Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
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Electronic Supplementary Information for

Concave octahedral Pd@PdPt electrocatalysts integrating core–shell, alloy and concave structures for high-efficiency oxygen reduction and hydrogen evolution reactions

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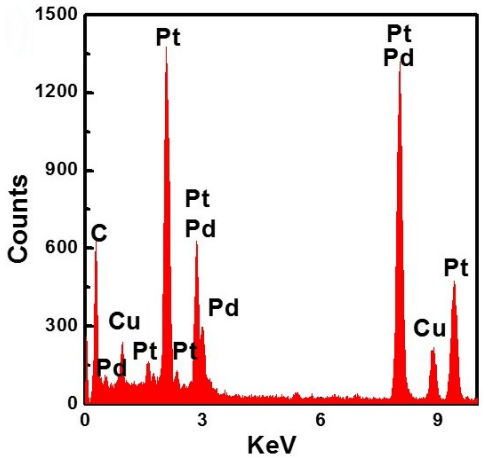

Figure S1. EDS image of the product.

Table S1. The Atomic Percentage of Pd and Pt

Catalysts	Characterization methods	Pd atom%	Pt atom%
Pd@PdPt	ICP	87.0	13.0
	XPS	57.7	42.3
	EDS	91.5	8.5
PdPt alloy	ICP	32.4	67.6
	XPS	37.6	62.4
	EDS	41.4	58.6

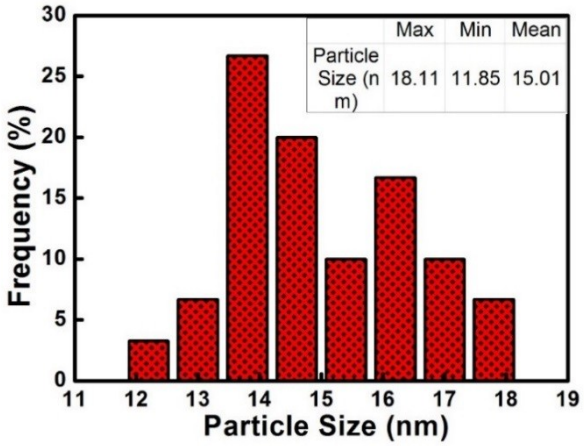

Figure S2. Particle size distribution image of concave octahedral Pd@PdPt.

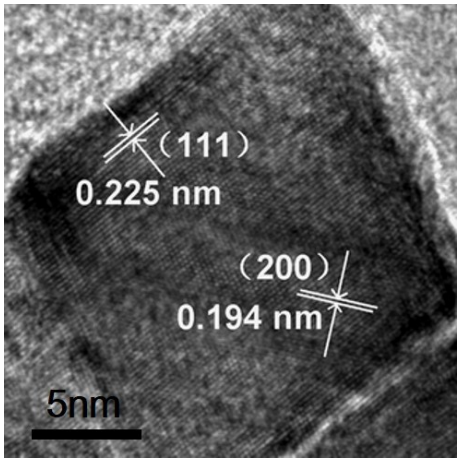

Figure S3. HRTEM interplanar spacing image of concave octahedral Pd@PdPt.

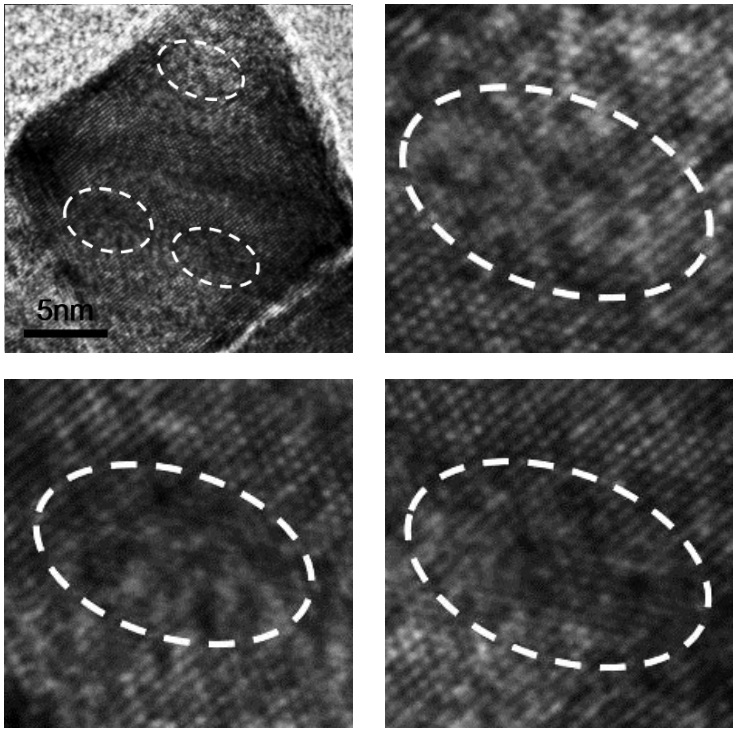

Figure S4. Enlarged HRTEM dislocation images of concave octahedral Pd@PdPt.

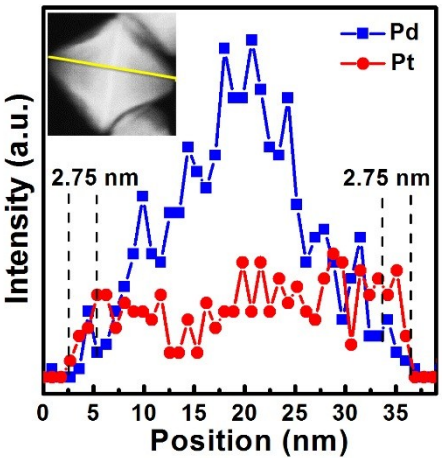

Figure S5. EDS line-scan image across the single concave octahedral Pd@PdPt shown in the inset.

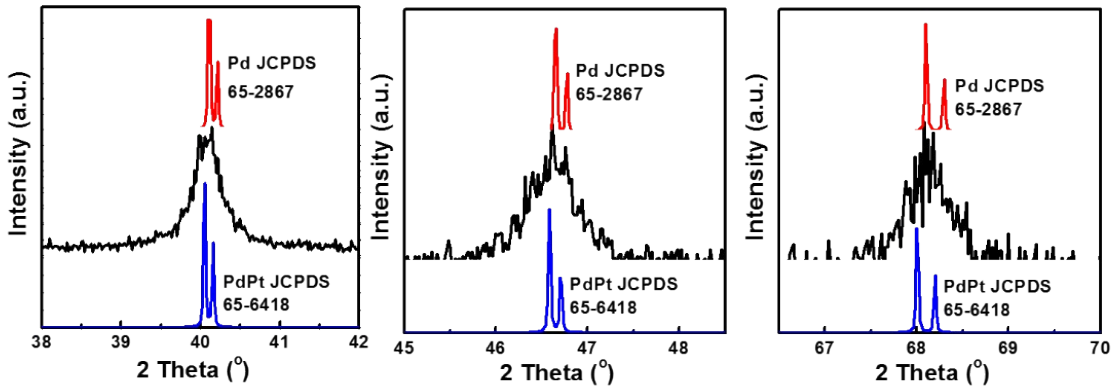

Figure S6. Enlarged XRD patterns of concave octahedral Pd@PdPt.

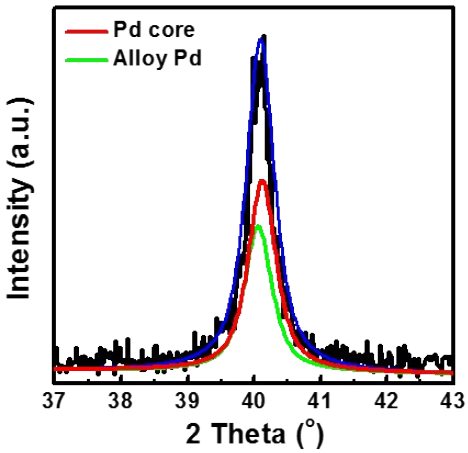

Figure S7. High-resolution XRD pattern of concave octahedral Pd@PdPt of the first diffraction peak shown in Figure 2a.

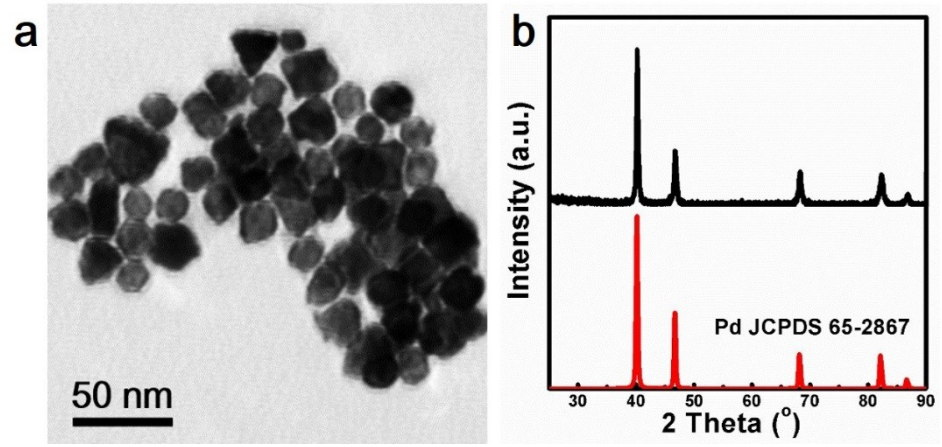

Figure S8. (a) TEM and (b) XRD images of Pd.

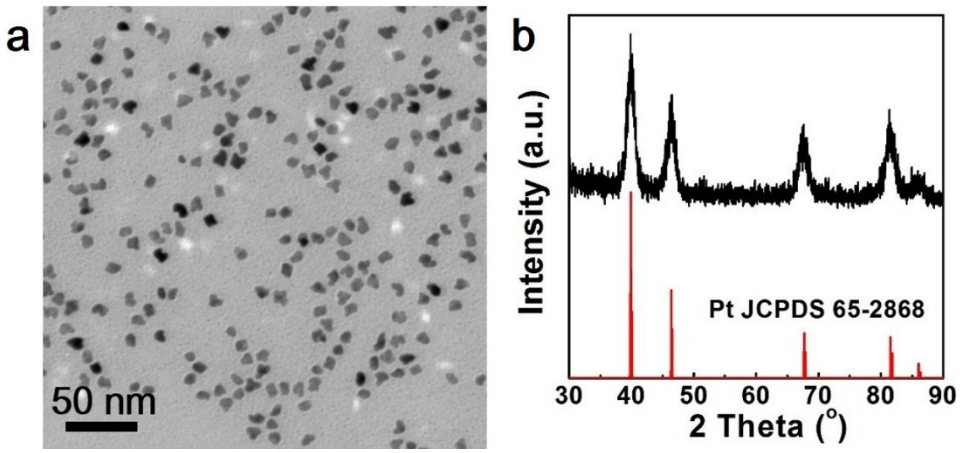

Figure S9. (a) TEM and (b) XRD images of Pt.

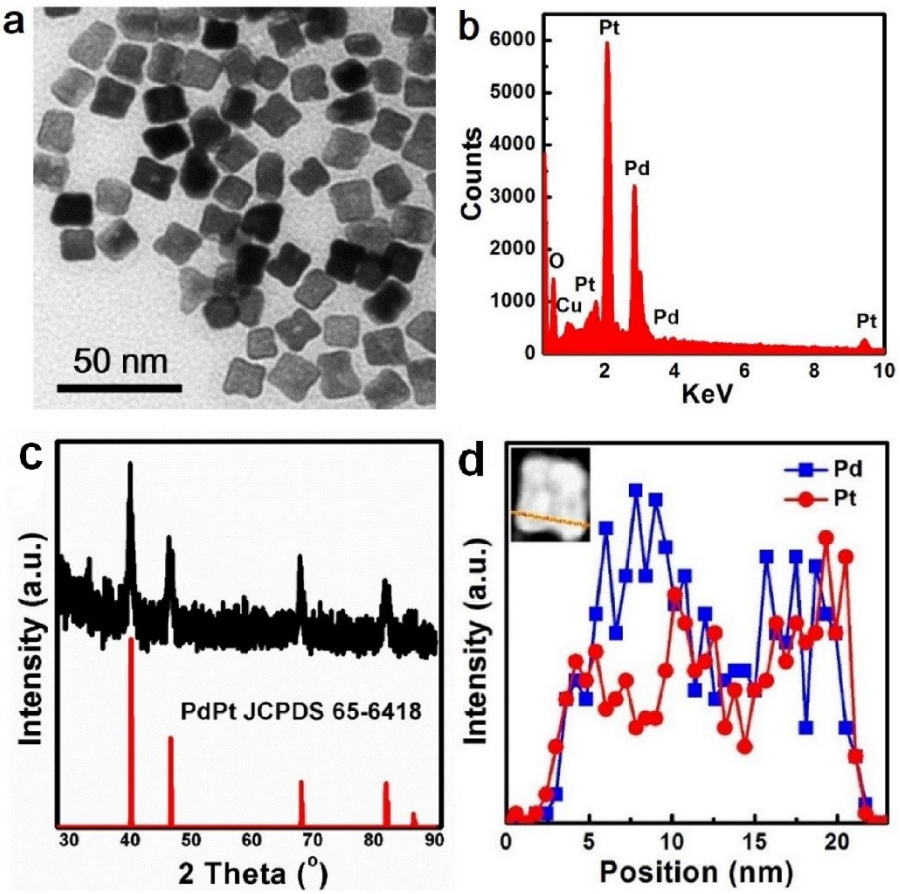

Figure S10. (a) TEM and (b) EDS images of PdPt alloy. (c) XRD pattern of PdPt alloy. (d) EDS line-scan image across the single PdPt alloy in the inset.

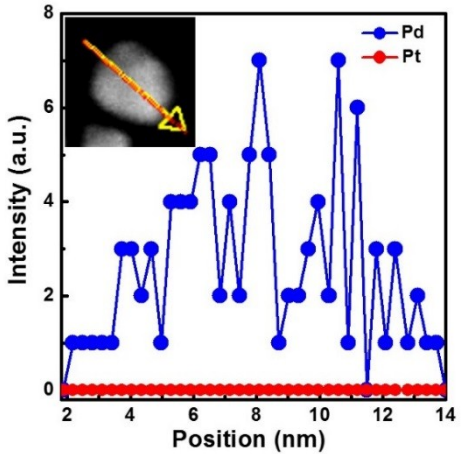

Figure S11. EDS line-scan image across the single NC shown in the inset.

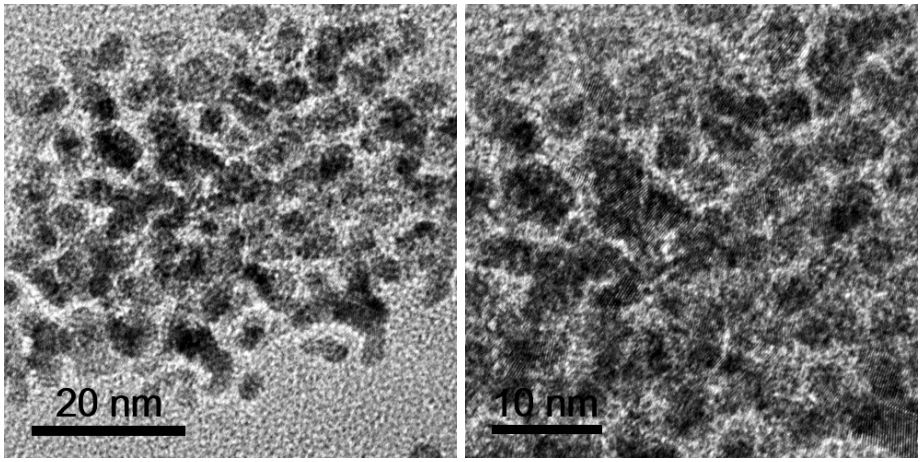

Figure S12. TEM image of the product by using hexadecyldimethylamine instead of CTAB as surfactant reaction.

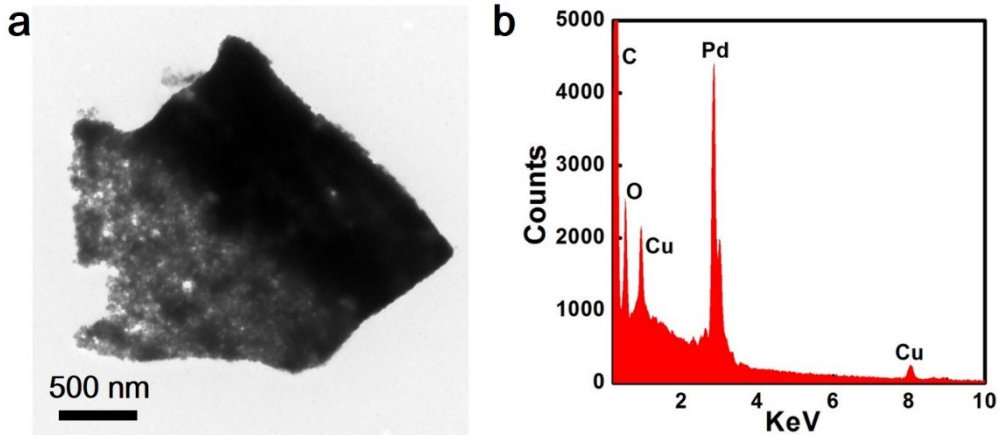

Figure S13. (a) TEM and (b) EDS images of the product by using DMF instead of EG as reducing agent and solvent.

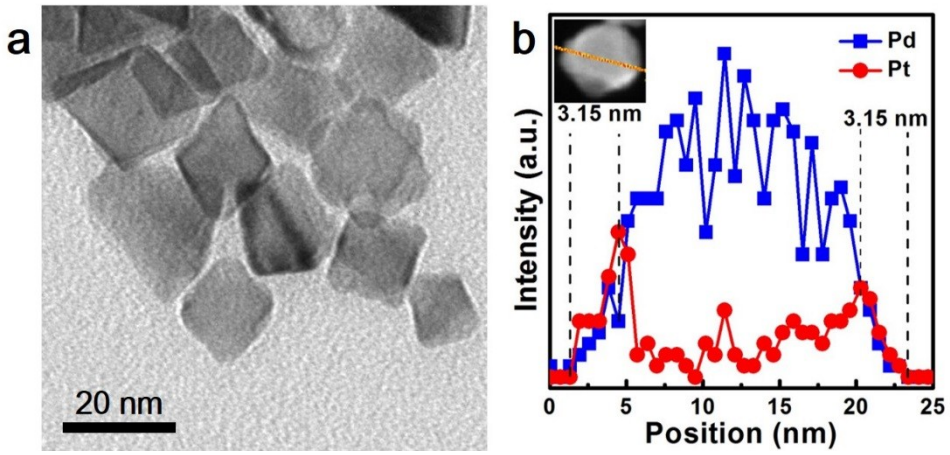

Figure S14. (a) TEM image and (b) EDS line-scan image across a single PdPt NC (The feeding raio of 1:1 for Pd/Pt) shown in the inset.

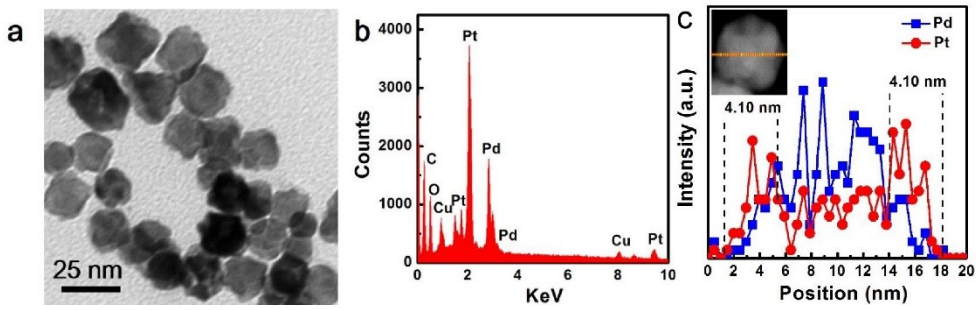

Figure S15. (a) TEM and (b) EDS images of PdPt NCs. (c) EDS line-scan image across a single PdPt NC shown in the inset (The feeding raio of 1:2 for Pd/Pt).

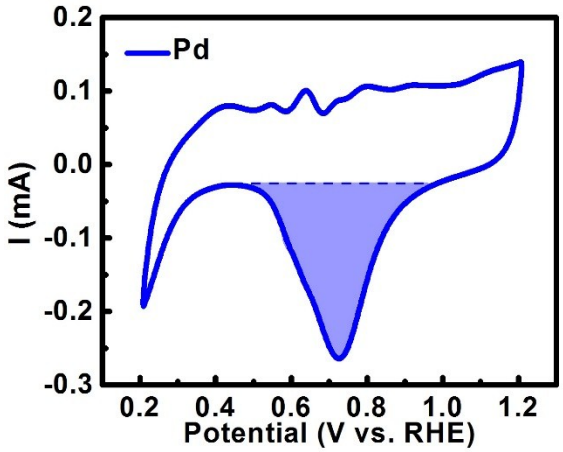

Figure S16. ORR cyclic voltammetry curve of Pd recorded in N_2-saturated 0.1 M KOH solution.

Table S2. Comparisons of catalytic properties of different ORR catalysts

Catalyst	$E_{1/2}$ [V][1]	Tafel slope [mV dec^{-1}]	J_m [at 0.9V, A $mg_{Pt\ or\ Pd}^{-1}$]	Electrolyte solution	Ref.
20% Pt/C	0.84	69	0.13	0.1 M KOH	This work
Pd@PdPt	0.91	66	0.95		This work
PdPt Alloy	0.89	87	0.037		This work
Pd	0.81	~	0.0014		This work
Pd/rPOM	~	72	0.315 (at 0.95 V)	0.1 M KOH	*J. Mater. Chem. A,* 2015, **3**, 13962.
Mo_2C–C-5	0.713	72.2	~	0.1 M KOH	*J. Mater. Chem. A*, 2016, **4**, 12583.
Ni_3C-GNRs	0.77	45	~	0.1 M KOH	*ACS Nano,* 2015, **9**, 7407.
CoP	0.7	51	~	0.1 M KOH	*Nano Lett.,* 2015, **15**, 7616.
Pd-P	0.88	~	1.34	0.1 M KOH	*J. Am. Chem. Soc.*, 2014, **136**, 5217.
$Pd/W_{18}O_{49}$	0.875	~	0.216	0.1 M KOH	*J. Am. Chem. Soc.*, 2014, **136**, 11687.
c-$CoMn_2$/C	0.83	~	0.0663 (at 0.85 V)	0.1 M KOH	*Nat. Commun.,* 2015, **6**, 7345.
PdMn/C-BAE	0.87	83	0.093 (at 0.85 V)	0.1 M KOH	*J. Mater. Chem. A,* 2016, **4**, 8337.
Ordered Pd_3Pb/C	0.92	~	0.1689	0.1 M KOH	*Nano Lett.,* 2016, **16**, 2560.
PtCu NFs	~	~	0.211	0.1 M KOH	*Adv. Mater., 2*016, DOI:10.1002/adma.201603075.
AuPdCo/C Intermetallic	~	~	0.13	0.1 M KOH	*Nat. Commun.,* 2014, **5**, 5185.
rGO-Pd	0.734	~	0.088 (at 0.765 V)	1 M KOH	*ACS Appl. Mater. Interfaces,* 2014, **6**, 15795.
C_{PANI} /Mn_2O_3	0.784	73	0.066 (at 0.3 V)	0.1 M KOH	*ACS Appl. Mater. Interfaces,* 2016, **8**, 6040.

[1] The potential measured versus RHE.

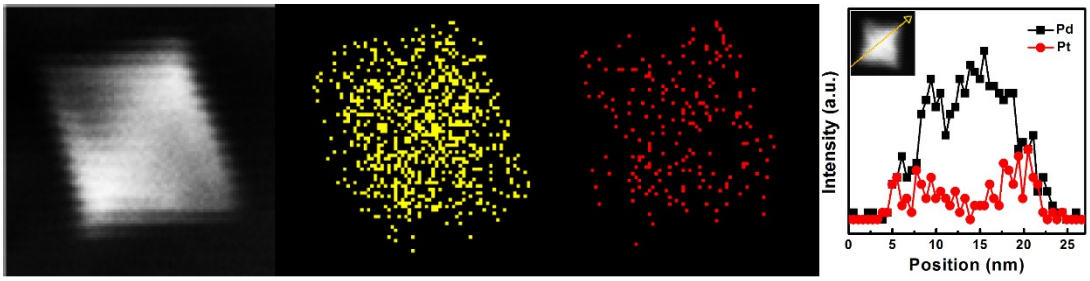

Figure S17. The elemental mapping and EDS line-scan profiles of Pd@PdPt catalyst after accelerated durability test.

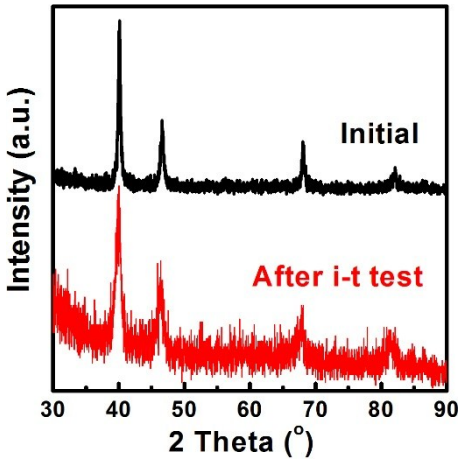

Figure S18. The XRD pattern of Pd@PdPt catalyst after accelerated durability test.

Table S3. Comparisons of catalytic properties of different HER catalysts

Catalyst	Tafel slope [mV dec^{-1}]	η_{10} [mV][1]	j_0 [mA cm^{-2}][2]	Electrolyte solution	Ref.
20% Pt/C	33	39	0.64	0.5 M H_2SO_4	This work
Pd@PdPt	38	39	0.91		This work
PdPt Alloy	38	50	0.48		This work
Pd	92	171	0.14		This work
Pd-Mn_3O_4	42	14	7.74	0.5 M H_2SO_4	*Chem. Commun.,* 2016, **52**, 6095.
Co-NG	82	147	0.125	0.5 M H_2SO_4	*Nat. Commun.,* 2015, **6**, 8668.
GCE-Ni/Pt	43	36	~	0.5 M H_2SO_4	*ACS Appl. Mater. Interfaces,* 2015, **7**, 26101.
$WO_{2.9}$	50	70	0.4	0.5 M H_2SO_4	*Nat. Commun.,* 2015, **6**, 9064.
Porous MoC_x octahedrons	53	142	0.023	0.5 M H_2SO_4	*Nat. Commun.,* 2015, **6**, 6512.
Fe-Co_2P/NCNTs	68	104	0.33	0.5 M H_2SO_4	*ACS Appl. Mater. Interfaces,* 2016, **8**, 13890.
Phosphorus modified WN/rGO	54	85	0.35	0.5 M H_2SO_4	*Angew. Chem. Int. Ed.,* 2015, **54**, 6325.
CoP	50	~	0.14	0.5 M H_2SO_4	*Angew. Chem. Int. Ed.,* 2014, **53**, 5427.
Mo_2C/CNT-graphene	58	130	0.062	0.5 M H_2SO_4	*ACS Nano,* 2014, **8**, 5164.
Pd_4Se	~50	94	0.23	0.5 M H_2SO_4	*Chem. Commun.,* 2016, **52**, 206.
rGO-PdPS	46	90	0.14	0.5 M H_2SO_4	*Chem. Commun.,* 2014, **50**, 7359.
Fe-Co_2P/NCNTs	68	104	0.33	0.5 M H_2SO_4	*ACS Appl. Mater. Interfaces,* 2016, **8**, 13890.
MoS_x/NCNT	40	110	0.033	0.5 M H_2SO_4	*Nano Lett.,* 2014, **14**, 1228.
u-CoP/Ti	49.3	45	~	0.5 M H_2SO_4	*J. Mater. Chem. A,* 2016, **4**, 10114.

[1] The potential measured versus RHE.

[2] j_0 values were calculated from tafel curves using an extrapolation method.

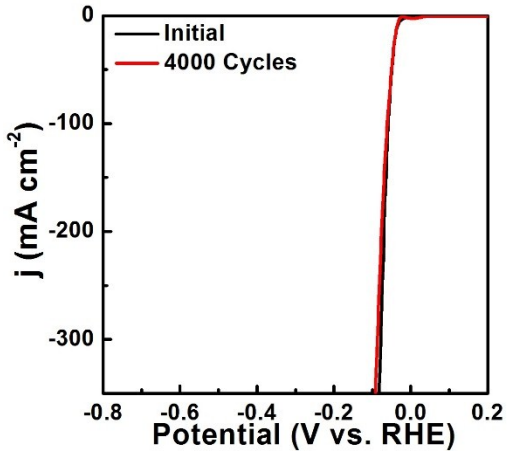

Figure S19. The accelerated durability test of Pd@PdPt catalyst performed in N_2-saturated 0.5 M H_2SO_4 solution.