Supporting Information

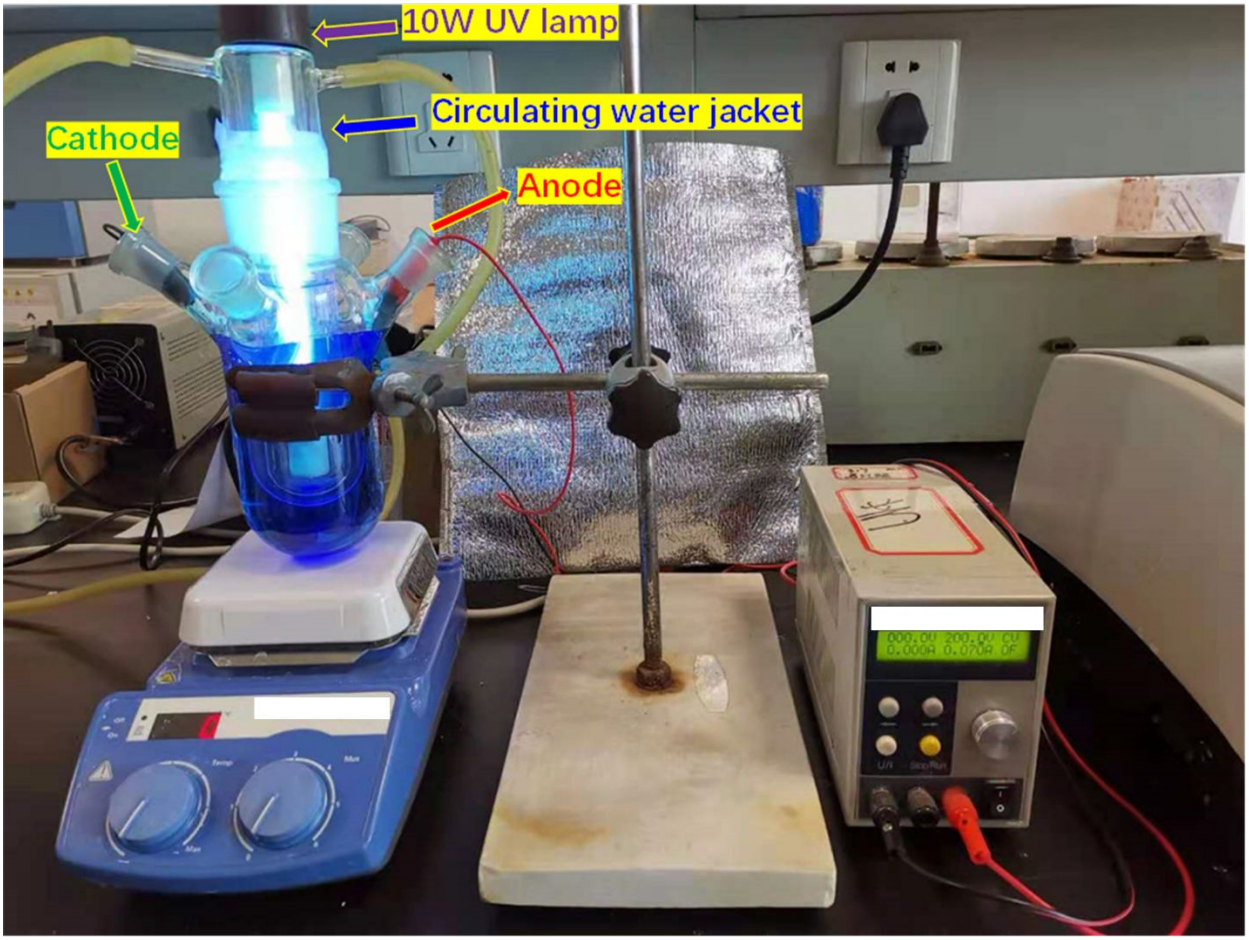
Engineering cationic sulfur-doped Co_3O_4 architectures with exposing high-reactive (112) facets for PEC water purification

Yanwei D[1]i, Chun Ma[1], Yinghuan Fu[1], Xiaoli Dong[1], Xinghui Liu[2*], Hongchao Ma[1*]

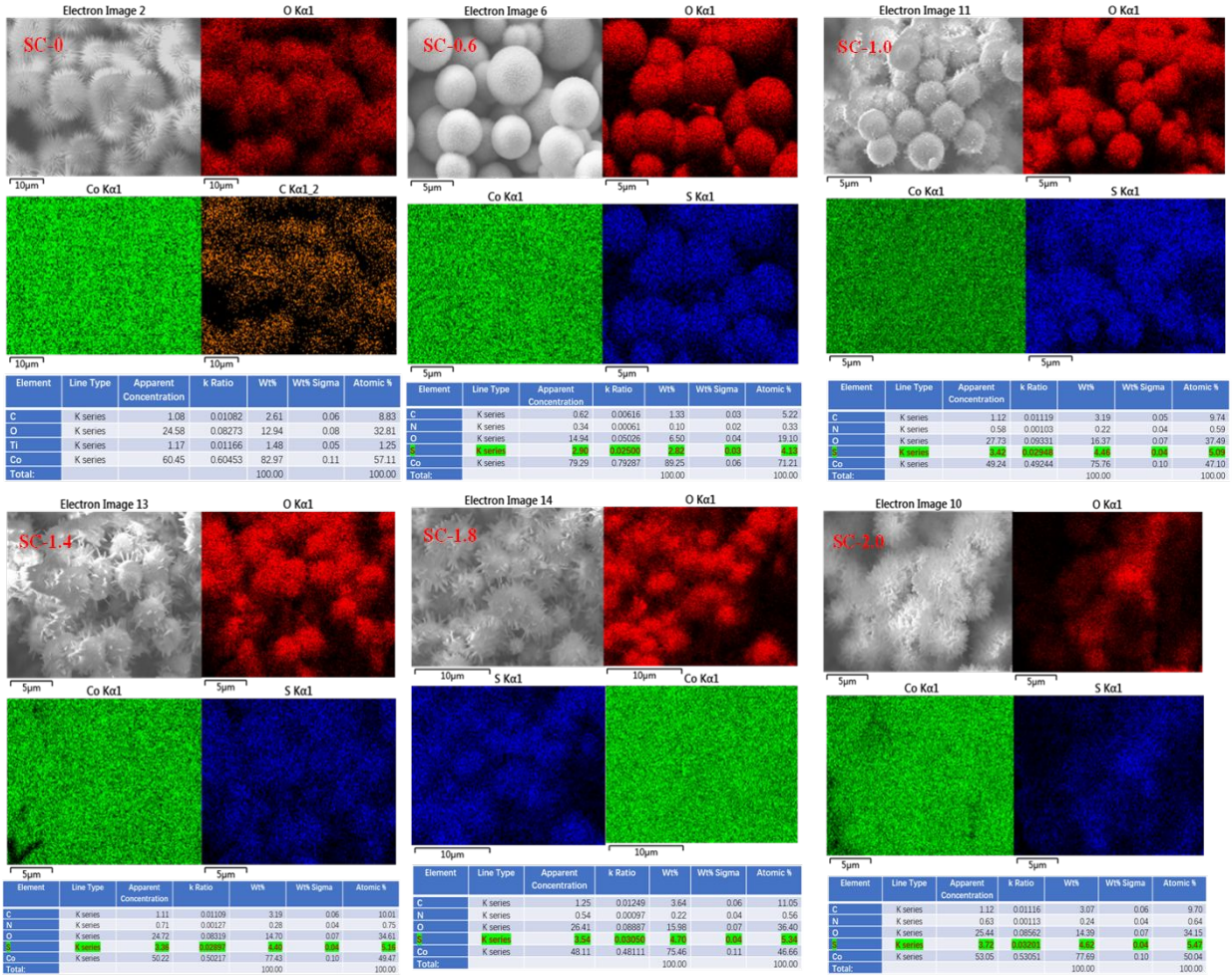
1 School of Light Industry and Chemical Engineering, Dalian Polytechnic University, Ganjingzi District, Dalian 116034, P.R. China

2 Department of Chemistry, Sungkyunkwan University (SKKU), Jangan-Gu, Suwon 16419, Republic of Korea

***Corresponding Authors email:** Xinghui Liu: liuxinghui119@gmail.com; Hongchao Ma: m-h-c@sohu.com.



Scheme S1. The diagram of the reactor during the PEC process.



Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Atomic %
C	K series	1.08	0.01082	2.61	0.06	8.83
O	K series	24.58	0.08273	12.94	0.08	32.81
Ti	K series	1.17	0.01166	1.48	0.05	1.25
Co	K series	60.45	0.60453	82.97	0.11	57.11
Total:				100.00		100.00

Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Atomic %
C	K series	0.62	0.00616	1.33	0.03	5.22
N	K series	0.34	0.00061	0.10	0.02	0.33
O	K series	14.94	0.05026	6.50	0.04	19.10
S	K series	2.90	0.02500	2.82	0.03	4.13
Co	K series	79.29	0.79287	89.25	0.06	71.21
Total:				100.00		100.00

Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Atomic %
C	K series	1.12	0.01119	3.19	0.05	9.74
N	K series	0.58	0.00103	0.22	0.04	0.59
O	K series	27.73	0.09331	16.37	0.07	37.49
S	K series	1.42	0.02948	4.46	0.04	5.09
Co	K series	49.24	0.49244	75.76	0.10	47.10
Total:				100.00		100.00

Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Atomic %
C	K series	1.11	0.01109	3.19	0.06	10.01
N	K series	0.71	0.00127	0.28	0.04	0.75
O	K series	24.72	0.08319	14.70	0.07	34.61
S	K series	2.38	0.02887	4.48	0.04	5.48
Co	K series	50.22	0.50217	77.43	0.10	49.47
Total:				100.00		100.00

Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Atomic %
C	K series	1.25	0.01249	3.64	0.06	11.05
N	K series	0.54	0.00097	0.22	0.04	0.56
O	K series	26.41	0.08887	15.98	0.07	36.40
S	K series	3.54	0.03050	4.70	0.04	5.34
Co	K series	48.11	0.48111	75.46	0.11	46.66
Total:				100.00		100.00

Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Atomic %
C	K series	1.12	0.01116	3.07	0.06	9.70
N	K series	0.63	0.00113	0.24	0.04	0.64
O	K series	25.44	0.08562	14.39	0.07	34.15
S	K series	2.72	0.03203	4.48	0.04	5.47
Co	K series	53.05	0.53051	77.69	0.10	50.04
Total:				100.00		100.00

Figure S1. the EDS mapping analysis of Ti/Co_3O_4 samples with or without L-cysteine modification.

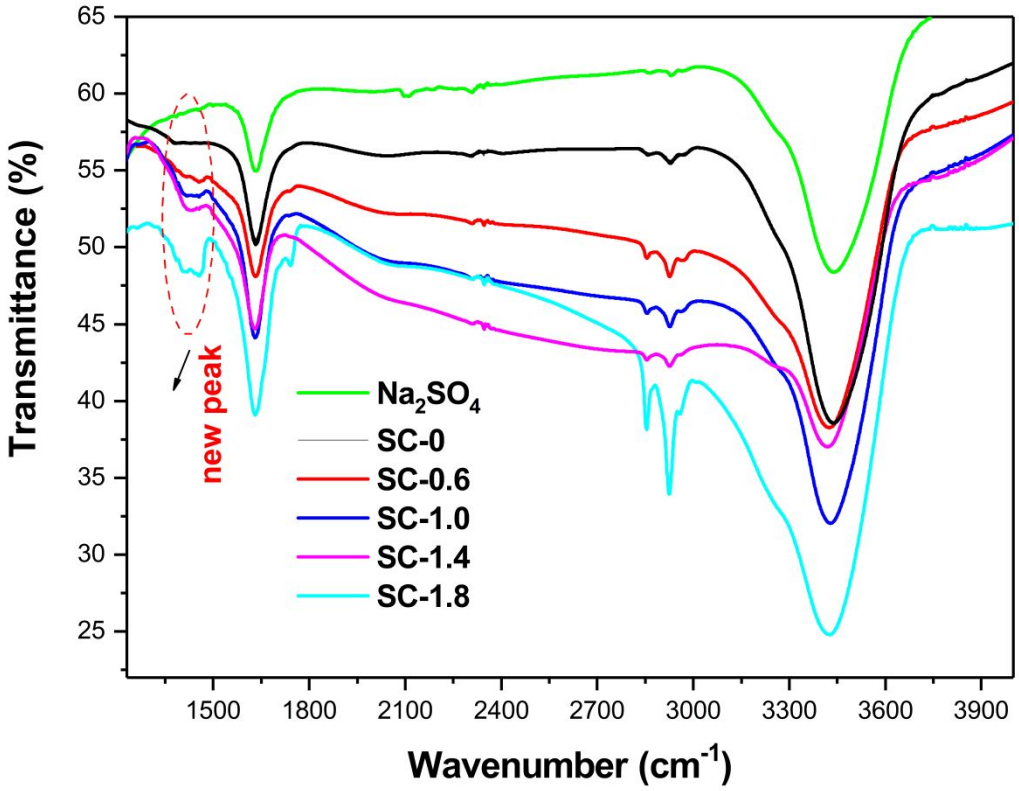


Figure.S2. FT-IR spectra of Ti/Co_3O_4 reference and L-cysteine modified Ti/Co_3O_4.

Figure. S2 shows the results of FT-IR analysis. It was observed that a new peak at 1420-1450 cm^{-1} was formed. The intensity of the new peak became stronger with enhancing S amount. The appearance of the peak at 1420-1450 cm^{-1} is an indicative of a new interaction of $Co–O–S^{6+}$.[1-4] To validate the XPS results, the FT-IR results also indicated that the doped S^{6+} was incorporated into Co_3O_4 lattice by replacing the Co ion after heat treatment, which is the evidence for proving the forming of the Co-O-S bonds.

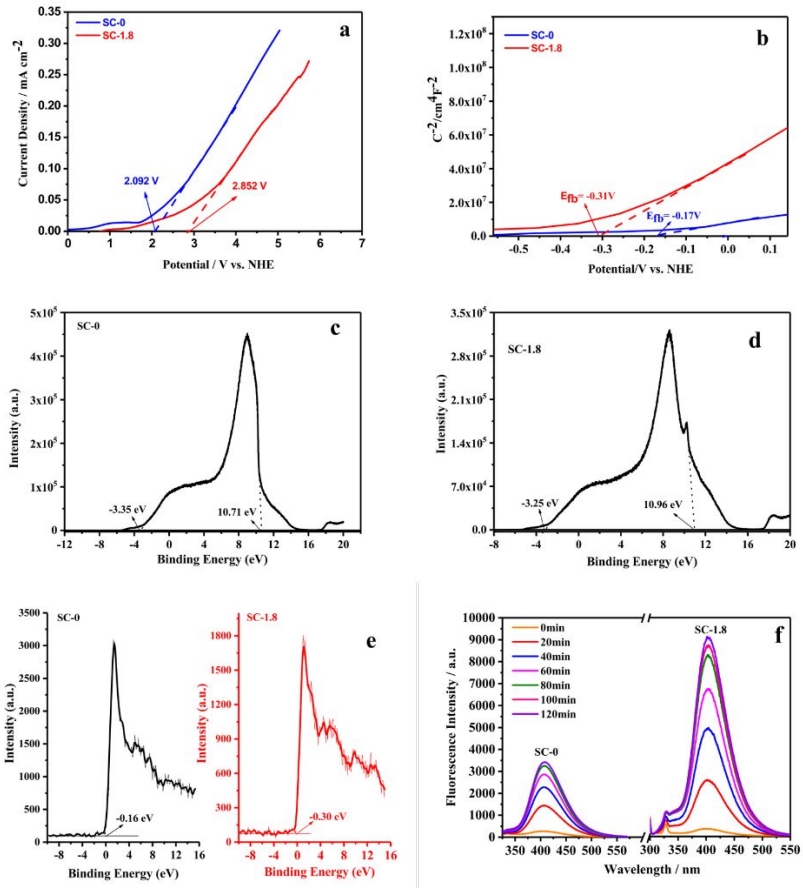


Figure S3. (a) Steady-state polarization curves of Ti/Co_3O_4-reference and L-cysteine-modified Ti/Co_3O_4 electrode in a 0.1 mol L^{-1} Na_2SO_4 solution (the potential was swept from 0.0 to 6.0 V vs. SCE); (b) Mot-Schottky plots of Ti/Co_3O_4-reference and L-cysteine-modified Ti/Co_3O_4 electrode; (c) UPS spectra (under -3.0 V bias) of the Ti/Co_3O_4-reference; (d) UPS spectra (under -3.0 V bias) of the L-cysteine modified Ti/Co_3O_4; (e) VB-XPS spectra of the Ti/Co_3O_4-reference and L-cysteine modified Ti/Co_3O_4; (f) Fluorescence spectra of Ti/Co_3O_4-reference and L-cysteine-modified Ti/Co_3O_4 electrode during the photoelectrolysis of benzoic acid (200 mg L^{-1} benzoic acid and 0.5 mol L^{-1} Na_2SO_4 as a supporting electrolyte).

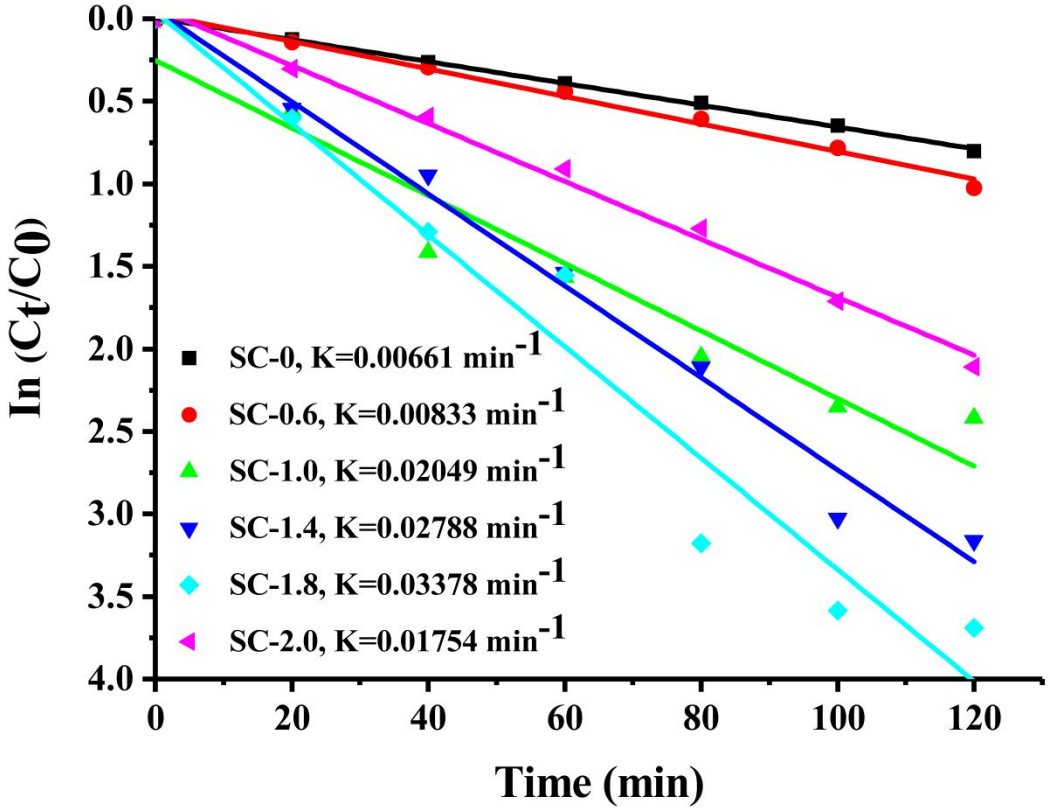


Figure S4. Kinetic analysis of the degradation of KN-R for the current electrodes.

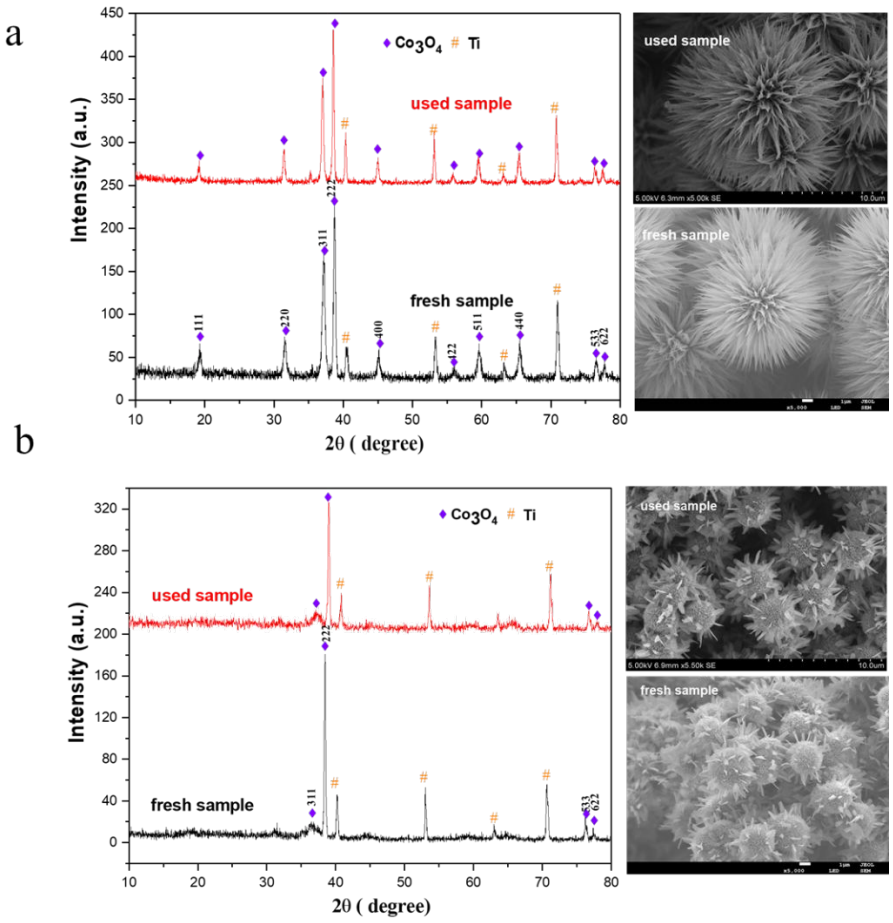
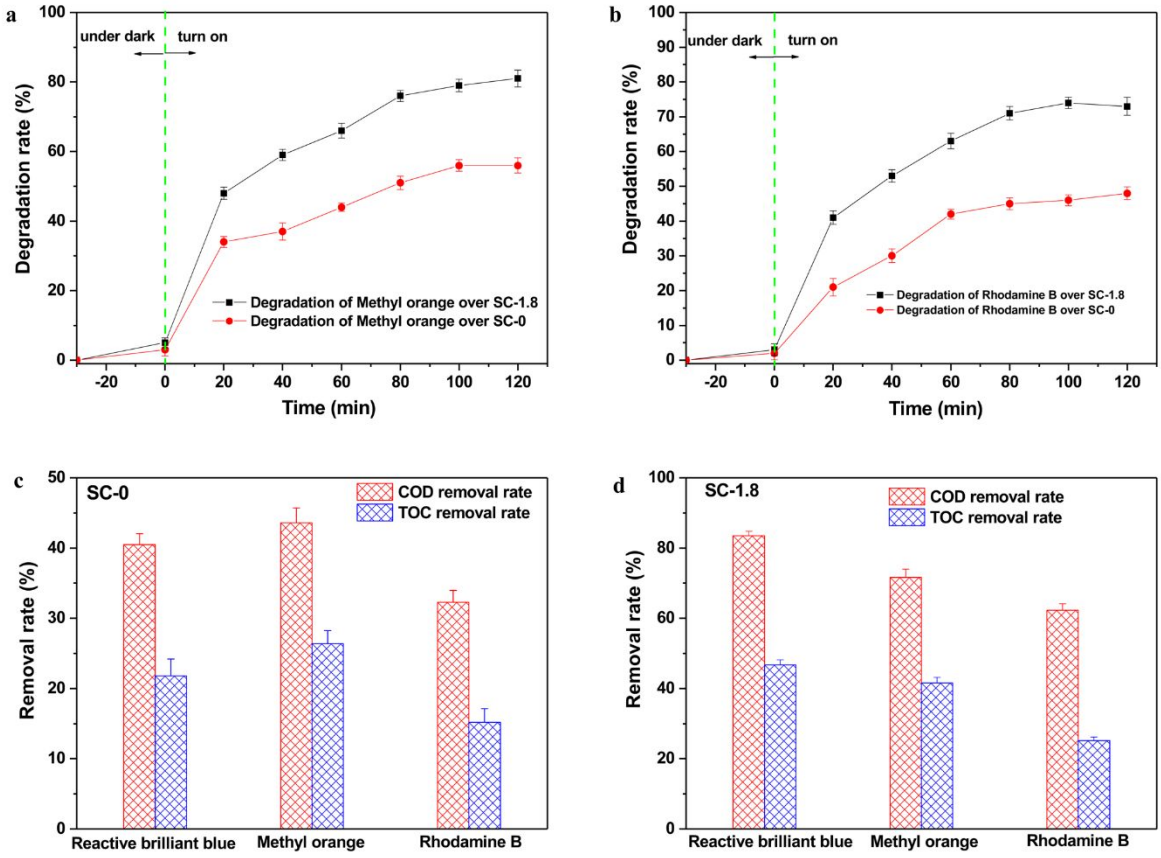
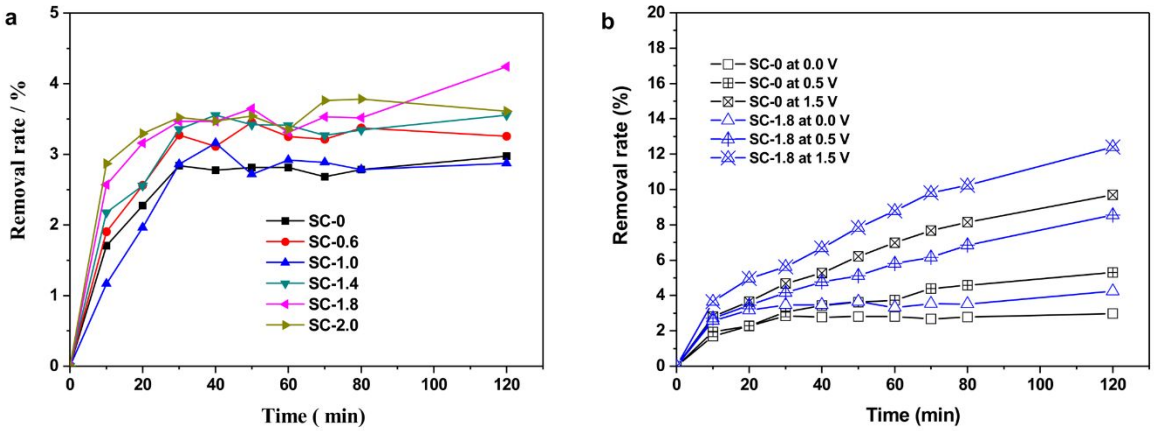


Figure S5. The XRD and SEM characterization for (a) Ti/Co3O4 samples and (b) L-cysteine modified Ti/Co3O4 samples before/after usage.



Figures S6. The analysis of the decolorization, COD and TOC for the degradation process of different pollutants over (a and c) for SC-0 and (b and d) for SC-1.8.



Figures S7. (a) absorption and (b) electrosorption removal of various electrodes.

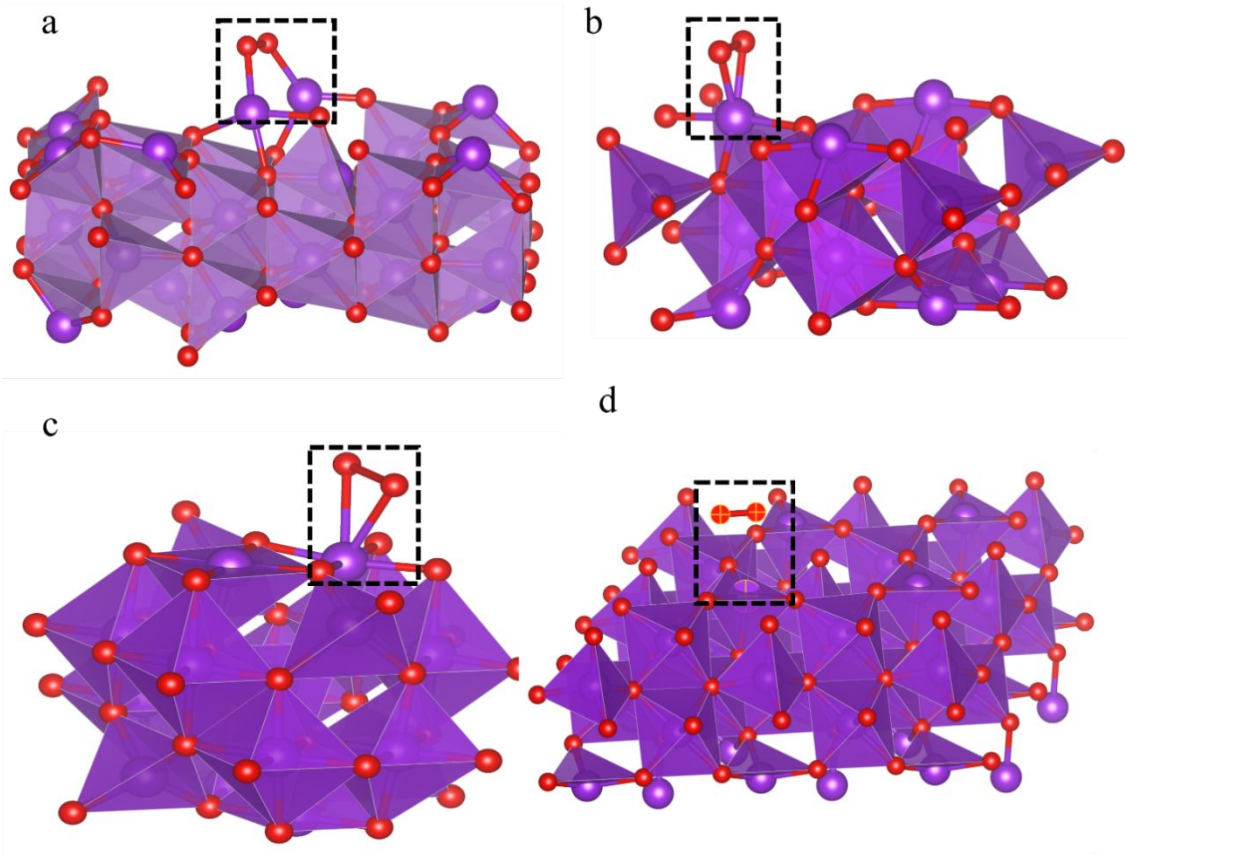


Figure S8. The DFT calculation-simulated interaction of $\cdot O_2^-$ with Co site on the different facets: (a) (112) facet, (b) (110) facet, (c) (001), (d) (111) facet.

Reference:

1. Liu, S.; Chen, X., A visible light response TiO2 photocatalyst realized by cationic S-doping and its application for phenol degradation. *J. Hazard. Mater.* **2008,** *152* (1), 48-55.
2. Han, C.; Pelaez, M.; Likodimos, V.; Kontos, A. G.; Falaras, P.; O'Shea, K.; Dionysiou, D. D., Innovative visible light-activated sulfur doped TiO2 films for water treatment. *Appl Catal. B* **2011,** *107* (1), 77-87.
3. Chen, X.; Sun, H.; Zhang, J.; Guo, Y.; Kuo, D.-H., Cationic S-doped TiO2/SiO2 visible-light photocatalyst synthesized by co-hydrolysis method and its application for organic degradation. *J. Mol. Liq.* **2019,** *273*, 50-57.
4. Nishikiori, H.; Hayashibe, M.; Fujii, T., Visible light-photocatalytic activity of sulfate-doped titanium dioxide prepared by the Sol− Gel method. *Catalysts* **2013,** *3* (2), 363-377.