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

Supporting information

Colloidal $Ni_{2-x}Co_xP$ nanocrystals for the hydrogen evolution reaction

Junfeng Liu,[a] Zhenxing Wang,[b] Jeremy David,[c] Jordi Llorca,[d] Junshan Li,[a] Xiaoting Yu,[a] Alexey Shavel,[a] Jordi Arbiol,[ce] Michaela Meyns,*[a] Andreu Cabot*[ae]

[a] Catalonia Institute for Energy Research (IREC), Sant Adrià de Besòs, 08930 Barcelona, Spain

[b] State Key Laboratory of Electrical Insulation and Power Equipment, Xi'an Jiaotong University, 710049, Xi'an, China

[c] Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Campus UAB, Bellaterra, 08193 Barcelona, Catalonia, Spain

[d] Institute of Energy Technologies, Department of Chemical Engineering and Barcelona Research Center in Multiscale Science and Engineering, Universitat Politecnica de Catalunya, Eduard Maristany 10-14, 08019 Barcelona, Spain

[e] ICREA, Pg. Lluis Companys 23, 08010 Barcelona, Catalonia, Spain

* Corresponding author

E-mail: michaela.meyns@awi.de, acabot@irec.cat

Contents

1. DFT calculations 2
2. Size distribution and geometric surface area 4
3. Additional HRTEM characterization 5
4. XPS survey 8
5. Crystal structure 9
6. Cl-free precursor 10
7. Additional electrochemical measurements 11
8. Comparison of catalysts 12
9. References 14

1. **DFT calculations**

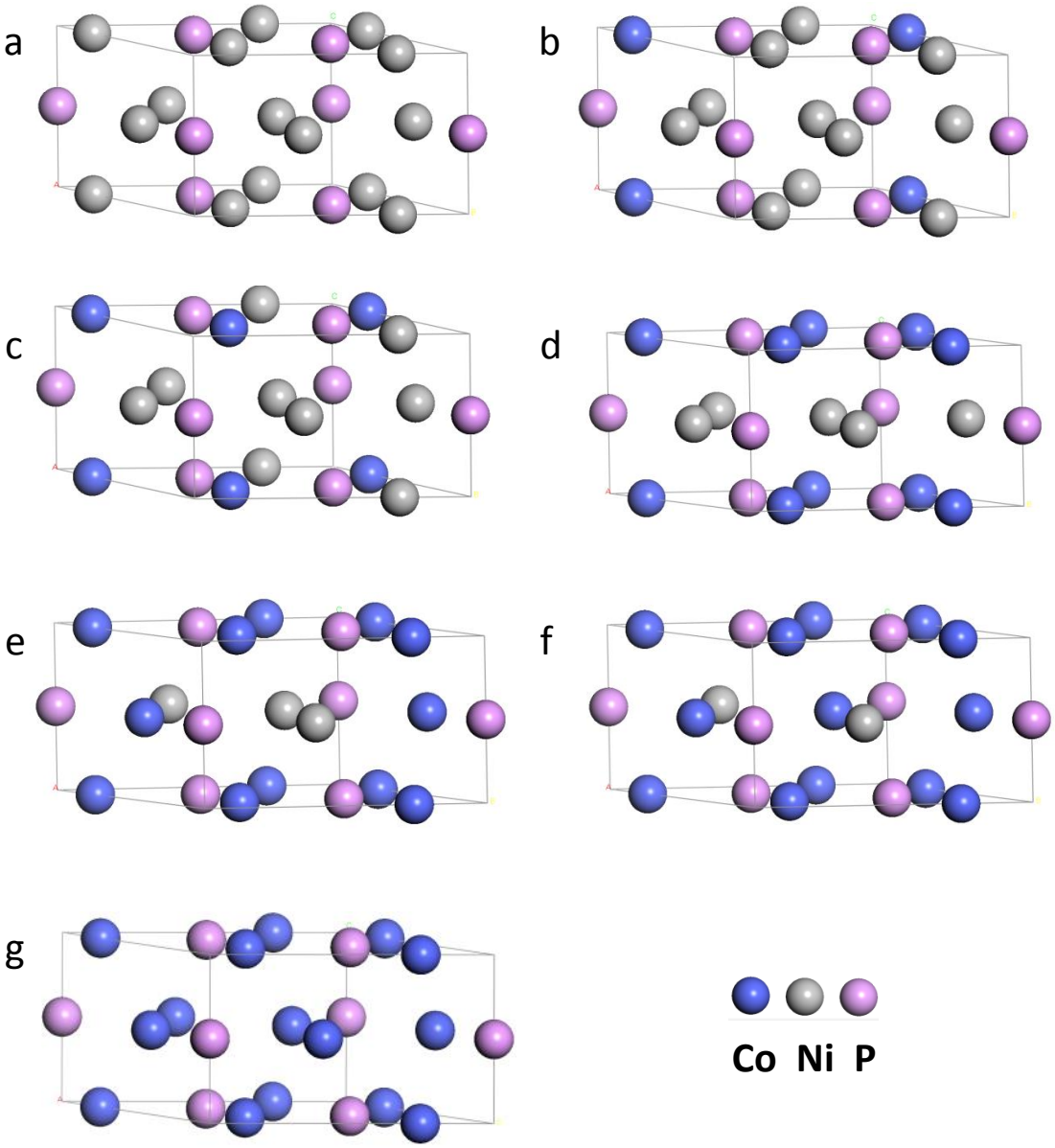


Figure S1. Hexagonal crystal structures of the $Ni_{2-x}Co_xP$: (a) Crystal structure of Ni_2P(a = b = 5.884 Å, c = 3.369 Å); (b) Crystal structure of $Ni_{1.67}Co_{0.33}P$ (a = b = 5.871Å, c = 3.338 Å); (c) Crystal structure of $Ni_{1.33}Co_{0.67}P$ (a = 5.838 Å, b = 5.849 Å, c = 3.325Å); (d) Crystal structure of NiCoP (a = b = 5.805 Å, c = 3.344 Å); (e) Crystal structure of $Ni_{0.67}Co_{1.33}P$ (a = 5.729, b = 5.893 Å, c = 3.363Å); (f) Crystal structure of $Ni_{0.33}Co_{1.67}P$ (a = 5.673 Å ,b = 5.794 Å, c = 3.389 Å); (g) Crystal structure of Co_2P (a = b = 5.725 Å, c = 3.409 Å).

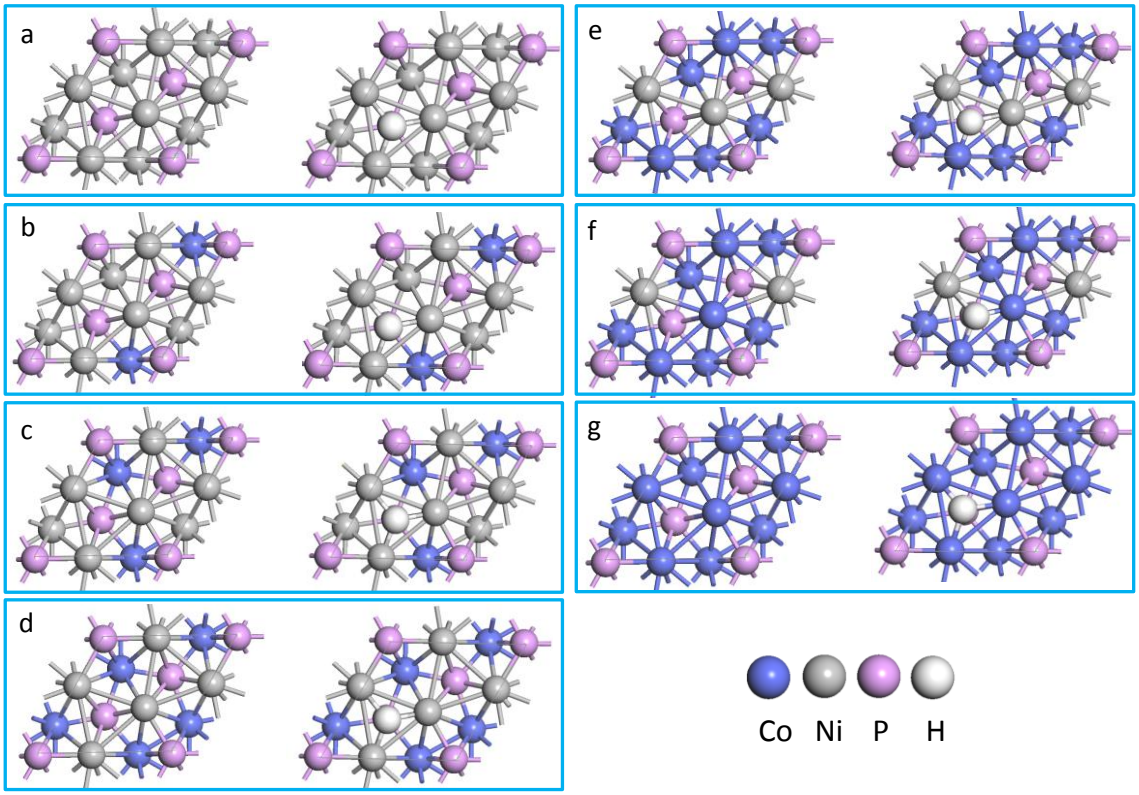


Figure S2. Top view of the (0001) surface of $Ni_{2-x}Co_xP$ (left panel) and the (0001) surface on which H*absorbed (right panel).(a) the (0001) surface of Ni_2P (d_{Ni-H} = 1.793 Å); (b) the (0001) surface of $Ni_{1.67}Co_{0.33}P$ (d_{Ni-H} = 1.801 Å); (c) the (0001) surface of $Ni_{1.33}Co_{0.67}P$ (d_{Ni-H} = 1.804 Å); (d) the (0001) surface of NiCoP (d_{Ni-H} = 1.792 Å); (e) the (0001) surface of $Ni_{0.67}Co_{1.33}P$ (d_{Ni-H} = 1.821 Å, d_{Co-H} = 1.747 Å); (f) the (0001) surface of $Ni_{0.33}Co_{1.67}P$ (d_{Ni-H} = 1.874 Å, d_{Co-H} = 1.769 Å); (g) the (0001) surface of Co_2P(d_{Co-H} = 1.801 Å).

Table S1. Calculated adsorption energies and Gibbs free energies of H adsorption on $Ni_{2-x}Co_xP$ (0001) surface.

Composition	ΔE_H (eV)	ΔE_{ZPE} (eV)	$\Delta_{0\rightarrow298.15K}\Delta H_H$ (eV)	$-T\Delta S_H$ (eV)	ΔG_{H^*} (eV)
Ni_2P	-0.228	0.067	0.052	0.205	0.096
$Ni_{1.67}Co_{0.33}P$	-0.196	-0.014	0.052	0.205	0.047
$Ni_{1.33}Co_{0.67}P$	-0.211	-0.005	0.052	0.205	0.041
NiCoP	-0.325	0.043	0.052	0.205	-0.025
$Ni_{0.67}Co_{1.33}P$	-0.508	0.039	0.052	0.205	-0.212
$Ni_{0.33}Co_{1.33}P$	-0.565	0.038	0.052	0.205	-0.270
Co_2P	-0.699	0.058	0.052	0.205	-0.384

2. Size distribution and geometric surface area

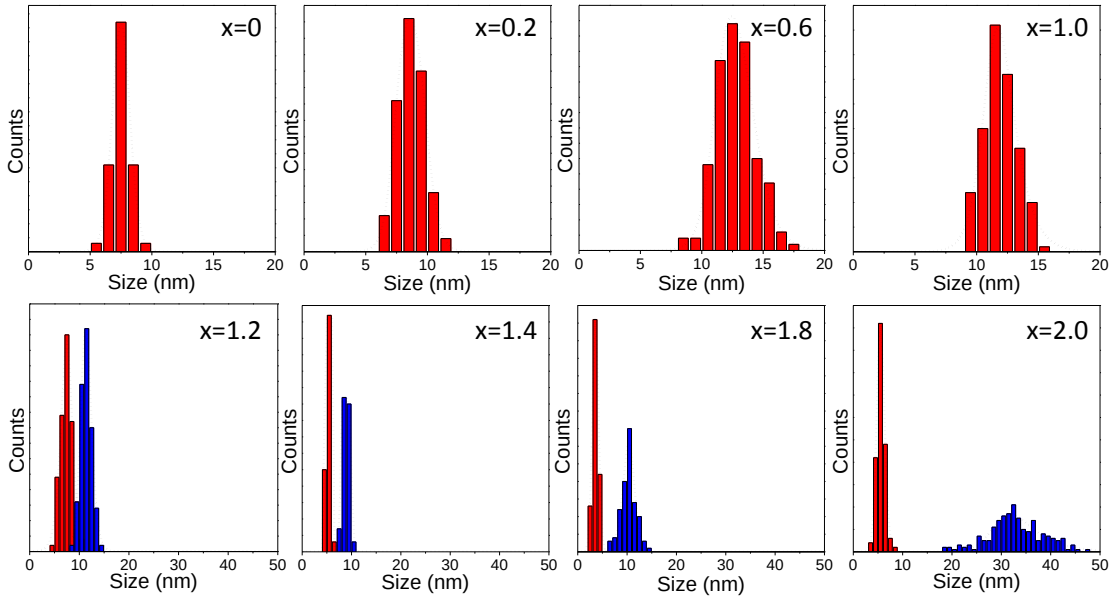


Figure S3. Size distributions of $Ni_{2-x}Co_xP$ (x = 0, 0.2, 0.6, 1.0, 1.2, 1.4, 1.8 and 2.0) NCs.

Table S2. Volume, surface and mass per NC, and geometric specific surface area of $Ni_{2-x}Co_xP$ NCs calculated from their geometry and estimated density.

Catalysts	V (nm^3)	S (nm^2)	m (10^{-21} g)	s/m (m^2 g^{-1})
Ni_2P	230	181	1702	107
$Ni_{1.8}Co_{0.2}P$	382	254	2832	90
$Ni_{1.4}Co_{0.6}P$	1150	531	8566	62
NiCoP	904	450	6762	67
$Ni_{0.8}Co_{1.2}P$	423	319	3168	101
$Ni_{0.6}Co_{1.4}P$	198	194	1485	131
$Ni_{0.2}Co_{1.8}P$	102	133	768	173
Co_2P	933	678	7032	96

The density of Ni_2P and Co_2P is 7.41 and 7.54 g/cm^3, respectively. The density of $Ni_{2-x}Co_xP$ is calculated by the following equation:

$$\rho = \frac{7.41(2-x) + 7.54x}{2}$$

3. Additional HRTEM characterization

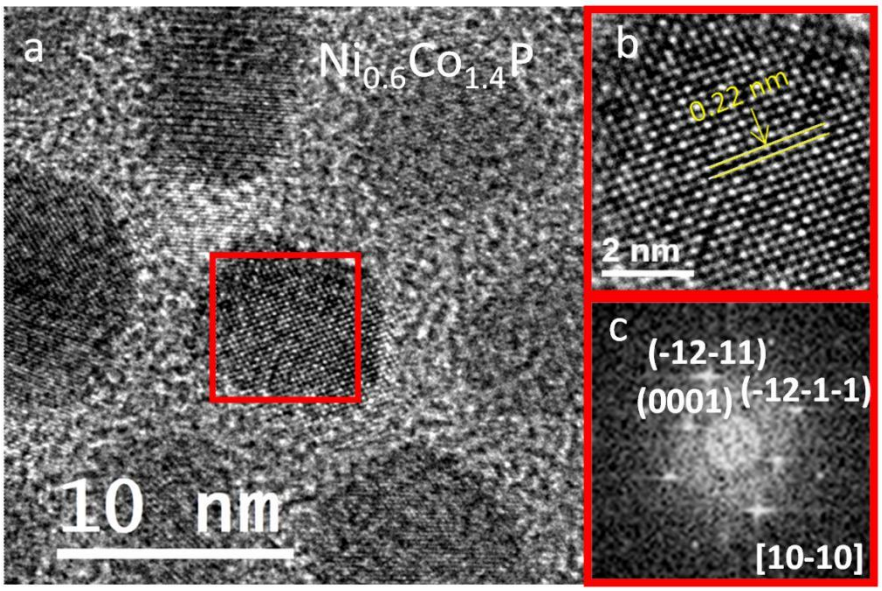


Figure S4. HRTEM micrograph of $Ni_{0.6}Co_{1.4}P$ NCs (a), detail of the NC in red (b) and its corresponding power spectrum (c).

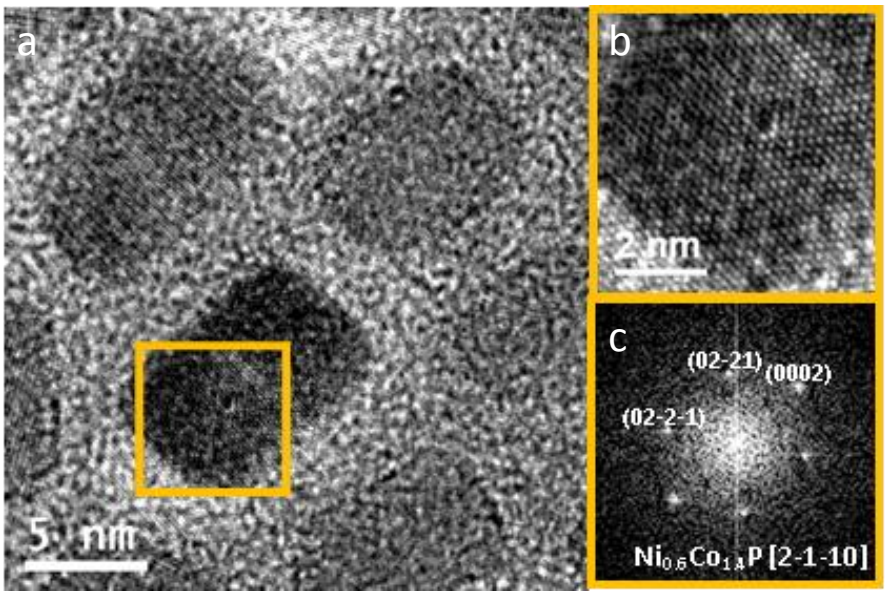


Figure S5. HRTEM micrograph of $Ni_{0.6}Co_{1.4}P$ NCs (a), detail of the NC in yellow (b) and its corresponding power spectrum (c).

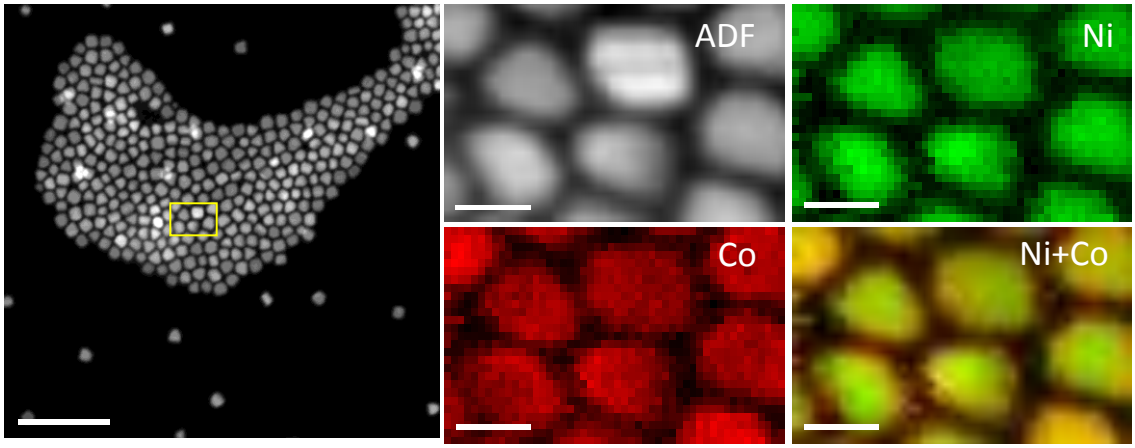
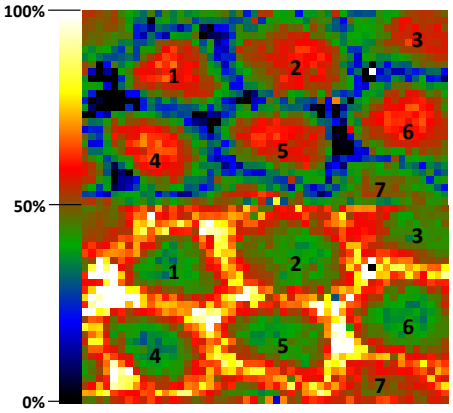


Figure S6. STEM – EELS elemental composition maps of a selected area of NiCoP nanocrystals on the left image: Ni (green), Co (red) and combination Ni+Co.



Target/Particle	Ni (%)	Co (%)	Composition
Target	*50*	*50*	*NiCo*
1	56.00	44.00	$Ni_{1.12}Co_{0.88}$
2	57.93	42.07	$Ni_{1.16}Co_{0.84}$
3	52.02	47.98	$Ni_{1.04}Co_{0.96}$
4	61.29	38.71	$Ni_{1.23}Co_{0.77}$
5	54.97	45.03	$Ni_{1.1}Co_{0.9}$
6	57.19	42.81	$Ni_{1.14}Co_{0.86}$
7	45.81	54.19	$Ni_{0.92}Co_{1.08}$

Figure S7. Ni and Co quantification maps obtained in the squared area of the STEM images in Figure S6, together with a table representing the quantification of the numbered particles.

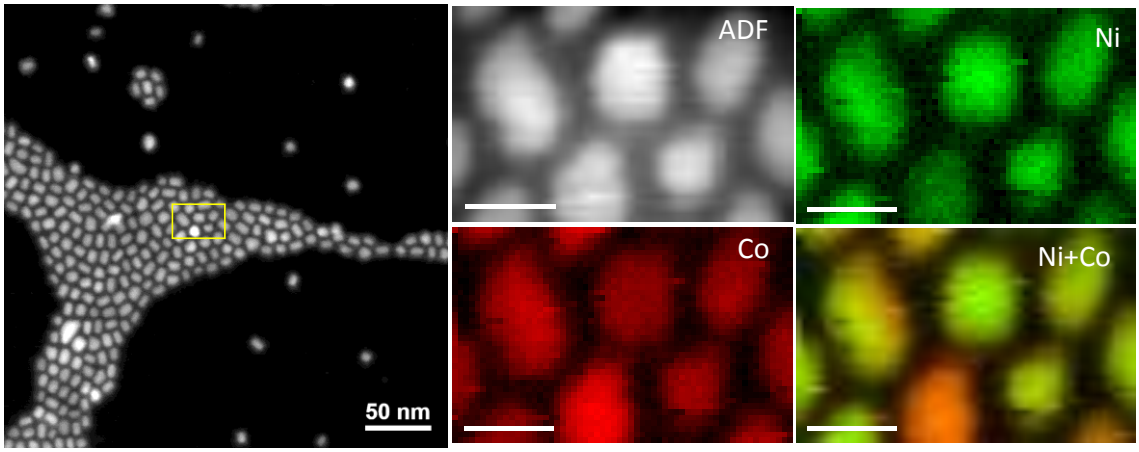
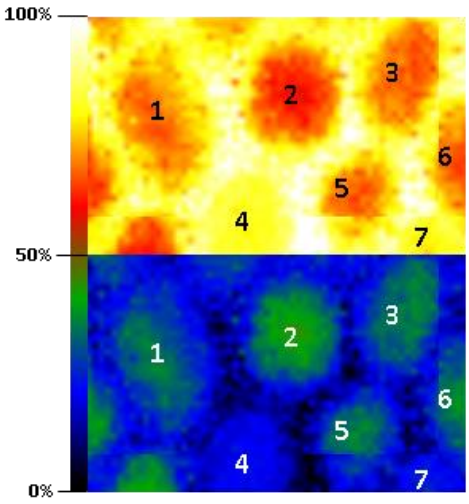


Figure S8. STEM – EELS elemental composition maps of a selected area of $Ni_{0.4}Co_{1.6}P$ nanocrystals on the left image: Ni (green), Co (red) and combination Ni+Co.



Target/Particle	Ni (%)	Co (%)	Composition
Target	*30*	*70*	*$Ni_{0.6}Co_{1.4}$*
1	30.02	69.98	$Ni_{0.6}Co_{1.4}$
2	37.54	62.46	$Ni_{0.75}Co_{1.25}$
3	31.54	68.46	$Ni_{0.63}Co_{1.37}$
4	17.46	82.54	$Ni_{0.35}Co_{1.65}$
5	31.58	68.42	$Ni_{0.63}Co_{1.37}$
6	32.91	67.09	$Ni_{0.66}Co_{1.33}$
7	20.67	79.33	$Ni_{0.4}Co_{1.6}$

Figure S9. Ni and Co quantification maps obtained in the squared areas of the STEM images in Figure S8, together with a table representing the quantification of the numbered particles.

4. XPS survey

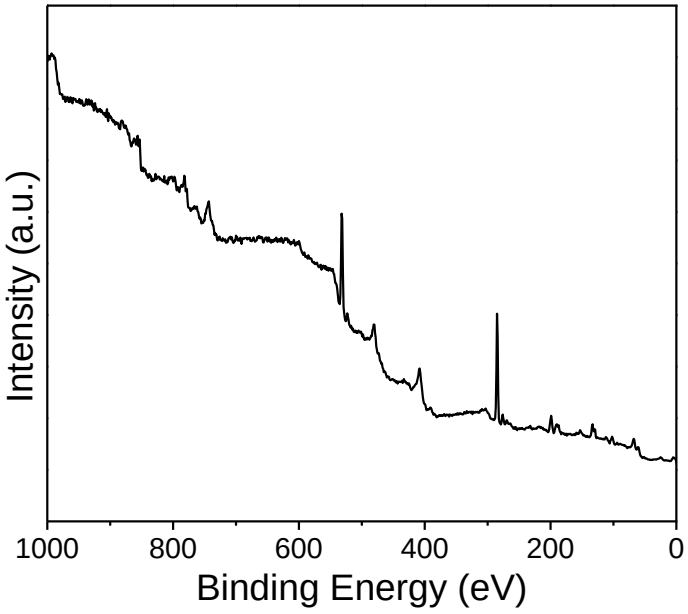


Figure S10. XPS survey of NiCoP nanocrystals.

5. Crystal structure

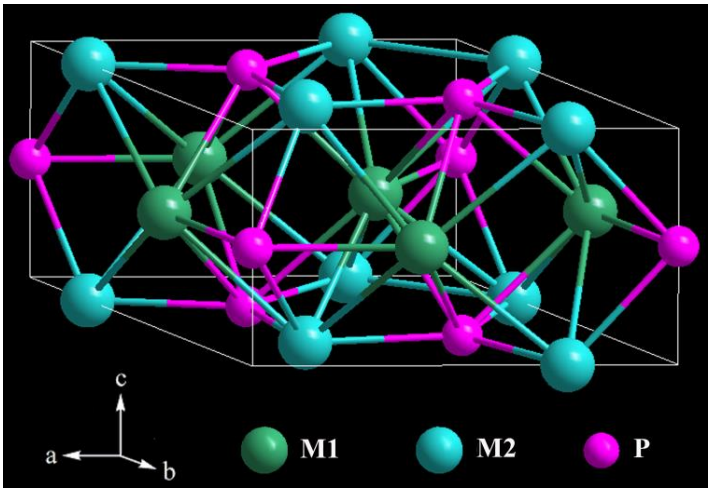


Figure S11. Hexagonal $Ni_{2-x}Co_xP$ structure type.

6. Cl-free precursor

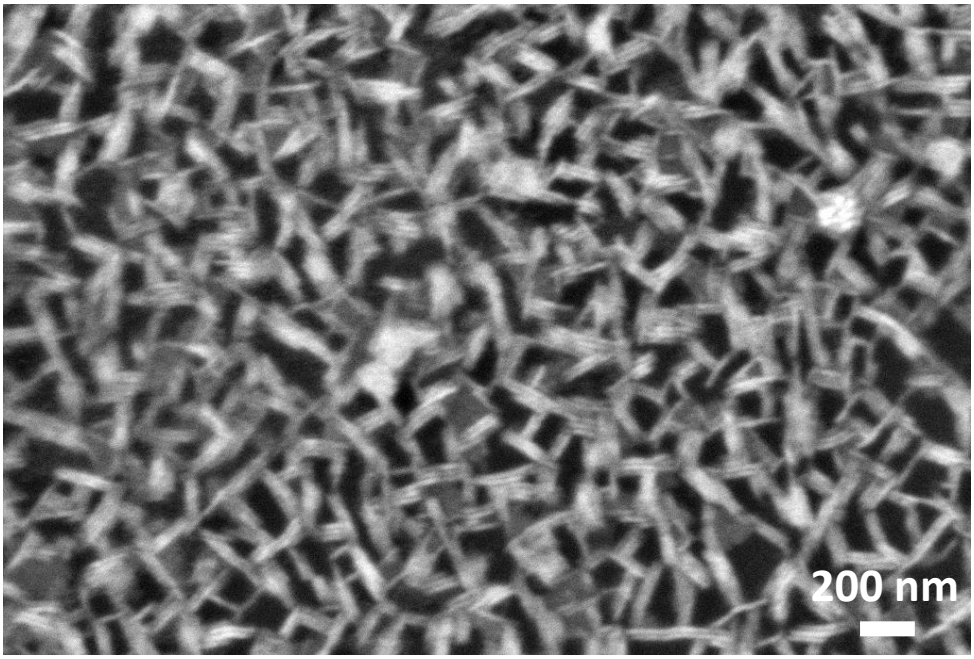


Figure S12. SEM micrograph of Co_2P nanorods obtained using $Co(NO_3)_2 \cdot 6H_2O$ instead of $CoCl_2$ as cobalt precursor ($Co(NO_3)_2 \cdot 6H_2O$: HDA : TPP = 1 : 10 : 10)

7. Additional electrochemical measurements

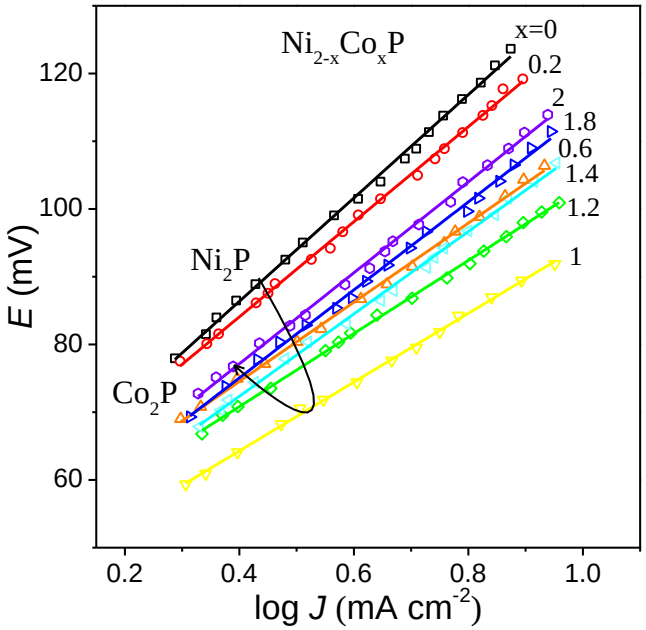


Figure S13. Tafel plots for the $Ni_{2-x}Co_xP$ NCs. Tafel slopes for $Ni_{2-x}Co_xP$ (x from 0 to 0.2, 0.6, 1, 1.2, 1.4, 1.6, 1.8, 2) are: 76, 70, 58, 51, 54, 61, 65, 67 mV dec^{-1}.

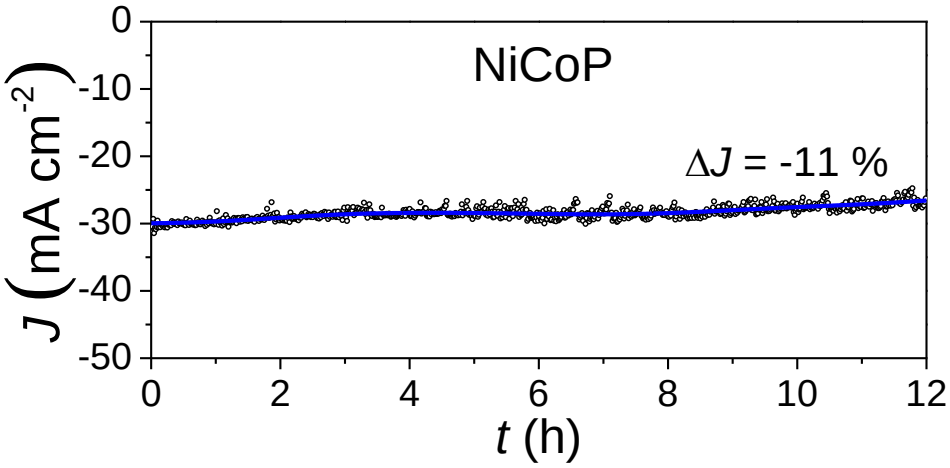


Figure S14. Time-dependent current density curve of NiCoP at an overpotential of 150 mV for 12 h.

8. Comparison of catalysts

Table S3. References of electrocatalysts for HER.

Catalyst	Substrate	Electrolyte	η at 10 mA cm^{-2}	References
MoS_2	Carbon fiber	0.5 M H_2SO_4	104	1
Mo_2C	GCE	0.5 M H_2SO_4	70	2
MoN	GCE	0.5 M H_2SO_4	125	3
MoN	GCE	1.0 M KOH	139	3
$CoSe_2$	Carbon fiber	0.5 M H_2SO_4	137	4
WS_2	GCE	0.5 M H_2SO_4	100	5
Ni_3S_2	Ni foam	1.0 M KOH	200	6
Co_2P	Ti foil	0.5 M H_2SO_4	134	7
FeP	GCE	0.5 M H_2SO_4	100	8
MoC-Mo_2C	GCE	0.5 M H_2SO_4	126	9
Fe_3C@NCNT	GCE	0.5 M H_2SO_4	154	10
Fe_3C@NCNT	GCE	1.0 M KOH	378	10
WC/graphene	Ga-W foil	0.5 M H_2SO_4	120	11
MoS_2/rGO	GCE	0.5 M H_2SO_4	120	12
$W(S_{0.48}Se_{0.52})_2$	Carbon fiber	1 M H_2SO_4	298	13
$WS_{2(1-x)}P_{2x}$	Carbon fiber	0.5 M H_2SO_4	98	14
Co_9S_8-MoS_x	Carbon fiber	0.5 M H_2SO_4	98	15
$Mn_{0.05}Co_{0.95}Se_2$	GCE	0.5 M H_2SO_4	174	16
$CoMoS_3$	GCE	0.5 M H_2SO_4	171	17
NiCoP	GCE	0.5 M H_2SO_4	97	This work

NCNT: N-doped carbon nanotubes

rGO: reduce graphene oxide

GCE: glassy carbon electrode

Table S4. References for synthesis of NiCoP.

Materials	Method	Metal precursors	P precursor	Controlled			η_{10}	Ref.
				Composition	Size	Shape		
NiCoP	Plasma-assisted	NiCo hydroxide	PH_3 gas	No	No	No	32	18
Ni-Co-P	Electro-deposition	$NiCl_2$, $Co(NO_3)_2$	NaH_2PO_2	No	No	No	30	19
NiCoP	Annealing	Ni-Co-salt	NaH_2PO_2	No	No	No	101	20
NiCoP	Annealing	Ni-Co carbonate	NaH_2PO_2	No	No	No	118	21
NiCoP	Annealing	NiCo hydroxide	NaH_2PO_2	No	No	No	124	22
NiCoP	Annealing	NiCo hydroxide	NaH_2PO_2	No	No	No	104	23
NiCoP	Annealing	$Ni_{1-0.5x}Co_{0.5x}(OH)_2$	NaH_2PO_2	Yes	No	No	59	24
NiCoP	Annealing	NiCo hydroxide	NaH_2PO_2	No	No	No	185	25
Ni-Co-P	Annealing	Ni-Co-PBA	NaH_2PO_2	No	No	No	167	26
NiCoP	Annealing	$NiCo_2O_4$	NaH_2PO2	Yes	No	No	44	27
$NiCo_2P_x$	Annealing	$NiCo_2O_4$	NaH_2PO_2	No	No	No	104	28
$Ni_{0.69}Co_{0.31}P$	Annealing	$NiCoO_x$	NaH_2PO_2	Yes	No	No	100	29
NiCoP	Colloidal	$Ni(acac)_2$, $Co(acac)_2$	TOP	No	No	No	102	30
$Co_{1.6}Ni_{0.4}P$	Colloidal	$Ni(acac)_2$, $Co(acac)_2$	TOP	Yes	No	No	162	31
$Ni_{2-x}Co_xP$	Colloidal	$Ni(OAc)_2$, $Co(OAc)_2$	PPh_3	Yes	No	No	>250	32
NiCoP	Colloidal	$NiCl_2$, $CoCl_2$	TPP	Yes	Yes	Yes	97	This work

9. References

[1] J. Hu, B. Huang, C. Zhang, Z. Wang, Y. An, D. Zhou, H. Lin, M. K. H. Leung, S. Yang, *Energy Environ. Sci.* 2017, **10**, 593-603.

[2] L. Liao, S. Wang, J. Xiao, X. Bian, Y. Zhang, M. D. Scanlon, X. Hu, Y. Tang, B. Liu, H. H. Girault, *Energy Environ. Sci.* 2014, **7**, 387-392.

[3] J. Xiong, W. Cai, W. Shi, X. Zhang, J. Li, Z. Yang, L. Feng, H. Cheng, *J. Mater. Chem. A* 2017, **5**, 24193-24198.

[4] D. Kong, H. Wang, Z. Lu, Y. Cui, *J. Am. Chem. Soc.* 2014, **136**, 4897-900.

[5] L. Cheng, W. Huang, Q. Gong, C. Liu, Z. Liu, Y. Li, H. Dai, *Angew. Chem.* 2014, **53**, 7860-7863.

[6] C. Ouyang, X. Wang, C. Wang, X. Zhang, J. Wu, Z. Ma, S. Dou, S. Wang, *Electrochimi. Acta* 2015, **174**, 297-301.

[7] Z. Huang, Z. Chen, Z. Chen, C. Lv, M. G. Humphrey, C. Zhang, *Nano Energy* 2014, 9, 373-382.

[8] Y. Xu, R. Wu, J. Zhang, Y. Shi, B. Zhang, *Chem. Commun.* 2013, **49**, 6656-6658.

[9] H. Lin, Z. Shi, S. He, X. Yu, S. Wang, Q. Gao, Y. Tang, *Chem. Sci.* 2016, **7**, 3399-3405.

[10] L. Zhang, Y. Chen, P. Zhao, W. Luo, S. Chen, M. Shao, *Electrocatalysis* 2018, **9**, 264-270.

[11] M. Zeng, Y. Chen, J. Li, H. Xue, R. G. Mendes, J. Liu, T. Zhang, M. H. Rümmeli, L. Fu, *Nano Energy* 2017, **33**, 356-362.

[12] Y. Li, H. Wang, L. Xie, Y. Liang, G. Hong, H. Dai, *J. Am. Chem. Soc.* 2011, **133**, 7296-7299.

[13] K. Xu, F. Wang, Z. Wang X. Zhan, Q. Wang, Z. Chen, M. Safdar, J. He, *ACS Nano* 2014, **8**, 8468-8476.

[14] T. A. Shifa, F. Wang, K. Liu, Z. Cheng, K. Xu, Z. Wang, X. Zhan, C. Jiang, J. He, *Small* 2017, 1603706.

[15] X. Zhou, X. Yang, M. N. Hedhili, H. Li, S. Min, J. Ming, K. W. Huang, W. Zhang, L. J. Li, *Nano Energy* 2017, **32**, 470-478.

[16] Y. Liu, X. Hua, C. Xiao, T. Zhou, P. Huang, Z. Guo, B. Pan, Y. Xie, *J. Am. Chem. Soc.* 2016, **138**, 5087-5092.

[17] L. Yu, B. Y. Xia, X. Wang, X. W. Lou, *Adv. Mater.* 2016, **28**, 92-97.

[18] H. Liang, A. N. Gandi, D. H. Anjum, X. Wang, U. Schwingenschlogl, H. N. Alshareef, *Nano Lett.* 2016, **16**, 7718-7725.

[19] P. Zhang, H. Chen, M. Wang, Y. Yang, J. Jiang, B. Zhang, L. Duan, Q. Daniel, F. Li, L. Sun, *J. Mater. Chem. A* 2017, **5**, 7564-7570.

[20] X. Wang, R. Tong, Y. Wang, H. Tao, Z. Zhang, H. Wang, ACS Appl. *Mater. Inter.* 2016, **8**, 34270-34279.

[21] T. Liu, X. Yan, P. Xi, J. Chen, D. Qin, D. Shan, S. Devaramani, X. Lu, *Int. J. Hydrogen Energ.* 2017, **42**, 14124-14132.

[22] Y. Li, J. Liu, C. Chen, X. Zhang, J. Chen, *ACS Appl. Mater. Inter.* 2017, **9**, 5982-5991.

[23] J. Li, G. Wei, Y. Zhu, Y. Xi, X. Pan, Y. Ji, I. V. Zatovsky, W. Han, *J. Mater. Chem. A* 2017, **5**, 14828-14837.

[24] J. Li, M. Yan, X. Zhou, Z. Q. Huang, Z. Xia, C. R. Chang, Y. Ma, Y. Qu, *Adv. Funct. Mater.* 2016, **26**, 6785-6796.

[25] H. Zhang, X. Li, A. Hähnel, V. Naumann, C. Lin, S. Azimi, S. L. Schweizer, A. W. Maijenburg, R. B. Wehrspohn, *Adv. Funct. Mater.* 2018, 1706847.

[26] Y. Feng, X. Y. Yu, U. Paik, *Chem. Commun.* 2016, **52**, 1633-1636.

[27] C. Du, L. Yang, F. Yang, G. Cheng, W. Luo, *ACS Catal.* 2017, **7**, 4131-4137.

[28] R. Zhang, X. Wang, S. Yu, T. Wen, X. Zhu, F. Yang, X. Sun, X. Wang, W. Hu, *Adv. Mater.* 2017, 1605502.

[29] Z. Yin, C. Zhu, C. Li, S. Zhang, X. Zhang, Y. Chen, *Nanoscale* 2016, **8**, 19129-19138.

[30] C. Wang, J. Jiang, T. Ding, G. Chen, W. Xu, Q. Yang, *Adv. Mater. Inter.* 2016, **3**, 1500454.

[31] Y. Pan, Y. Chen, Y. Lin, P. Cui, K. Sun, Y. Liu, C. Liu, *J. Mater. Chem. A* 2016, **4**, 14675-14686.

[32] Q. Liang, K. Huang, X. Wu, X. Wang, W. Ma, S. Feng, *RSC Adv.* 2017, **7**, 7906-7913.