PdRu NFs, and commercial Pd/C catalysts towards (a) MOR and (b) EOR at the fixed potentials of -0.3 and -0.15 V, respectively. (c) The corresponding histograms of the retained mass activities of 3D-2D nanohybrids, 3D PdRu NFs, and commercial Pd/C catalysts.

Table S1 A literature survey of the activity and stability of electrocatalysts toward MOR.

Catalysts	Peaks currents from CV curves		Electrolyte	Cycling stability	References
	J_m (A/mg)	J_s (mA/cm^2)			
3D-2D hybrids	1.7	4.5	1.0 M KOH + 1.0 M methanol	72.4 % activity after 1000 cycles	This work
$Pd_3Ru_1P_{1.5}$ NCs	1.26	NA	1.0 M KOH + 1.0 M methanol	56 % activity after 1000 cycles	Int. J. Hydrogen Energy **2017**, *42*, 11229-11238
PtNi Concave Nanoctahedra	0.44	1.55	0.1 M $HClO_4$+ 1 M methanol	NA	Angew. Chem. Int. Ed. **2012**, *51*, 12524-12528
$PtRu/G_{85}(CN)_{15}$	0.91	NA	0.1 M H_2SO_4 + 0.5 M methanol	63.5 % activity after 1000 cycles	Carbon, **2015**, *93*, 105-115
$Fe_{28}Pt_{38}Pd_{34}$ NWs	0.48		0.1M $HClO_4$+ 0.2 M methanol	NA	J. Am. Chem. Soc. **2012**, *51*, 15354-15357
$Pt_{0.3}Ru_{0.6}Pd_{0.1}$	1.04	1.56	1 M KOH + 1 M methanol	48 % activity after 500 cycles	New J. Chem. **2017**, *41*, 3048-3054
PtNi/C	1.20		1 M NaOH + 1 M methanol	NA	Catal. Commun. **2010**, *12*, 67-70
AuPt/MWCNT	1.60	1.6	0.5 M KOH + 1 M methanol	NA	Electrochem. Commun. **2008**, *10*, 1748-1751
PtAu/RGO/GC	1.60		1 M KOH + 1 M methanol	69.8 % activity after 500 cycles	J. Mater. Chem. A **2013**, *1*, 7255-7261
$PtPb_{0.27}$ NWs/C	1.21	2.41	0.1 M $HClO_4$ + 0.15 M methanol	58.4 % activity after 1000 cycles	Chem. Mater. **2016**, *28*, 4447-4452
PtPb Nanorods/C	0.70		0.1 M H_2SO_4 + 0.5 M methanol	NA	J. Am. Chem. Soc. **2007**, *129*, 8684-8685
PtCu Nanotubes/C		4.7	0.1 M $HClO_4$ + 1 M methanol	NA	Angew. Chem. Int. Ed. **2009**, *48*, 4217-4221
$PtCu_{2.1}$ NWs	1.56	3.31	0.1 M $HClO_4$+	70.1 % activity	Nano Lett. **2016**,

			0.2 M methanol	after 1000 cycles	*16*, 5037--5043
Highly branched Pt–Ni	NA	0.93	0.1 M $HClO_4$+ 0.1 M methanol	67.3 % activity after 4000 cycles	Chem. Sci. **2012**, *3*, 1925-1929
PtZn Nanoparticles/C		~ 0.92	0.1 M H_2SO_4 + 0.5 M methanol	NA	ACS Nano **2012**, *6*, 5642-5647
THH PtNi NFs	0.84	2.19	0.1 M $HClO_4$+ 0.2 M methanol	20.0 % activity after 600 cycles	Nano Lett. **2016**, *16*, 2762-2767
Pt_3Cu/C	~ 0.70	~ 0.50	0.5 M $HClO_4$+ 1 M methanol	NA	ACS Appl. Mater. Interface **2014**, *6*, 17748-17752

Table S2 A literature survey of the activity and stability of electrocatalysts toward EOR.

Catalysts	Peaks currents from CV curves		Electrolyte	Cycling stability	References
	J_m (A/mg)	J_s (mA/cm^2)			
3D-2D hybrids	4.7	12.3	1.0 M KOH + 1.0 M ethanol	70.2 % activity after 1000 cycles	This work
Pt-Cu Nanocone	~ 0.4	2.97	0.5 M H_2SO_4 + 1.0 M ethanol	NA	J. Am. Chem. Soc. **2013**, *135*, 18304-18307
Pd/C promoted with $CaSiO_3$	1.5	NA	1.0 M KOH + 1.0 M ethanol	60 % activity after 1000 cycles	Electrochim. Acta **2015**, *158*, 18-23
Pd_7Ru_1 nanodendrites	1.15		1.0 M KOH + 1.0 M ethanol	67.7 % activity after 500 cycles	Nanoscale **2015**, *7*, 12445-12451
Tetrahexahedral PtNi Nanoframes/C	0.77	1.99	0.1M $HClO_4$+ 0.2 M ethanol	NA	Nano Lett. **2016**, *16*, 2762-2767
PdPt@Pt/rGO	0.074		0.5 M H_2SO_4 + 0.5 M Ethanol	NA	ACS Appl. Mater. Inter. **2014**, 6, 10549-10555
$PdCu_2$	1.6		1.0 M KOH + 1 M ethanol	70 % activity after 300 cycles	ACS Appl. Mater. Interfaces **2016**, *8*, 34497
Pt-Pd CNCS	1.07		1.0 M KOH + 1 M ethanol	NA	J. Mater. Chem. A **2014**, *2*, 13840-13844
PdNi	1.5		1.0 M KOH + 1 M ethanol	60 % activity after 500 cycles	J. Colloid Interface Sci. **2017**, *493*, 190-197
PtAu ANFs	1.21	0.95	0.5 M KOH + 0.5 M ethanol	NA	Int. J. Hydrogen Energy **2016**, *41*, 1645-1653
PtSn Nanocrystals/CNT		~ 0.741	0.5 M H_2SO_4 + 1 M ethanol	NA	Angew. Chem. Int. Ed. **2016**, *55*, 4952-4956
PtRu Nanoparticles/XC	0.189		0.5 M H_2SO_4 + 0.5 M	52 % activity after 500 cycles	Electrochim. Acta **2014**, *142*, 223-

			ethanol		227
$PtPb_{0.27}$ NPs/C	0.25	1.19	0.1 M $HClO_4$+ 0.2 M ethanol	31.6 % activity after 1000 cycles	Chem. Mater. **2016**, *28*, 4447-4452.
Pt-CoSn/C	0.55		0.5 M H_2SO_4 + 1 M ethanol	NA	J. Power Sources. **2011**, *196*, 8000-8003
PtAu NWs		~ 0.741	1 M KOH + 0.1 M ethanol	NA	Energy Environ. Sci., **2012**, *5*, 8328-8334
THH PtNi NFs	0.77	1.99	0.5 M $HClO_4$+ 0.2 M ethanol	30 % activity after 300 cycles	Nano Lett. **2016**, *16*, 2762-2767