

Supplementary Information

PtCo excavated rhombic dodecahedral nanocrystals for efficient electrocatalysis

Cong Shen,^a Xuemin Li,^a Yajing Wei,^a Zhenming Cao,^a Huiqi Li,^a Yaqi Jiang^{a,*} and Zhaoxiong Xie^{a,*}

^aState Key Laboratory of Physical Chemistry of Solid Surfaces & Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005 (P. R. China). E-mail: yqjiang@xmu.edu.cn; zzxie@xmu.edu.cn; Fax: (+) 86-592-2183047.

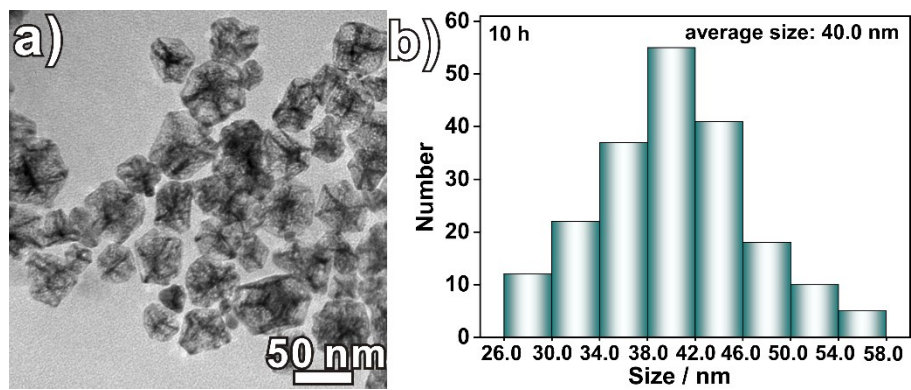


Fig. S1 (a) TEM image and (b) size distribution of the as-prepared PtCo ERD NCs based on statistics of 200 particles.

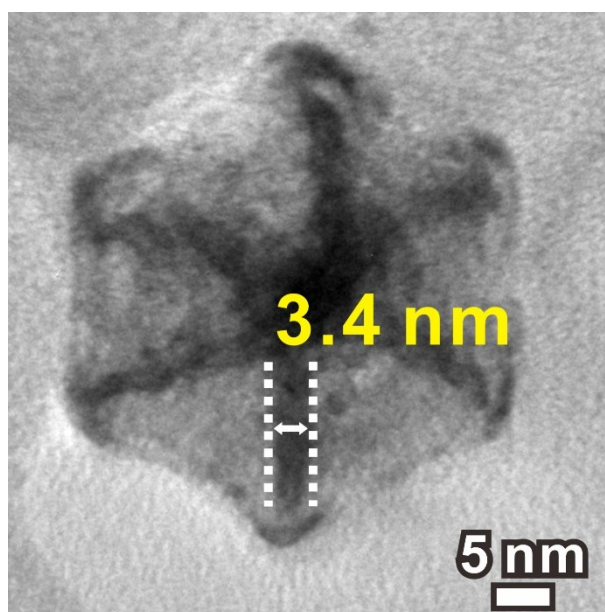


Fig. S2 High-magnification TEM image of a single PtCo ERD NC illustrating the thickness of a nanosheet.

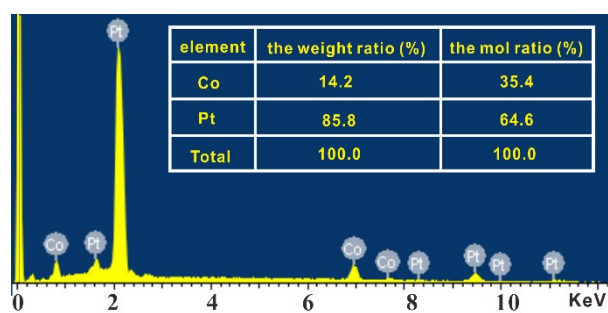


Fig. S3 EDS spectrum of the as-prepared PtCo ERD NCs.

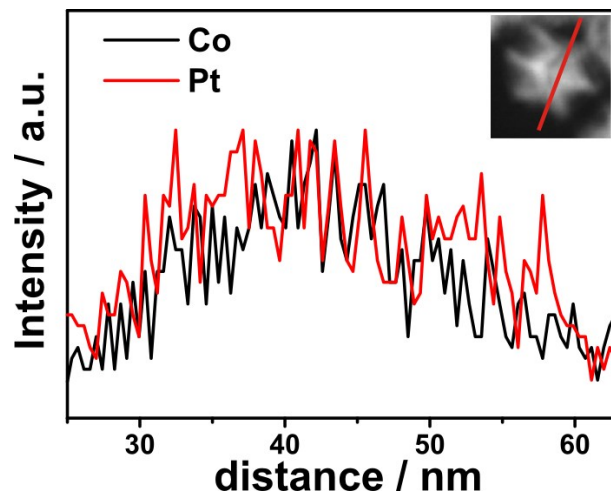


Fig. S4 Cross-sectional compositional line profiles of Pt and Co recorded across an individual PtCo ERD NC. The inset presents corresponding HAADF-STEM image.

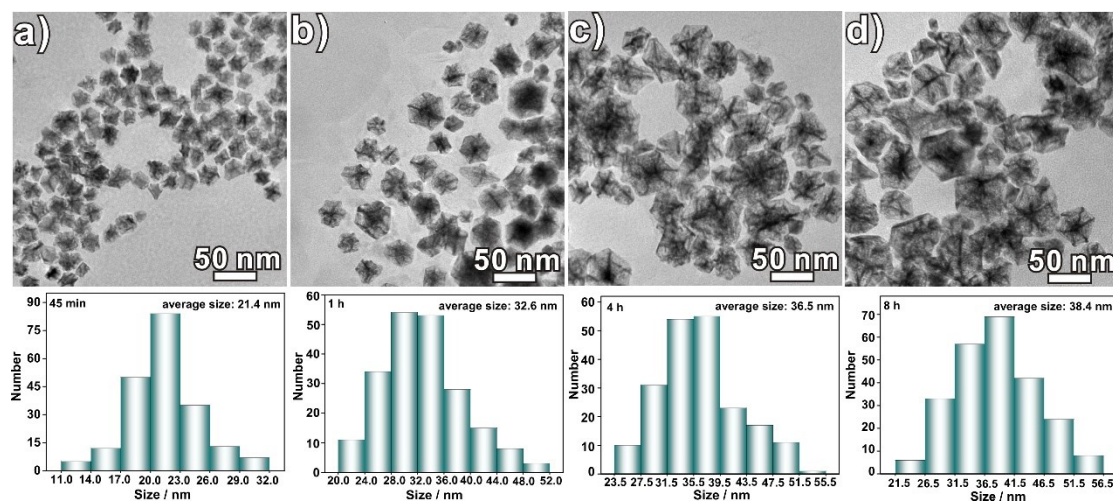


Fig. S5 TEM images and size distributions of the as-prepared PtCo ERD NCs obtained at different reaction time while keeping other conditions the same. (a) 45 min; (b) 1 h; (c) 4 h; (d) 8 h. The counted numbers of particles are 206, 206, 202, and 239, respectively.

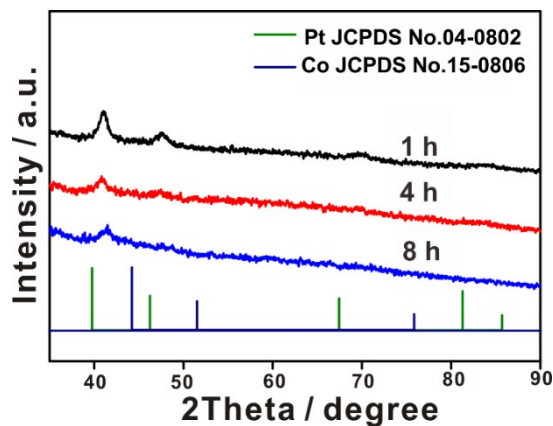


Fig. S6 XRD patterns of the as-prepared PtCo ERD NCs formed at different reaction times.

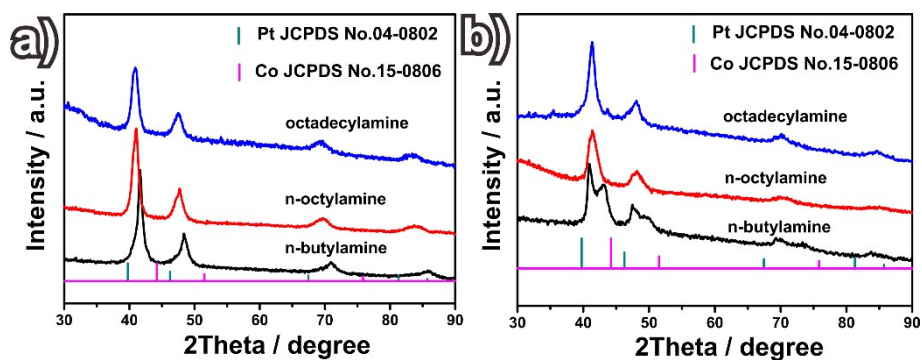


Fig. S7 XRD patterns of PtCo alloy NCs formed from different kinds of amines (a) with 300 μL of formaldehyde solution and (b) without formaldehyde solution while keeping other conditions the same.

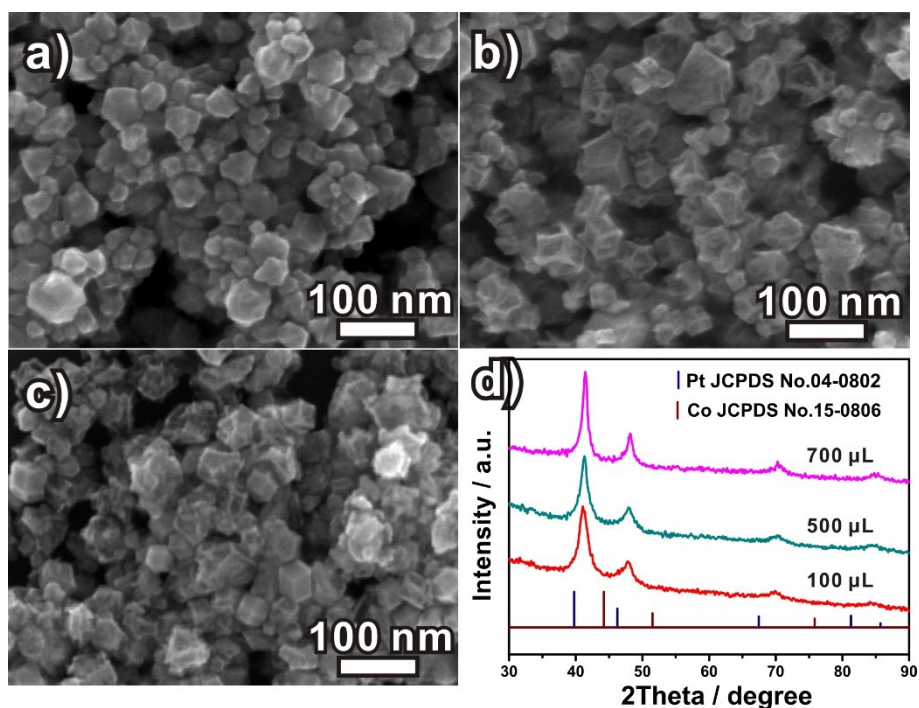


Fig. S8 SEM images of the PtCo NCs synthesized with different volume of formaldehyde while keeping other conditions the same. (a) 100 μL ; (b) 500 μL ; (c) 700 μL . (d) XRD patterns.

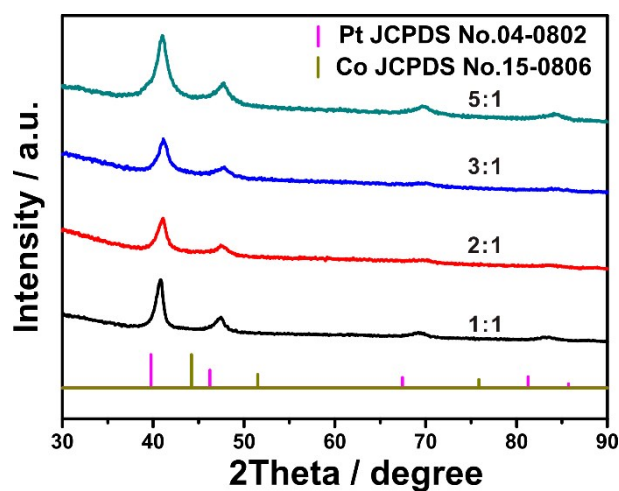


Fig. S9 XRD patterns of the PtCo alloy NCs synthesized from different molar ratios of Co and Pt precursors in the presence of 300 μL of formaldehyde.

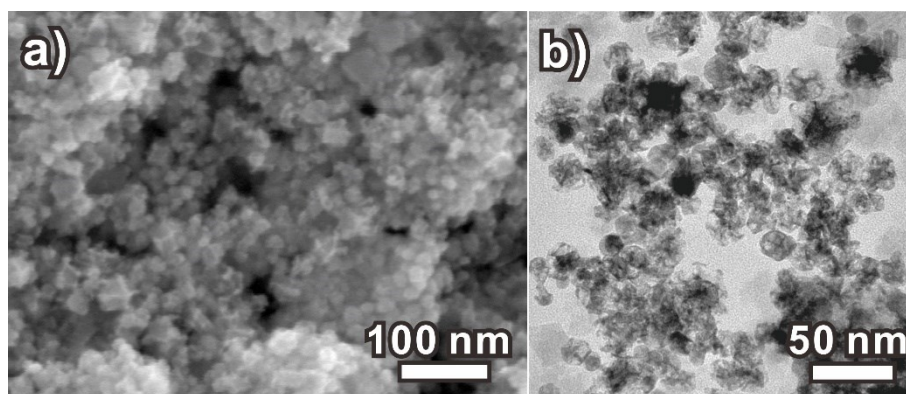


Fig. S10 (a) SEM image and (b) TEM image of the Pt-Co alloy NCs synthesized from Co/Pt molar ratio at 5:1 in the presence of 300 μL of formaldehyde while keeping other conditions the same.

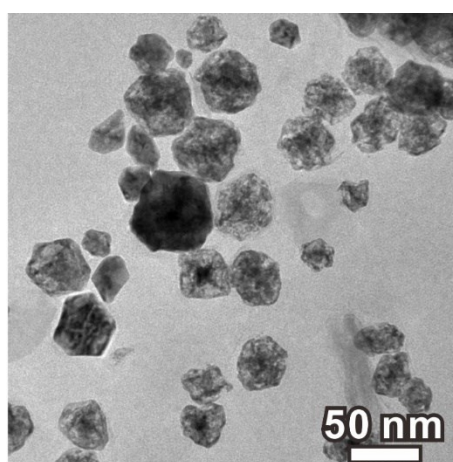


Figure S11 TEM image of product formed from the molar ratio of $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ at 5:1 in the absent of formaldehyde.

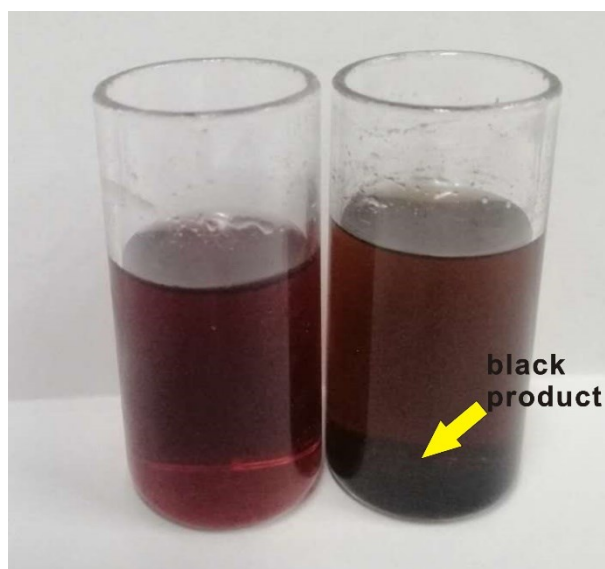


Fig. S12 The photography of the reactant solution obtained from the contrast synthetic experiment of 1 h of reaction, (left) without formaldehyde and (right) with 300 μL of formaldehyde solution.

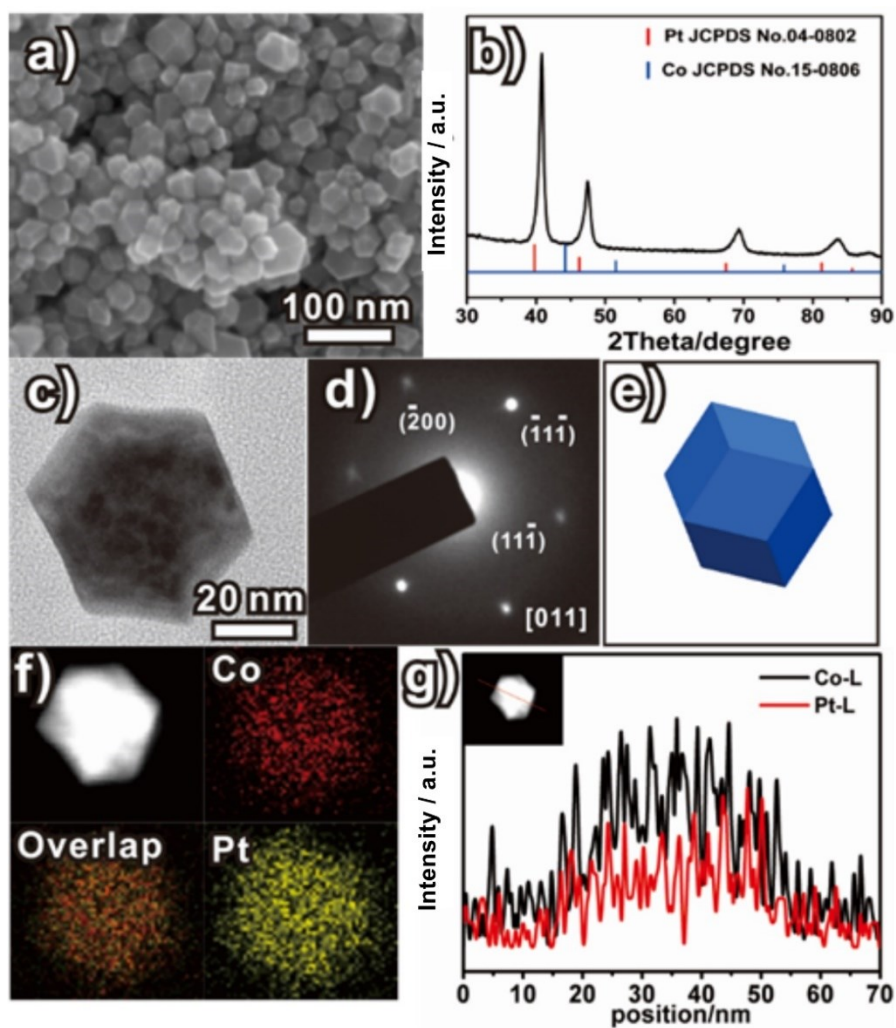


Fig. S13 (a) SEM image of PtCo RD NCs on a large scale; (b) XRD pattern of PtCo RD NCs; (c) TEM image and (d) the corresponding SAED image of an individual PtCo RD NC. (e) The schematic model of RD viewed along [011] direction. (f) HAADF-STEM image and HAADF-STEM-EDS maps of a single PtCo RD NC; (g) Cross-sectional compositional line profile of Pt and Co recorded across a single PtCo RD NC.

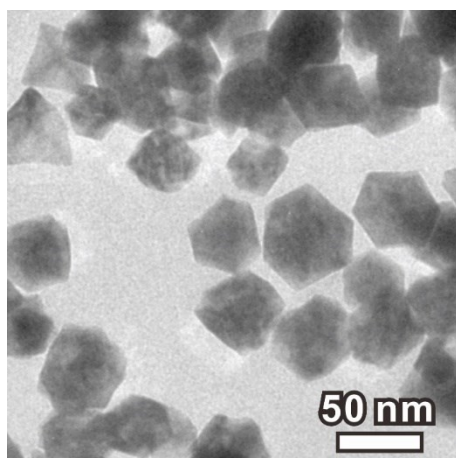


Fig. S14 TEM image of PtCo RD NCs on a large scale which obtained from molar ratio of $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ at 3:1 in the absent of formaldehyde.

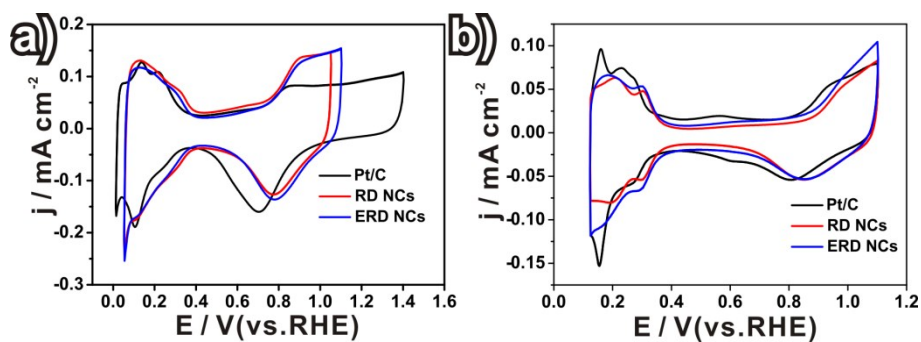


Fig. S15 (a) Cyclic voltammograms of as-prepared PtCo ERD NCs/C, RD NCs/C and Pt/C recorded in N₂-saturated HClO₄ solution (0.1 M) at scan rate of 100 mV s⁻¹ and a rotation rate of 1600 rpm; (b) CVs recorded in N₂-saturated H₂SO₄ solution (0.5 M) at a scan rate of 50 mV s⁻¹.

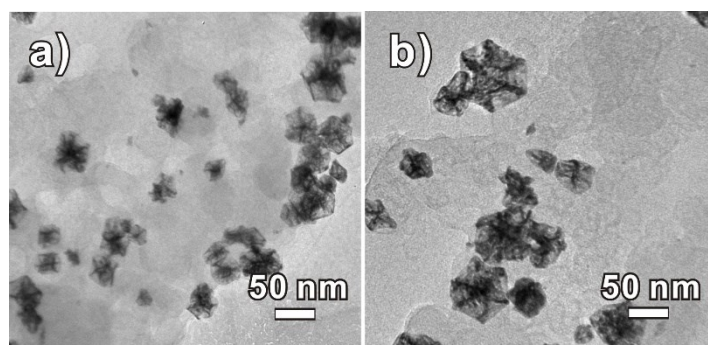


Fig. S16 (a-b) TEM images of PtCo ERD NCs/C catalyst after oxygen oxidation reaction.

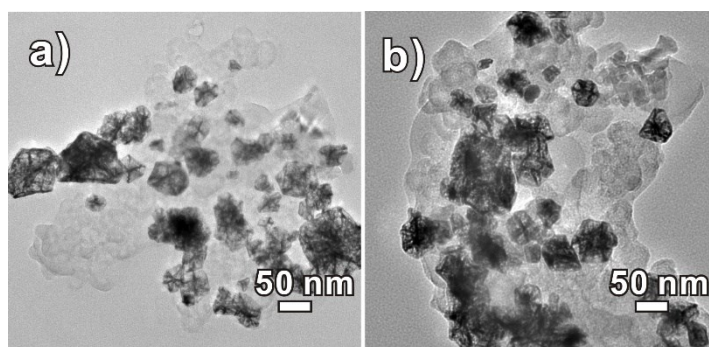


Fig. S17 (a-b) TEM images of PtCo ERD NCs/C catalyst after methanol oxidation reaction.

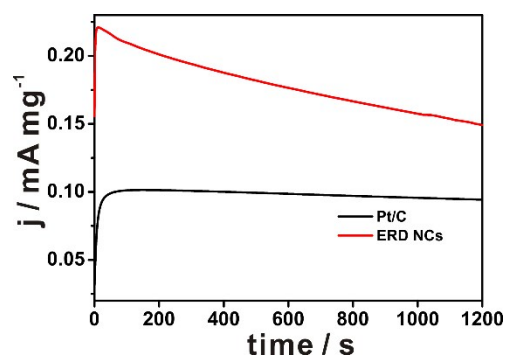


Fig. S18 Chronoamperometric measurements (i - t curves) of PtCo ERD NCs/C and commercial Pt/C in 0.5 M H₂SO₄ + 0.5 M CH₃OH at 0.4 V (vs. SCE).

Table S1 A comparison of the specific activities (SA) and mass activities (MA) of Pt-Co catalysts from literatures and this work.

Number	catalysts	electrolyte	SA@0.9V mA/cm ²	MA@0.9V A/mg _{Pt}	Ref.
1	PtCo@CNTs-MOF	0.1 M HClO ₄	1.38	0.852	[1]
2	Pt-Co/C-PANI-500 °C	0.1 M HClO ₄	1.29	1.33	[2]
3	PtCo/G-600	0.1 M HClO ₄	0.524	0.952	[3]
4	Excavated PtCo octahedron	0.1 M HClO ₄	1.53	0.35	[4]
5	Pt-Co NWs/C	0.1 M HClO ₄		0.2914	[5]
6	Pt-Co NWs	0.1 M HClO ₄	0.3564	0.179	[6]
7	leached PtCo/C_S#2	0.1 M HClO ₄		0.313	[7]
8	PtCo-Pt (chem)	0.1 M HClO ₄		0.38329	[8]
9	Ordered PtCo ₃ H600	0.1 M HClO ₄		0.72	[9]
10	PtCo ₃ /C	0.1 M HClO ₄	~2.25	~1.13	[10]
11	Pt-skin Pt ₃ Co z-NWs/C	0.1 M HClO ₄	5.6	2.2	[11]
12	Pt ₃ Co/C-N ₂ H ₄ ·H ₂ O	0.1 M HClO ₄	1.5	0.21	[12]
13	PtCo R-NW/C	0.1 M HClO ₄	~1.04	~0.98	[13]
14	Pt/40Co-NC-900	0.1 M HClO ₄	1.15	~0.24	[14]
15	H-PtCo@Pt ₁ N-C	0.1 M HClO ₄	2.39	1.2	[15]
16	PtCo@HGS	0.1 M HClO ₄	0.92 ± 0.16	0.97 ± 0.19	[16]
17	Concave cubic Pt-Co	0.1 M HClO ₄	0.439	0.237	[17]
18	PtCo@NC-10	0.1 M HClO ₄	1.32	0.82	[18]
19	Pt 75 Co 25 /C(500)	0.1 M HClO ₄	2.06	0.97	[19]
20	Pt-Co/C-PNIPAM	0.1 M HClO ₄	1.45		[20]
21	PtCo RD NCs/C	0.1 M HClO ₄	1.43	0.54	this paper
22	PtCo ERD NCs/C	0.1 M HClO ₄	2.68	0.94	this paper

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