Supporting Information

$Bi(OH)_3$/PdBi Composite Nanochains as Highly Active and Durable Electrocatalysts for Ethanol Oxidation

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Author Contributions

X.Y., Y.Z. and M.C. contributed equally to this work.

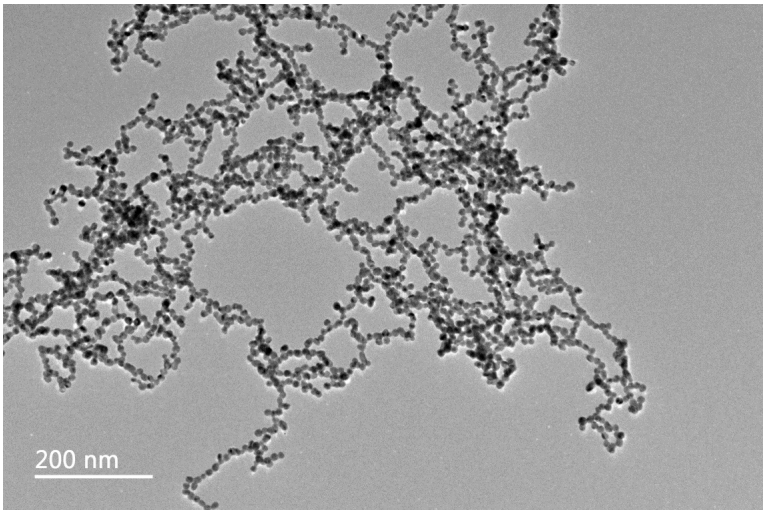

Figure S1. TEM image of PdBi-Bi$(OH)_3$ nanochains.

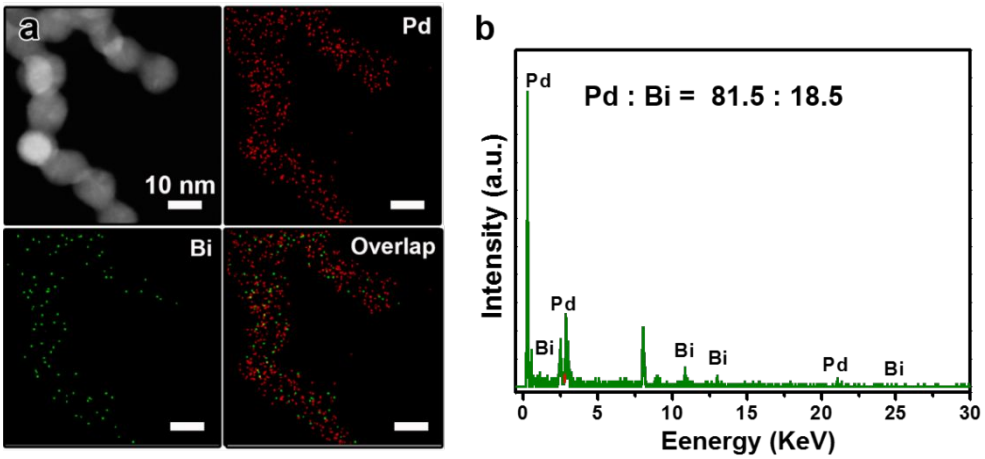

Figure S2. (a) EDS elemental mapping images of PdBi-$Bi(OH)_3$ nanochains showing the elemental distribution of Pd, Bi and overlapped elements. (b) EDS spectrum obtained from the EDS mapping results.

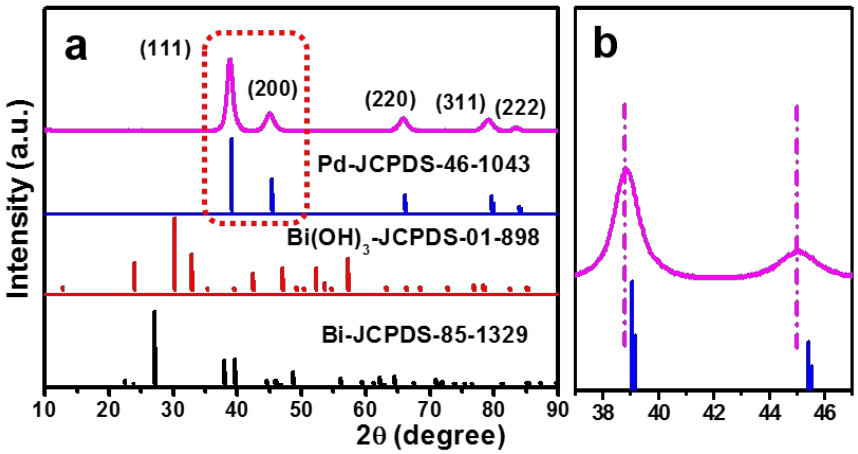

Figure S3. (a, b) XRD patterns of PdBi-$Bi(OH)_3$ nanocrystals.

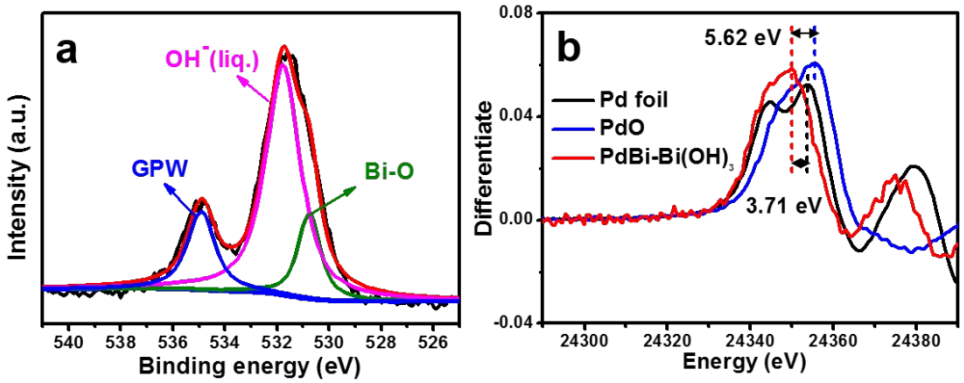

Figure S4. (a) XPS spectrum of PdBi-Bi$(OH)_3$ nanochains at O 1s. (b) Derivative function curves based on Pd K_3 edge in XANES spectra of PdBi-Bi$(OH)_3$ nanochains.

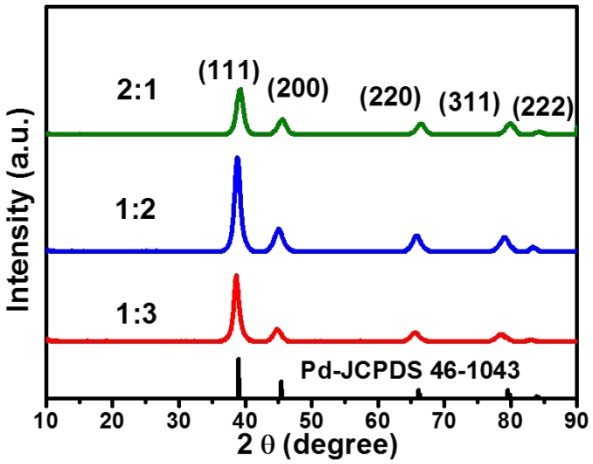

Figure S5. XRD patterns of PdBi-$Bi(OH)_3$ nanocrystals with different feeding Pd:Bi ratios. The sample with a feeding ratio of 1:1 was denoted as PdBi-$Bi(OH)_3$ nanochains in our work.

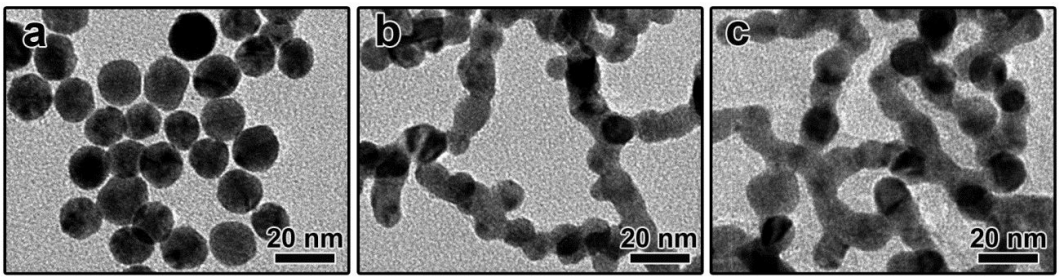

Figure S6. TEM images of PdBi-$Bi(OH)_3$ nanocrystals with different Pd:Bi feeding ratios: (a) 2:1, (b) 1:2 and (c) 1:3.

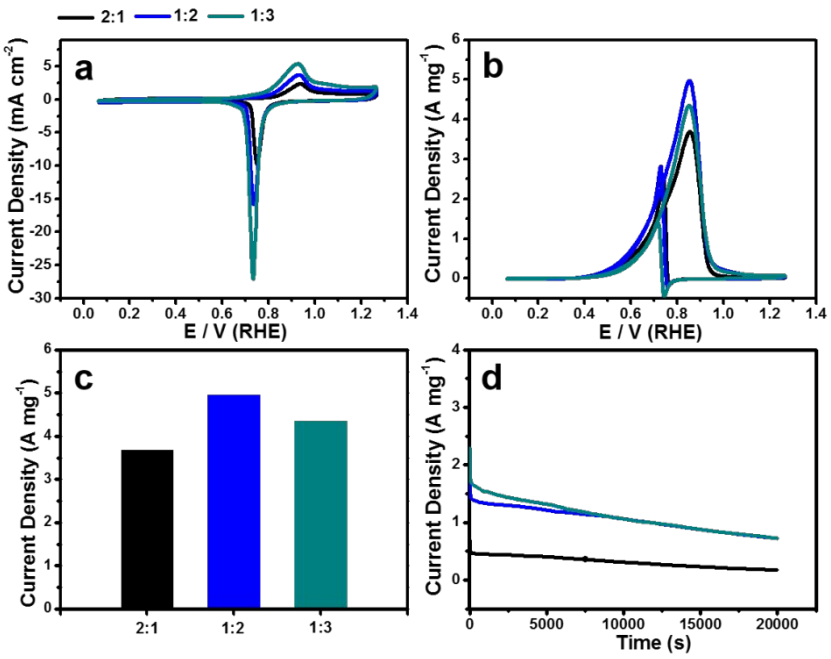

Figure S7. CV curves of different samples measured in N_2-saturated (a) 1 M NaOH and (b) 1 M NaOH containing 1 M ethanol solution at a scan of 50 mV s^{-1}. (c) Mass activities of different samples in N_2-saturated 1 M NaOH solution containing 1 M ethanol. (d) CA curves of different samples measured in N_2-saturated 1 M NaOH solution containing 1 M ethanol, recorded at 0.86 V *vs.* RHE.

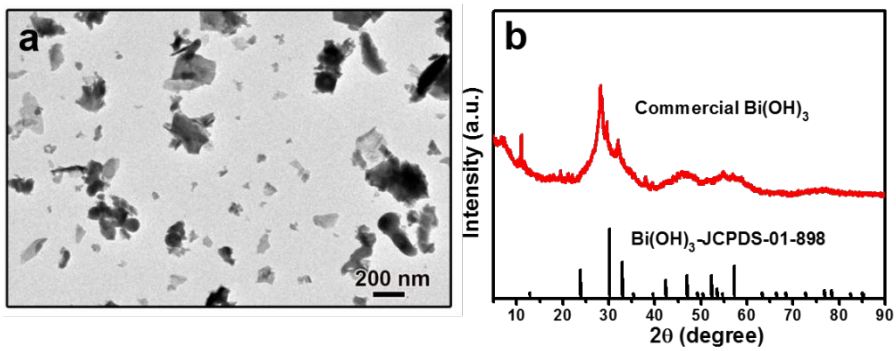

Figure S8. (a) TEM image and (b) XRD pattern of commercial $Bi(OH)_3$ nanocrystals.

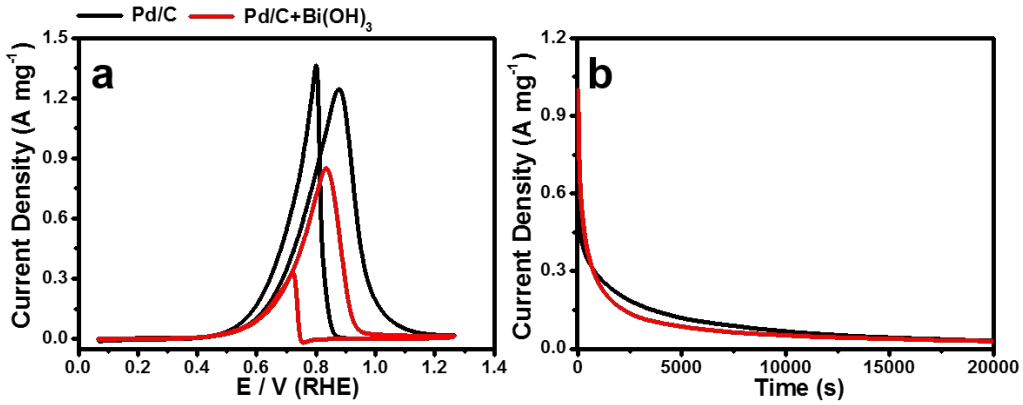

Figure S9. (a) CV curves of physically mixed commercial Pd/C and commercial $Bi(OH)_3$ in N_2-saturated 1 M NaOH containing 1 M ethanol. (b) CA tests of mixture of commercial Pd/C and commercial $Bi(OH)_3$ in N_2-saturated 1 M NaOH containing 1 M ethanol at 0.86 V.

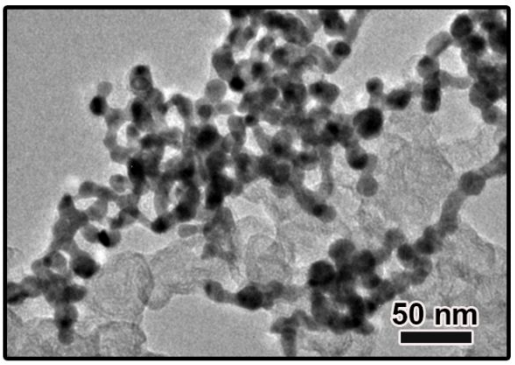

Figure S10. TEM images of PdBi nanochains obtained from acid treatment.

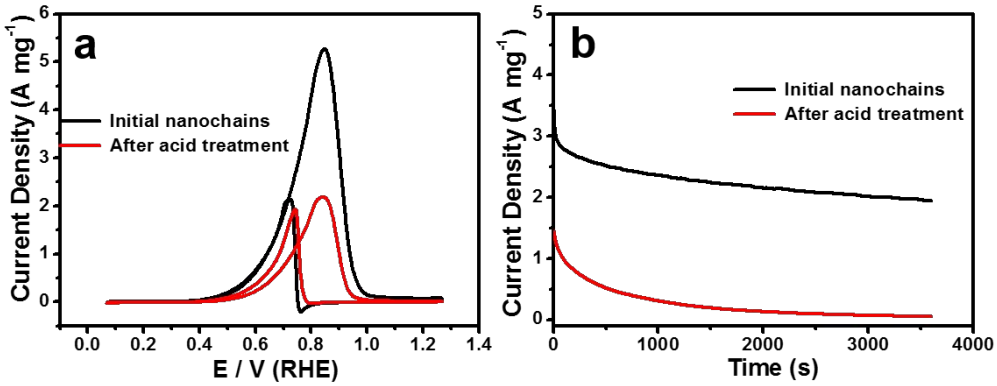

Figure S11. (a) CV curves of PdBi-$Bi(OH)_3$ nanochains before and after acid treatment in N_2-saturated 1 M NaOH containing 1 M ethanol. (b) CA tests of PdBi-$Bi(OH)_3$ nanochains before and after acid treatment in N_2-saturated 1 M NaOH containing 1 M ethanol at 0.86 V.

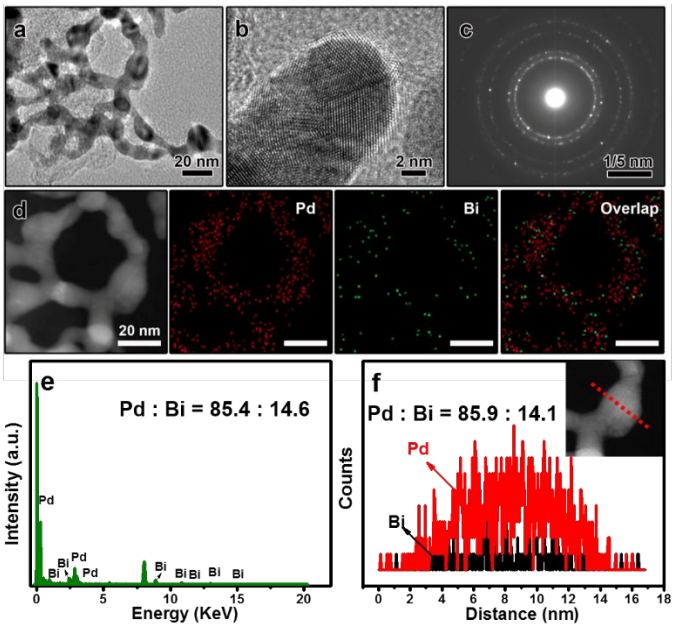

Figure S12. Structural characterizations of PdBi-Bi$(OH)_3$ nanochains after CA test for 200,000 s. (a) TEM image; (b) HRTEM image; (c) SAED pattern; (d) EDS mappings of Pd and Bi element; (e) EDS spectrum obtained from the EDS mapping result; (f) EDS line scans along the line in the inset.

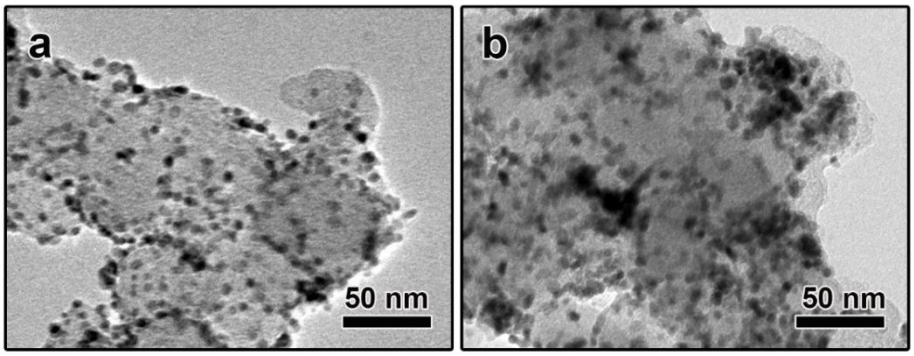

Figure S13. TEM images of commercial Pd/C (a) before and (b) after 80,000 s durability test.

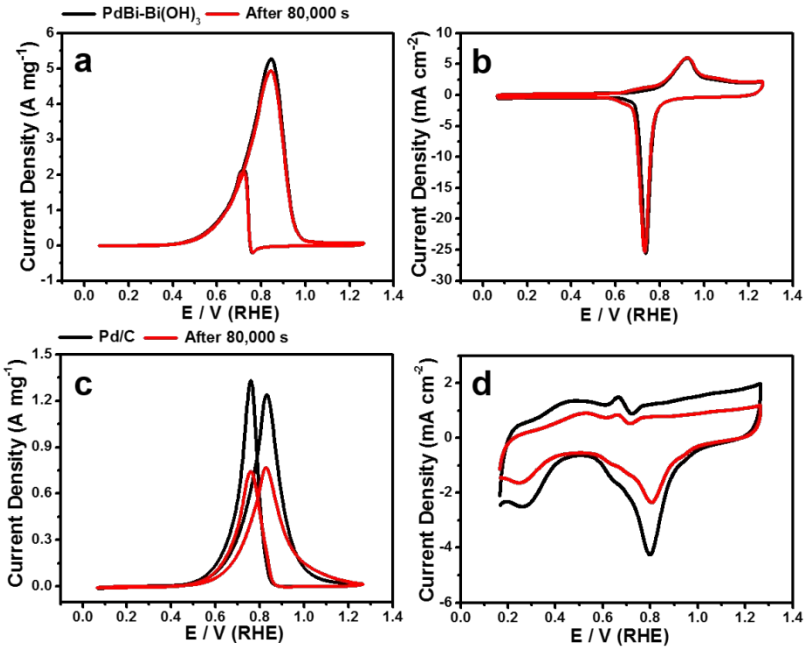

Figure S14. CV curves of (a, b) PdBi-$Bi(OH)_3$ nanochains and (c, d) commercial Pd/C as indicated (black) before and (red) after 80,000 s CA measurements in N_2-saturated (a, c) 1 M NaOH containing 1 M ethanol and (b, d) 1 M NaOH solution.

Table S1. The activity and stability of Pd-based EOR electrocatalysts in alkaline solution.

Electrocatalyst	Electrolyte	Activity	CA stability	Ref.
PdBi-Bi$(OH)_3$ nanochains	1 M NaOH+1 M ethanol	5.30 A mg^{-1}	76 % (2.12 A mg^{-1}) activity retention after 3,600 s, 36 % (1.00 A mg^{-1}) activity retention after 20,000 s	This work
PdP_2/rGO	0.5 M KOH +0.5 M ethanol	1.60 A mg^{-1}	~6% (0.05 A mg^{-1}) activity retention after 10,000 s	*Appl. Catal. B-Environ.* **2019**, *242*, 258-266.
Pd-Ru/TiO_2	1 M NaOH +1 M ethanol	2.70 A mg^{-1}	~29% (0.38 A mg^{-1}) activity retention after 10,000 s	*Nanoscale,* **2019**, *11*, 3311-3317.
Pd/Black Phosphorus−graphene	1 M NaOH +1 M ethanol	6.00 A mg^{-1}	~12% (0.71 A mg^{-1}) activity retention after 20,000 s	*ACS Appl. Mater. Interfaces* **2019**, *11*, 5136-5145.
PdAg Nanodendrites	1 M KOH +1 M ethanol	2.63 A mg^{-1}	52% (0.78 A mg^{-1}) activity retention after 10,000 s	*Adv. Mater.* **2018**, *30*, 1706962.
Pd/TiO_2-nanosheets-black P	1 M NaOH +1 M ethanol	5.02 A mg^{-1}	31% (0.87 A mg^{-1}) activity retention after 3,600 s	*Adv. Energy Mater.* **2018**, *8*, 1701799.
Pd/carbon nanocages	1 M KOH +1 M ethanol	2.41 A mg^{-1}	~9% (~0.06 A mg^{-1}) activity retention after 3,600 s	*ACS Sustainable Chem. Eng.* **2018**, *6*, 7507-7514.
Pd-Ni-P	1 M NaOH +1 M ethanol	4.95 A mg^{-1}	15% (0.22 A mg^{-1}) activity retention after 2,000 s	*Nat. Commun.* **2017**, *8*, 14136.
Au@Pd Nanorods	1 M NaOH +1 M ethanol	2.92 A mg^{-1}	32% (0.96 A mg^{-1}) activity retention after 1,200 s	*Adv. Mater.* **2017**, *29*,1701331.
Pd/$Ni(OH)_2$/rGO	1 M KOH +1 M ethanol	1.55 A mg^{-1}	76 % (0.61 A mg^{-1}) activity retention after 3,600 s, 55 % (0.44 A mg^{-1}) activity retention after 20,000 s	*Adv. Mater.* **2017**, *29*, 1703057.
PtPdBi Hollow Catalyst	1 M KOH +1 M ethanol	5.26 A mg^{-1}	38% (~0.99 A mg^{-1}) activity retention after 3,600 s	*Catalysts* **2017**, *7*, 208.
PdAg/rGO	1 M KOH + 1 M ethanol	3.14 A mg^{-1}	47% (~0.39 A mg^{-1}) activity retention after 5,000 s	*Electrocatal.* **2017**, *8*, 430-441.
PdCu/rGO	0.5 M KOH + 0.5 M ethanol	2.42 A mg^{-1}	33% (0.15 A mg^{-1}) activity retention after 3,000 s	*Nanoscale Res.Lett.* **2017**, *12*, 521.
$PdCu_2$	1 M KOH +1 M ethanol	1.60 A mg^{-1}	43 % (0.28 A mg^{-1}) activity retention after 1,000 s	*ACS Appl. Mater. Interfaces* **2016**, *8*, 34497-34505.

Pd_2Sn Nanorods	0.5 M KOH +0.5 M ethanol	50.0 mA cm^{-2}	56 % (10 mA cm^{-2}) activity retention after 7,200 s	*J. Mater. Chem. A* **2016**, *4*, 16706-16713.
PdS_x/C	1 M KOH+1 M ethanol	1.62 A mg^{-1}	Dropped to zero after 3,600 s	*J. Power Sources* **2016**, *336*, 1-7.
Pd_2Ge	1 M KOH+1 M ethanol	4.00 mA cm^{-2}	44 % (~1.8 mA cm^{-2}) activity retention after 1,000 s	*Chem. Mater.* **2015**, *27*, 7459-7467.
Pd/Carbon Black	1 M NaOH+ 1 M ethanol	5.00 A mg^{-1}	20 % (0.70 mA mg^{-1}) activity retention after 3,600 s	*Int. J. Hydrogen Energy* **2015**, *40*, 12382-12391.
Pd-Ag Bimetallic Alloy Networks	1 M NaOH+ 1 M ethanol	2.00 A mg^{-1}	40 % (~0.50 A mg^{-1}) activity retention after 1,000 s	*ACS Appl. Mater. Interfaces* **2015**, *7*, 13842-13848.
Pd-Co Films	2 M KOH + 10 *wt*% ethanol	23.0 mA cm^{-2}	60 % (~14 mA cm^{-2}) activity retention after 1,800 s	*J. Power Sources* **2015**, *293*, 815-822.
Pd_xCu_{100-x} networks	1 M KOH + 1 M ethanol	3.01 A mg^{-1}	33 % (~0.65 A mg^{-1}) activity retention after 7,200 s	*J. Mater. Chem. A* **2014**, *2*, 20933-20938.
Pd-Au/C	1 M NaOH+ 1 M ethanol	25.0 mA cm^{-2}	Dropped to zero after 3,600 s	*Electrochim. Acta* **2014**, *144*, 50-55.
PtPd/GO	1 M KOH + 1 M ethanol	1.16 A mg^{-1}	18 % (~0.10 A mg^{-1}) activity retention after 3,600 s	*ACS Appl. Mater. Interfaces* **2014**, *6*, 3607-3614.
Pd-MgO/C	1 M KOH + 1 M ethanol	85.0 mA cm^{-2}	Dropped to zero after 1,800 s	*Int. J. Hydrogen Energy* **2014**, *39*, 16015-16019.
Pd-Ag nanoparticles	1 M KOH + 1 M ethanol	1.60 A mg^{-1}	55 % (~0.40 A mg^{-1}) activity retention after 2,000 s	*J. Power Sources* **2014**, *263*, 13-21.
Pd_3Ni	1 M KOH + 1 M ethanol	0.01 A mg^{-1}	Dropped to zero after 14,400 s	*Int. J. Hydrogen Energy* **2013**, *38*, 4474-4482.
Pt/PdCu	1 M KOH + 1 M ethanol	183 mA cm^{-2}	36 % (~20 mA cm^{-2}) activity retention after 6,000 s	*Adv. Mater.* **2012**, *24*, 5493-5498.
Au_3Pd	1 M KOH + 1 M ethanol	4.00 mA cm^{-2}	Dropped to zero after 500 s	*Electrochim. Acta* **2012**, *81*, 8-13.
PdBi/C	1 M KOH + 1 M ethanol	~0.02 A mg^{-1}	78 % (0.01 A mg^{-1}) activity retention after 1,800 s	*Int. J. Hydrogen Energy* **2011**, *36*, 10522-10526.
Pd-CeO_2	1 M KOH + 1 M ethanol	230 mA cm^{-2}	66 % (~40 mA cm^{-2}) activity retention after 1,800 s	*J. Catal. Lett.* **2010**,*138*, 46-49.