Electronic Supplementary Information (ESI)

Homologous Co_3O_4‖CoP nanowires grown on carbon cloth as a high-performance electrode pair for triclosan degradation and hydrogen evolution

Chaojie Lyu,[a] Jinlong Zheng,[#,a] Rui Zhang,[a] Ruqiang Zou,[b] Bin Liu,[c] and Wei Zhou*,[a]

[a]*School of Chemistry, Beihang University, Beijing 100191, China*
[b]*Beijing Key Laboratory for Theory and Technology of Advanced Battery Materials, Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing 100871, China*
[c]*Institute for Food & Bioresource Engineering, College of Engineering, Peking University, Beijing 100871, China*
[#]*The author contributed equally to the first author.*
E-mail: zhouwei@buaa.edu.cn

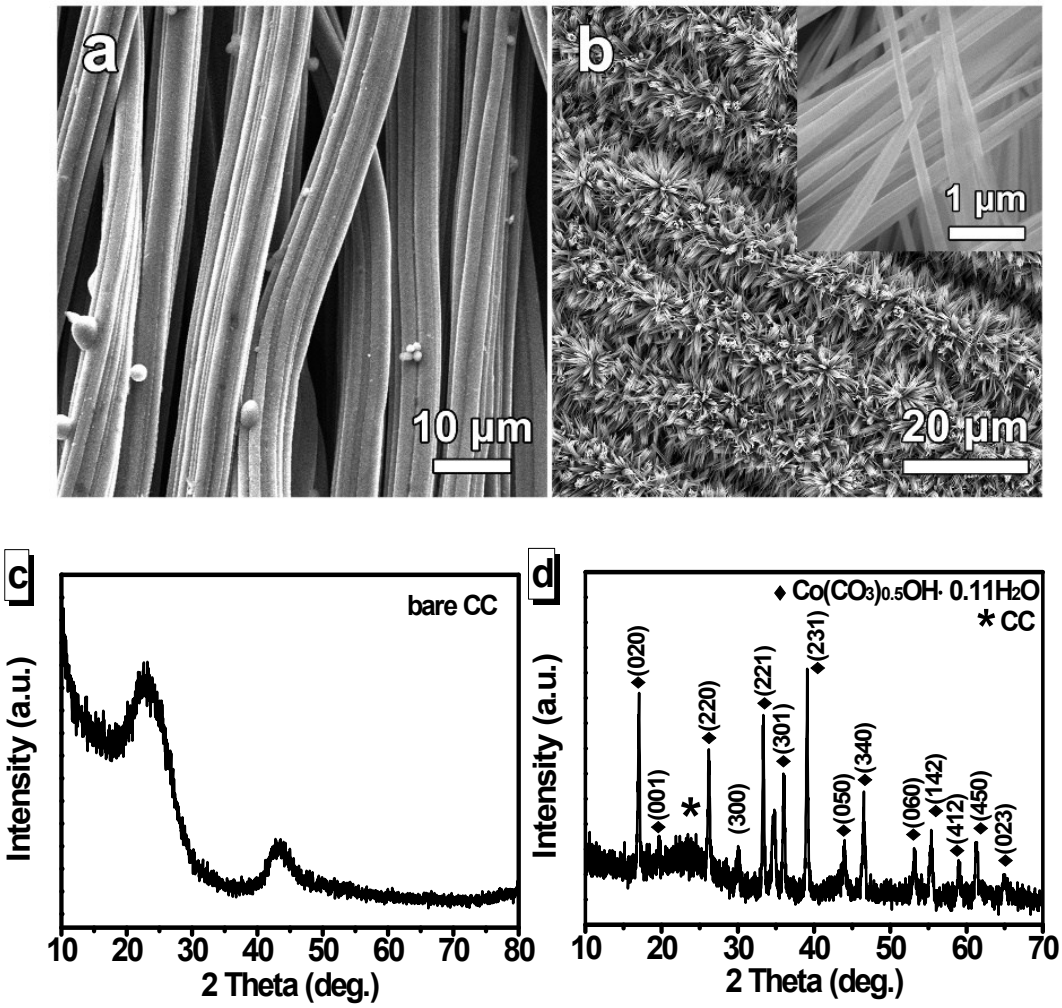

Fig. S1 (a) SEM image of the bare carbon cloth (CC). (b) SEM image of the precursor/CC with magnified nanowires inserted, indicating the whole surface of the CC was uniformly coated with nanowires with diameters of 100-200 nm. (c, d) XRD patterns of the bare CC and the precursor/CC. The marked diffraction peaks of the Co precursor in Fig. S1d can be well indexed to $Co(CO_3)_{0.5}OH{\cdot}0.11H_2O$ (JCPDS No. 48-0083), in agreement with reported references. The peak marked with asterisk at ~24.5° came from CC. [S1, S2]

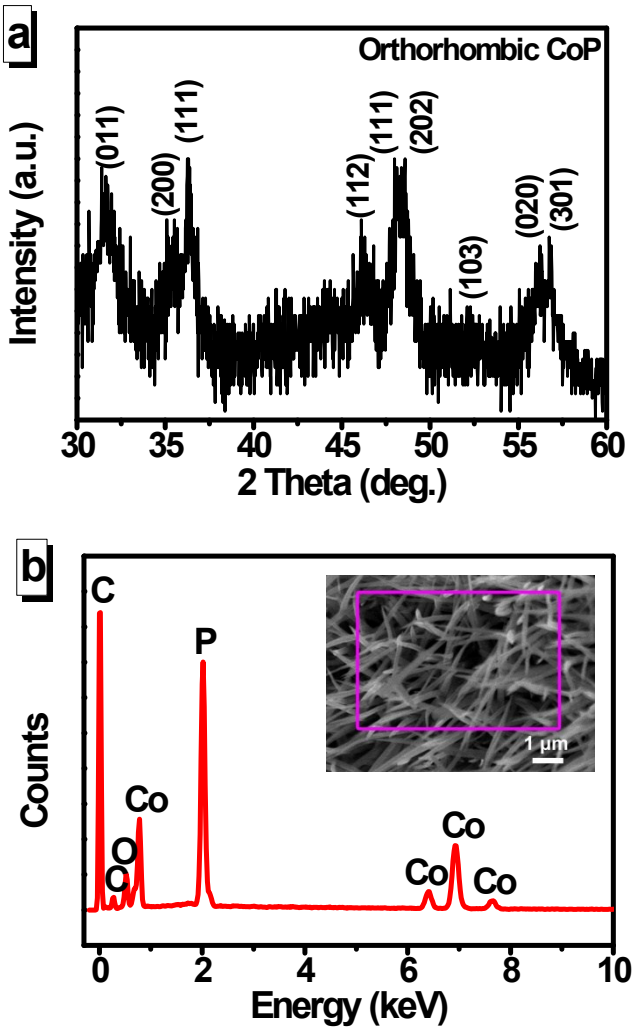

Fig. S2 (a) XRD patterns of the CoP NWs/CC with these diffraction peaks corresponding to orthorhombic CoP (JCPDS No. 29-0497). (b) EDX spectrum of the CoP NWs/CC with the selected area inserted, revealing the existence of Co and P with atomic ratio of 1:1.2, in agreement with the result of XRD pattern.

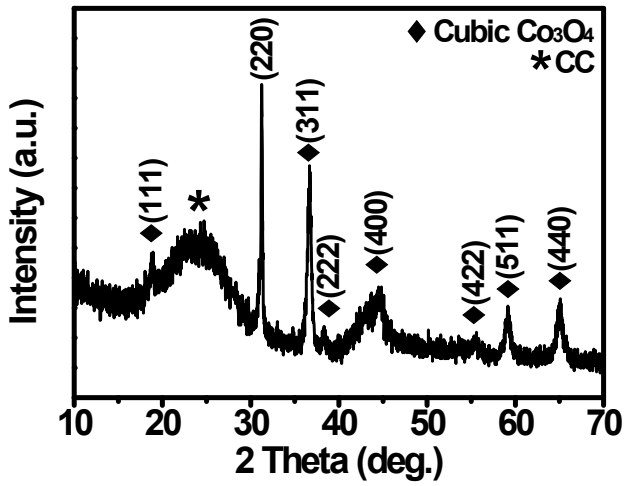

Fig. S3 XRD pattern of the Co_3O_4 NWs/CC, confirming the heat-treated product was transformed to cubic Co_3O_4 (JCPDS No. 43-1003). The peak marked with asterisk at ~24.5° came from CC.

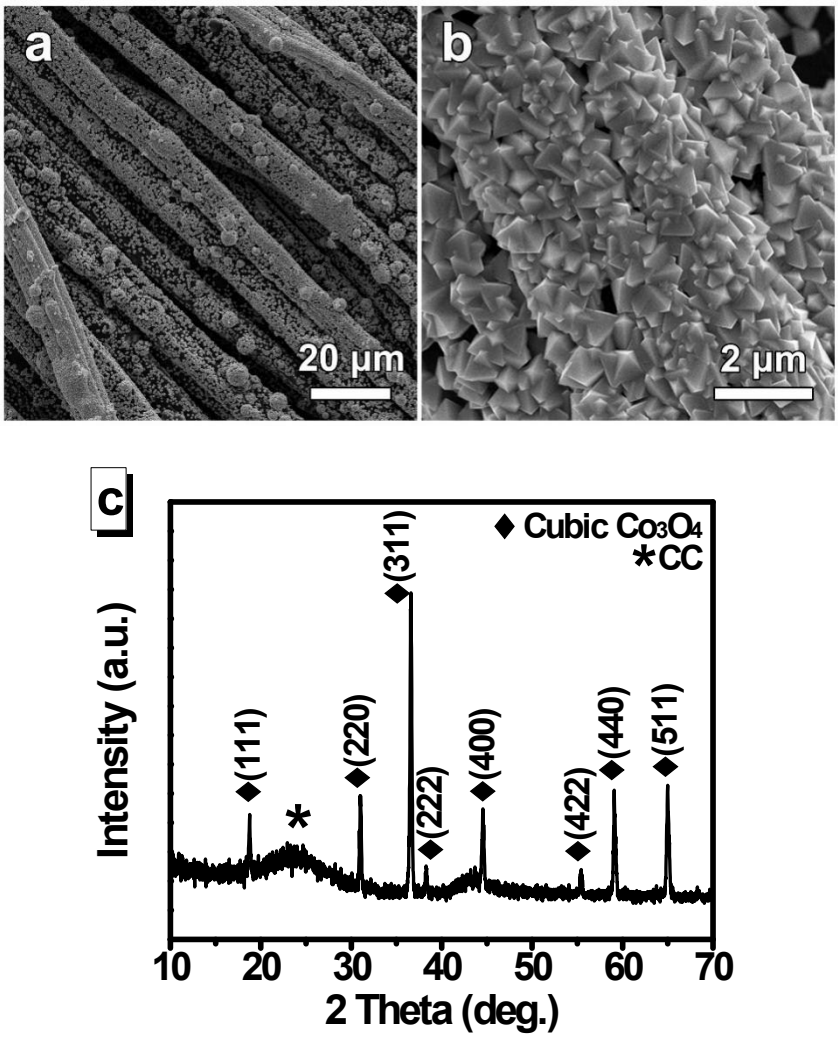

Fig. S4 (a, b) Low- and high-magnification SEM images of the Co_3O_4 Oct/CC, showing the octahedron with an average size of ~500 nm. (c) XRD pattern of the Co_3O_4 Oct/CC. All the diffraction peaks could be indexed well with standard cubic Co_3O_4 (JCPDS No. 43-1003). The peak marked with asterisk at ~24.5° came from CC.

Table S1 Comparison of HER performance in 0.5 M H_2SO_4 (pH=0), 1 M PBS (pH =7), and 1 M KOH (pH=14) for CoP NWs/CC with other Co-based Electrocatalysts.

pH = 0

Catalyst	Electrolyte	η (mV) @ 10 mA cm^{-2}	Tafel slope (mV dec^{-1})	Reference
Co_9S_8/NC@MoS_2	0.5 M H_2SO_4	117	68.8	*ACS Appl. Mater. Inter.* 2017, **9**, 28394-28405 [S3]
$CoSe_2$@G	0.5 M H_2SO_4	210	42	*Chem. Eng. J.* 2017, **321,** 105-112 [S4]
CoP NPs@NPC	0.5 M H_2SO_4	134	79	*Nanoscale,* 2017, **9,** 3555-3560 [S5]
Ni_2P/NiCoP@NCCs	0.5 M H_2SO_4	136	79	*J. Mater. Chem. A*, 2017, **5,** 16568-16572 [S6]
CoP NRs	0.5 M H_2SO_4	123	63	*Mater. Lett.*, 2017,**202,** 146-149 [S7]
Co_2P	0.5 M H_2SO_4	240	76	*Nano Lett.,* 2016, **16,** 4691-4698 [S8]
CoP-Co	0.5 M H_2SO_4	135	66	*ACS Nano,* 2017, **11,** 4358-4364 [S9]
CoP NWs/CC	0.5 M H_2SO_4	119	73	**Our Work**

pH = 7

CoO/$CoSe_2$	1 M PBS	450	131	*Adv. Sci.* 2016, ***3,*** 1500426 [S10]
Co_2N/TM	1 M PBS	290	138	*Catal. Sci. Technol.*, 2017, **7,** 2689-2694 [S11]

Co_9S_8/CC	1 M PBS	175	\	*J. Mater. Chem. A*, 2016, **4,** 6860-6867 [S12]
Ni−Co−S	1 M PBS	280	73	*ACS Appl. Mater. Inter.* 2017, **9,** 19746-19755 [S13]
Co-B	1 M PBS	251	75	*J. Power Sources,* 2015, **279**, 620-625 [S14]
CoP NPs@NPC	1 M PBS	423	268	*Nanoscale,* 2017, **9,** 3555-3560 [S5]
CoP NWs/CC	1 M PBS	130	144	**Our Work**

pH = 14

Catalyst	**Electrolyte**	**η (mV) @ 10 mA cm^{-2}**	**Tafel slope (mV dec^{-1})**	**Potential Rention Rate (Testing time)**	**Reference**
Co@NC/NF	0.1 M KOH	240	\	92(45h)	*ChemElectroChem*, 2017, **4,** 188-193 [S15]
NiCo HNSs	1 M KOH	230	87.5	78.2(5h)	*J. Mater. Chem. A*, 2017, **5,** 7769-7775 [S16]
Co–Ni–B	1 M KOH	205	\	90(12h)	*J. Mater. Chem. A,* 2017, **5,** 12379-12384 [S17]
Co_4Mo_2@NC	1 M KOH	218	73.5	75(13h)	*J. Mater. Chem. A*, 2017, **5**, 16929-16935 [S18]
CoMnCH	1 M KOH	180	\	96.7(10h)	*J. Am. Chem. Soc.* 2017, **139,** 8320-8328 [S19]
CoP	1 M KOH	139	70.3	77.5(10h)	*Nano Energy,* 2017, **38,** 290-296 [S20]

Ni−Co−Ti	1 M KOH	106	41	88(150h)	*ACS Appl. Mater. Inter.*, 2017, **9,** 12416-12426 [S21]
Ce-CoP	1 M KOH	92	63.5	93.1(10h)	*Nano Energy,* 2017, **38**, 290-296 [S20]
CoP NWs/CC	1 M KOH	69	70	98.5% (24h)	**Our Work**

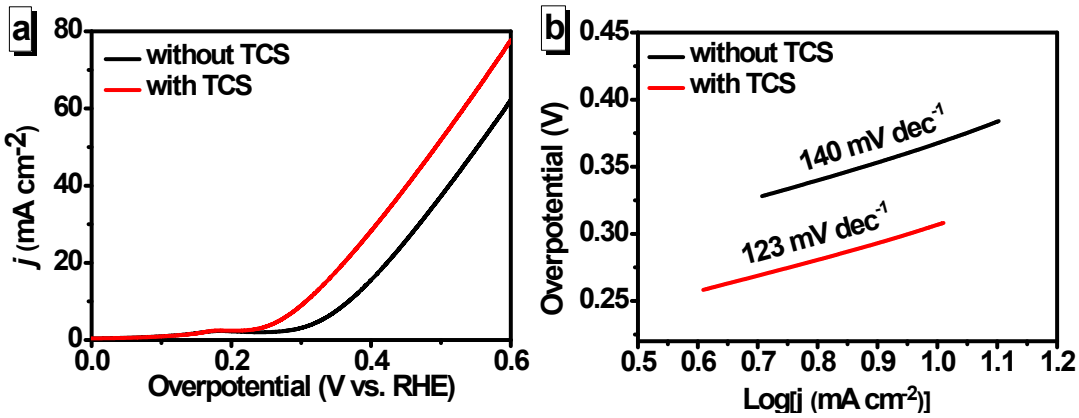

Fig. S5 (a) LSV curves of Co_3O_4 NWs/CC at a scan rate of 2 mV s^{-1} in 1 M KOH with and without TCS. (b) Corresponding Tafel plots of Co_3O_4 NWs/CC in 1 M KOH with and without TCS.

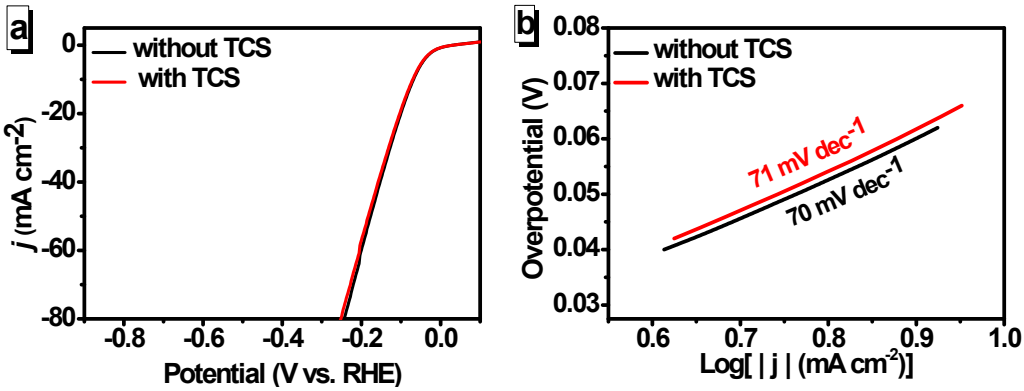

Fig. S6 (a) LSV curves of CoP NWs/CC for HER at a scan rate of 2 mV s^{-1} in 1 M KOH with and without TCS. (b) Corresponding Tafel plots of CoP NWs/CC in 1 M KOH with and without TCS.

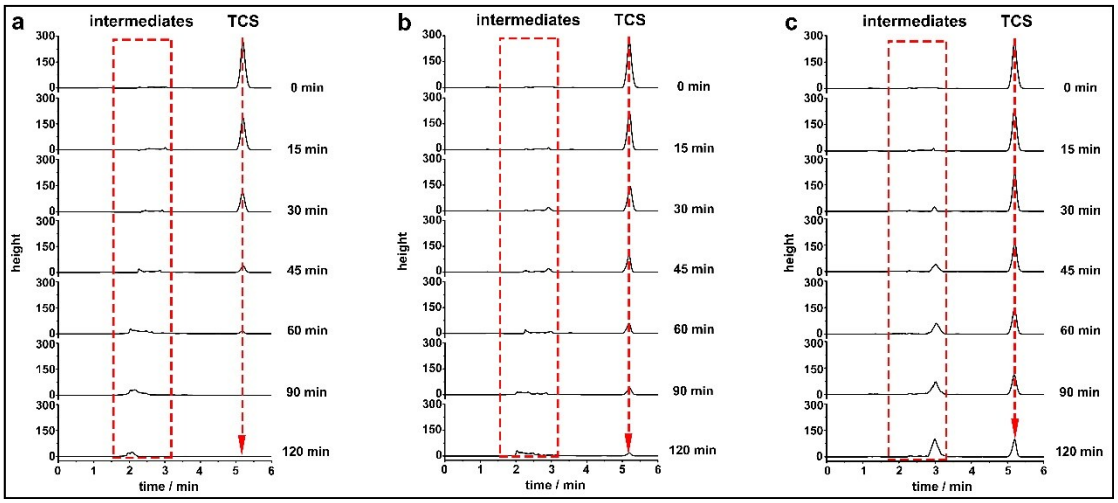

Fig. S7 Retention time of TCS solution (40 mg L^{-1}) and its intermediates during the electrochemical degradation process, using (a) the Co_3O_4 NWs/CC‖CoP NWs/CC pair, (b) the Co_3O_4 Oct/CC‖CoP NWs/CC pair, and (c) the CC‖CoP NWs/CC pair. Obviously, the peaks with retention time of ~5.2 min correspond to TCS while the peaks with retention time between 2 and 3 min correspond to the intermediates. Obviously, the rapid peak decrease of TCS using Co_3O_4 NWs/CC suggested its fast degradation rate.

Table S2 Comparison of TCS degradation with other literatures.

Electrode	TCS concentration (mg L^{-1})	Current density (mA cm^{-2})	Time (min)	Degradation Rates (%)	Reference
boron-doped diamond (BDD)	1.19	28.5	180	62	*J. Electroanal. Chem.,* 2016, **776**, 148-151 [S22]
Ti/SnO_2-Sb/Ce-PbO_2	4	10	5	99.9	*CLEAN-Soil, Air, Water.,* 2015, **43**, 958-966 [S23]
Ti/MMO	5	3	30	100	*Chemosphere,* 2013, **93**, 2796-2804 [S24]
p-Si-BDD	100	30	600	95	*Chem. Eng. Trans.,* 2014, **41**, 103-108 [S25]
Pt/carbon felt	5	13	10	100	*Electrochim. Acta.,* 2007, **52**, 5493-5503 [S26]
Co_3O_4 NWs/CC	40	10	60	95	**Our work**

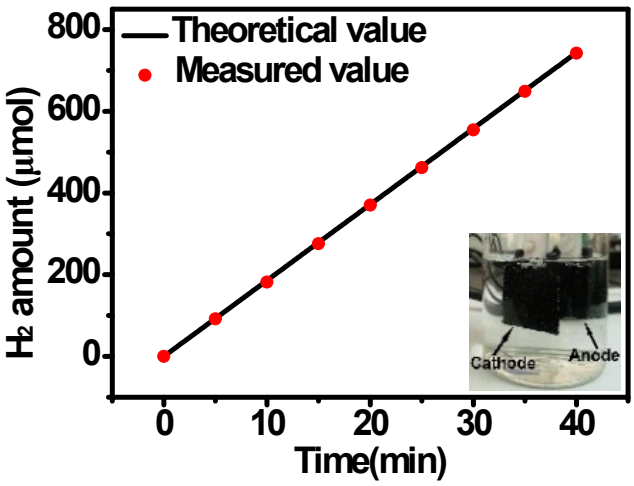

Fig. S8 Measured H_2 quantity compared with theoretically calculated H_2 quantity *vs*. time for CoP NWs/CC.

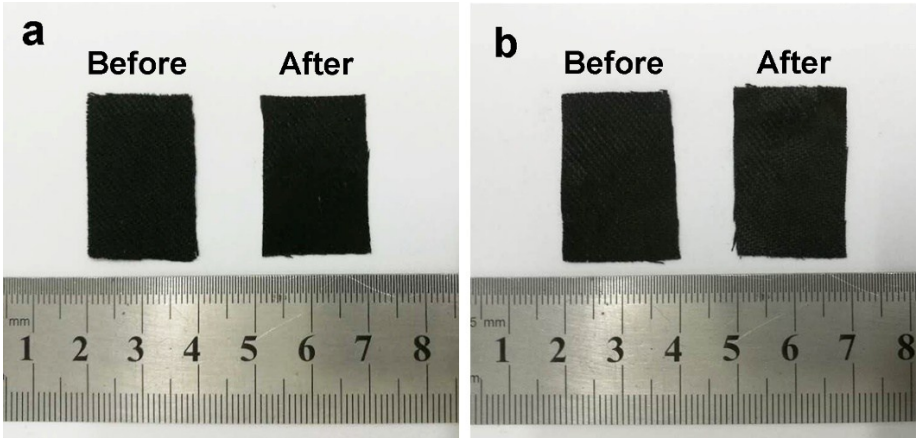

Fig. S9 Optical photos of (a) CoP NWs/CC and (b) Co_3O_4 NWs/CC electrodes before and after 6 successive electrolysis cycles.

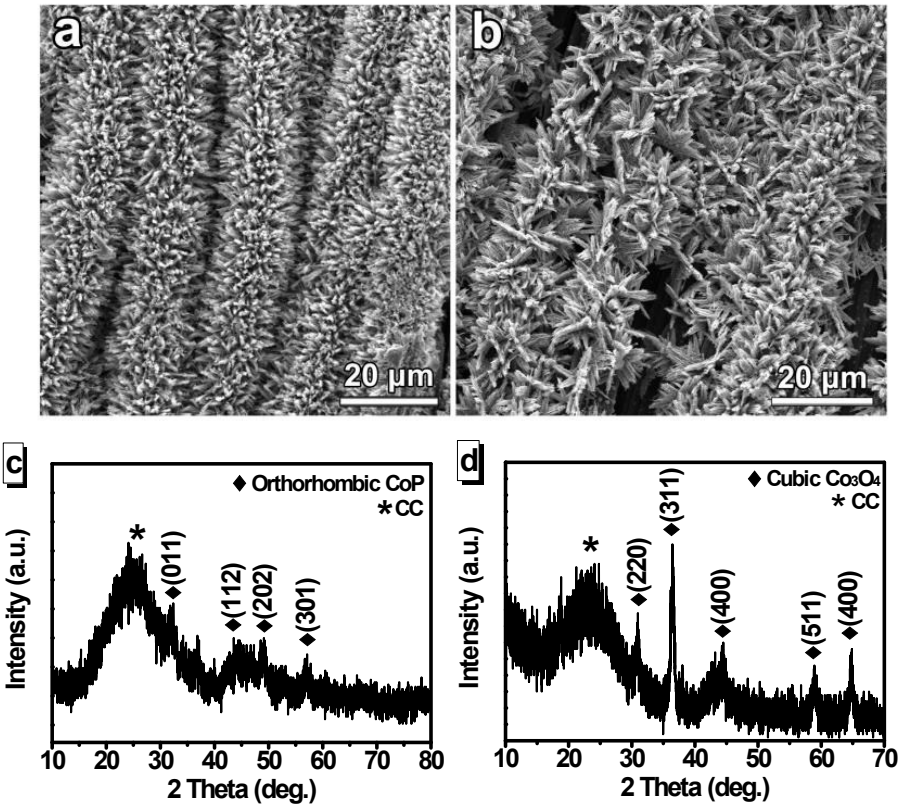

Fig. S10 (a-b) SEM images of CoP NWs/CC and Co_3O_4 NWs/CC after 6 successive electrolysis cycles. (c-d) XRD patterns of CoP NWs/CC and Co_3O_4 NWs/CC after 6 successive electrolysis cycles. The peaks marked with asterisks at ~24.5° came from CC.

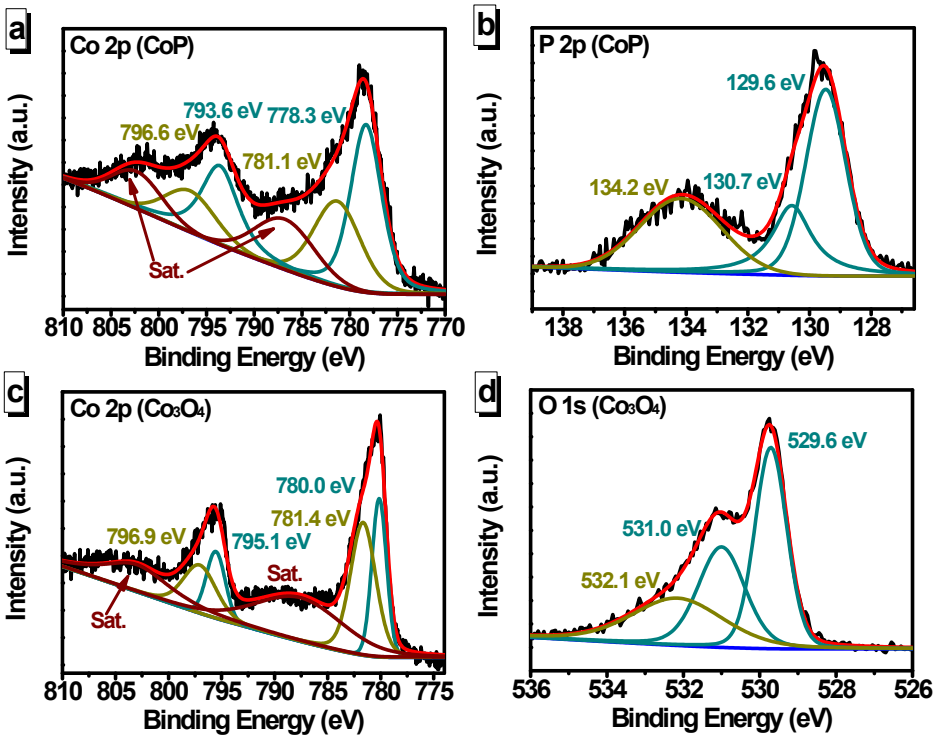

Fig. S11 High-resolution XPS spectra of (a) Co 2p and (b) P 2p for CoP. High-resolution XPS spectra of (c) Co 2p and (d) O 1s for Co_3O_4 after 6 successive electrolysis cycles.

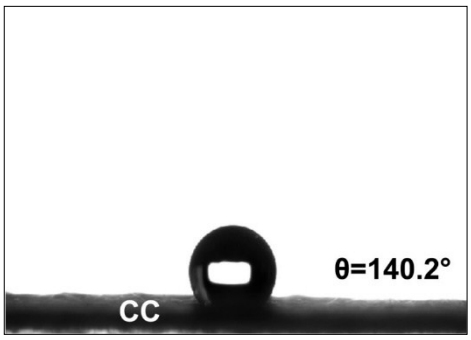

Fig. S12 Wettability test of the bare CC without treatment with contact angle of about 140.2 °, showing its very poor hydrophilicity.

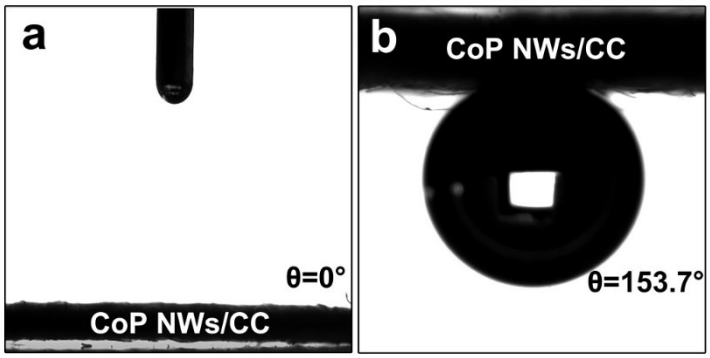

Fig. S13 Wettability tests of the CoP NWs/CC to TCS solution. (a) Liquid contact angle of ~0°, suggesting the surface of CoP NWs/CC was superhydrophilic. (b) Bubble contact angle of ~153.7°. As the bubble contact is larger than 150°, the surface of CoP NWs/CC is considered to be "superaerophobic".[S22, S23]

Table S3 Electrolysis time and corresponding peak area of the triclosan degradation intermediates by Chronopotentiometry at 10 mA cm^{-2}.

Identified intermediate compounds	Electrolysis time (min)	Peak area	Retention time (min)	Molecular weight (g/moL)
phenol	0	11.3	2.1	94.111
	15	21.5		
	30	45.8		
	45	90.3		
	60	163.2		
	90	148.9		
	120	79.5		
1,2-dihydroxybenzene	0	9.6	2.5	110.11
	15	15.6		
	30	23.6		
	45	48.9		
	60	31.2		
	90	12.4		
	120	0		
2-phenoxyphenol	0	12.5	3.0	186.22
	15	50.6		
	30	39.8		
	45	10.3		
	60	11.6		
	90	9.5		
	120	0		
triclosan	0	2542	5.2	289.54
	15	1727		
	30	1012		
	45	340		
	60	125		
	90	0		
	120	0		

References

(S1) H. Yang, Y. Zhang, F. Hu and Q. Wang, *Nano Lett.*, 2015, **15**, 7616-7620.

(S2) L. Cui, D. Liu, S. Hao, F. Qu, G. Du, J. Liu, A. Asiri and X. Sun, *Nanoscale*, 2017, **9**, 3752-3756.

(S3) H. Li, X. Qian, C. Xu, S. Huang, C. Zhu, X. Jiang, L. Shao and L. Hou, *ACS Appl. Mater.*

Inter., 2017, **9**, 28394-28405.
(S4) C. Dai, X. Tian, Y. Nie, C. Tian, C. Yang, Z. Zhou, Y. Li and X. Gao, *Chem. Eng. J.,* 2017, **321**, 105-112.
(S5) Z. Pu, I, S. Amiinu, C. Zhang, M. Wang, Z. Kou and S. Mu, *Nanoscale,* 2017, **9**, 3555-3560.
(S6) L. Han, T. Yu, W. Lei, W. Liu, K. Feng, Y. Ding, G. Jiang, P. Xu and Z. Chen, *J. Mater. Chem. A*, 2017, **5**, 16568-16572.
(S7) J. Zhang, X. Liang, X. Wang and Z. Zhuang, *Mater. Lett.*, 2017, **202**, 146-149.
(S8) M. Zhuang, X. Ou, Y. Dou, L. Zhang, Q. Zhang, R. Wu, Y. Ding, M. Shao and Z. Luo, *Nano Lett*., 2016, **16**, 4691-4698.
(S9) H. Wang, S. Min, Q. Wang, D. Li, G. Casillas, C. Ma, Y. Li, Z. Liu, L. J. Li, J. Yuan, M. Antonietti and T. Wu, *ACS Nano*, 2017, **11**, 4358-4364.
(S10) K. Li, J. Zhang, R. Wu, Y. Yu, and B. Zhang, *Adv. Sci.*, 2016, **3**, 1500426.
(S11) L. Zhang, L. Xie, M. Ma, F. Qu, G. Du, A. M. Asiri, L. Chen and X. Sun, *Catal. Sci. Technol.*, 2017, **7**, 2689-2694.
(S12) L. Feng, M. Fan, Y. Wu, Y. Liu, G. Li, H. Chen, W. Chen, D. Wang and X. Zou, *J. Mater. Chem. A*, 2016, **4**, 6860-6867.
(S13) A. Irshad, N. Munichandraiah, *ACS Appl. Mater. Inter.*, 2017, **9**, 19746-19755.
(S14) S. Gupta, N. Patel, A. Miotello and D. Kothari, *J. Power Sources*, 2015, **279**, 620-625.
(S15) A. Aijaz, J. Masa, C. Rçsler, W. Xia, P. Weide, R. A. Fischer, W. Schuhmann and M. Muhler, *ChemElectroChem*, 2017, **4**, 188-193.
(S16) X. Sun, Q. Shao, Y. Pi, J. Guo and X. Huang, *J. Mater. Chem. A*, 2017, **5**, 7769-7775.
(S17) N. Xu, G. Cao, Z. Chen, Q. Kang, H. Da and P. Wang, *J. Mater. Chem. A*, 2017, **5**, 12379-12384.
(S18) J. Jiang, Q. Liu, C. Zeng and L. Ai, *J. Mater. Chem. A*, 2017, **5**, 16929-16935.
(S19) T. Tang, W. Jiang, S. Niu, N. Liu, H. Luo, Y. Chen, S. Jin, F. Gao, L. Wan, and J. Hu, *J. Am. Chem. Soc*., 2017, **139**, 8320-8328.
(S20) W. Gao, M. Yana, H. Y. Cheung, Z. Xia, X. Zhou, Y. Qin, C. Y. Wong, J. C. Hob, C. Chang and Y. Qu, *Nano Energy*, 2017, **38**, 290-296.
(S21) P. Ganesan, A. Sivanantham and S. Shanmugam, *ACS Appl. Mater. Inter*., 2017, **9**, 12416-12426.
(S22) J. A. Barrios, A.Cano, J. E. Becerril and B. Jiménez, *J. Electroanal. Chem.,* 2016,**776**, 148-151.
(S23) D. Maharana, J. Niu, N. N. Rao, Z. Xu and J. Shi, *CLEAN-Soil, Air, Water.*, 2015, **43**, 958-966.
(S24) S. Yuan, N. Gou, A. N. Alshawabkeh and A. Z. Gu, *Chemosphere*., 2013, **93**, 2796-2804.
(S25) C. Sáez, M. J. M. Vidales, P. Cañizares and S. Cotillas, *Chem. Eng. Trans*., 2014, **41**, 103-108.
(S26) I. Sirés, N. Oturan, M. A. Oturan, R. M. Rodríguez, J. A. Garrido and E. Brillas, *Electrochim.Acta*., 2007, **52**, 5493-5503.