Supporting Information

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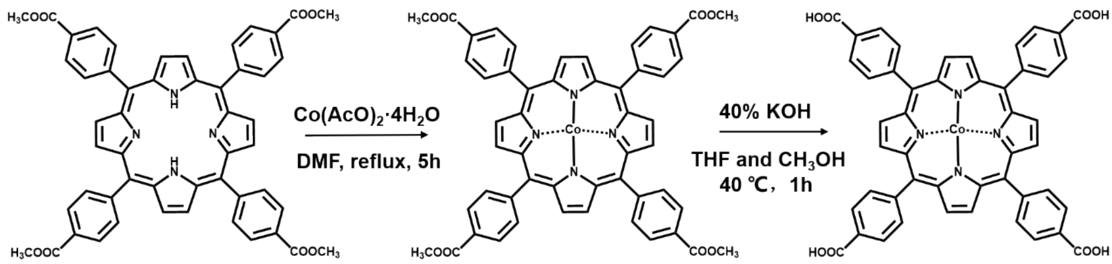
Contents

Figures



Scheme S1 The synthesis of cobalt 5, 10, 15, 20 - meso - tetra (4-carboxyphenyl) porphyrin.

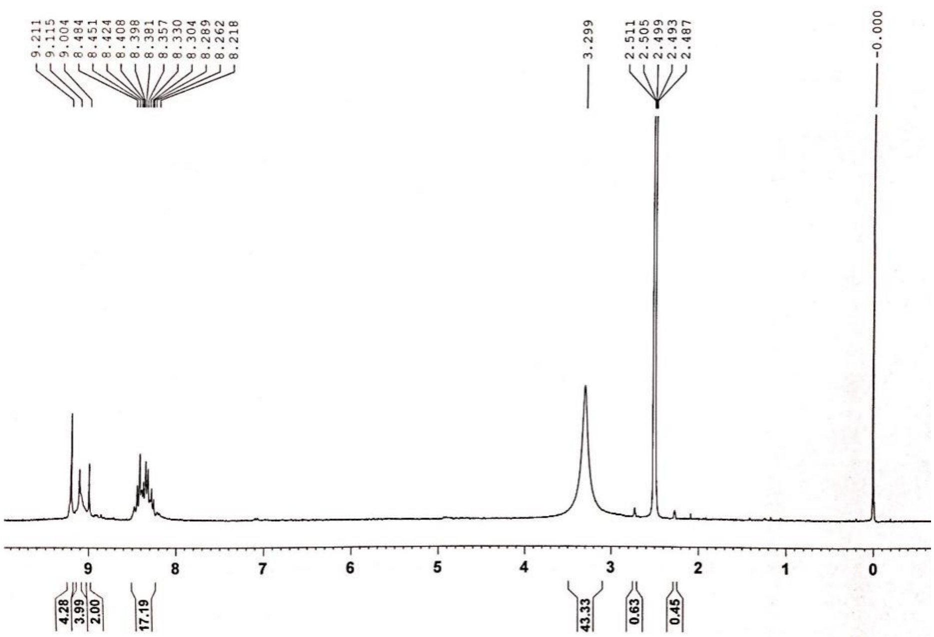


Fig. S1 1H NMR spectra of CoTCPP monomer.

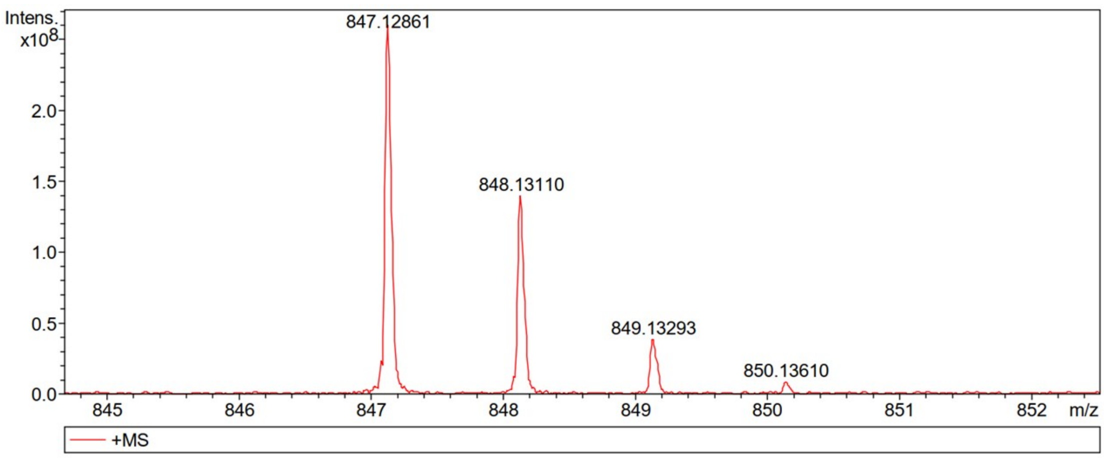


Fig. S2 HRMS spectrum of CoTCPP monomer dissolved in CH_3OH.

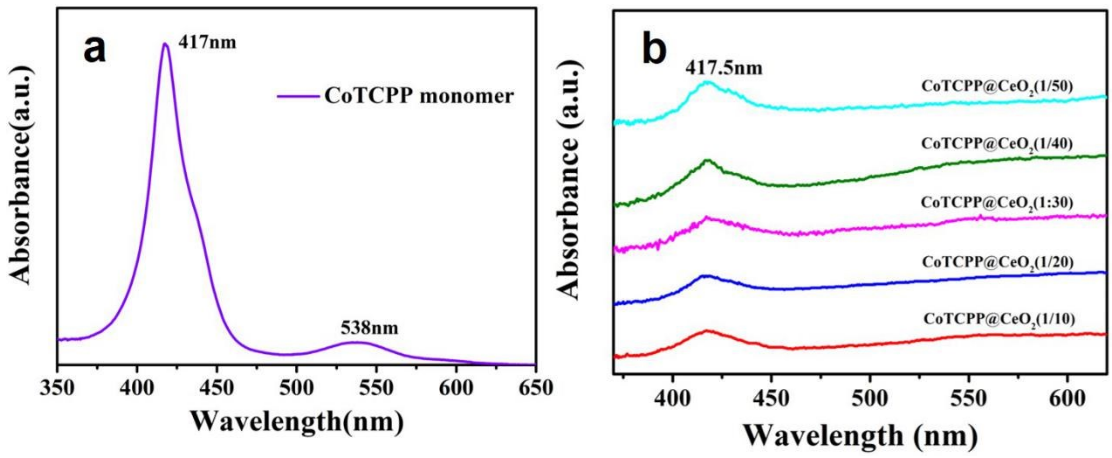


Fig. S3 Ultraviolet visible absorption spectrum of (a) CoTCPP monomer and (b) **CoTCPP@CeO$_2$**.

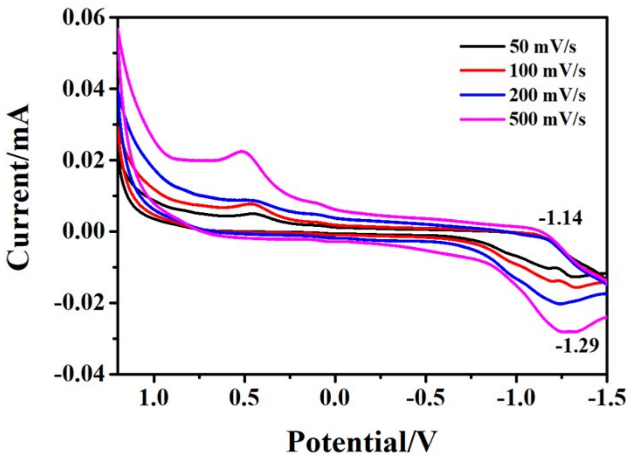


Fig. S4 Cyclic voltammetry curves of CoTCPP monomer at different sweep speeds, the samples were dissolved in DMF.

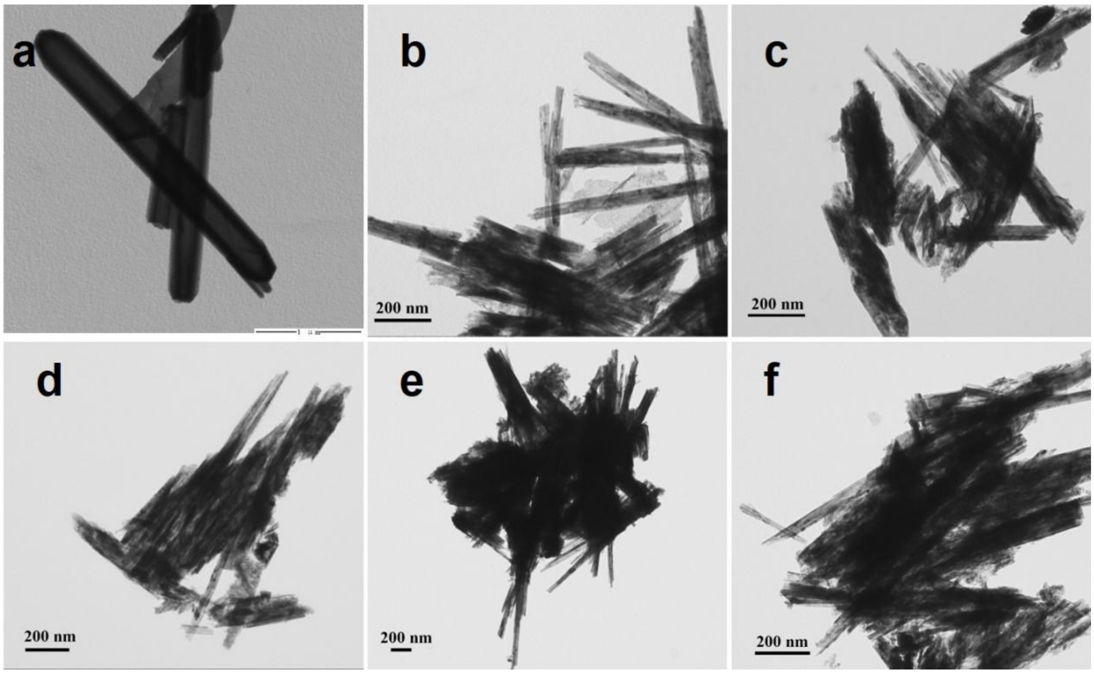


Fig. S5 TEM images of ceria hollow nanorobs (a), composite materials in different mass ratio (**CoTCPP@CeO$_2$**) (b) 1/10, (c) 1/20, (d) 1 /30, (e) 1/40, (f) 1/50, just synthesized.

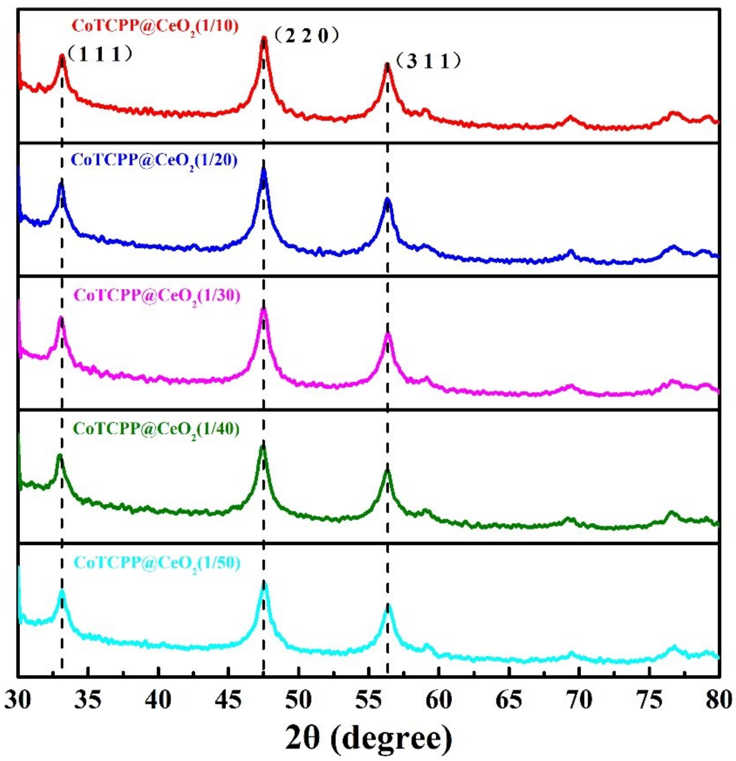


Figure S6 XRD patterns of a series of **CoTCPP@CeO$_2$**.

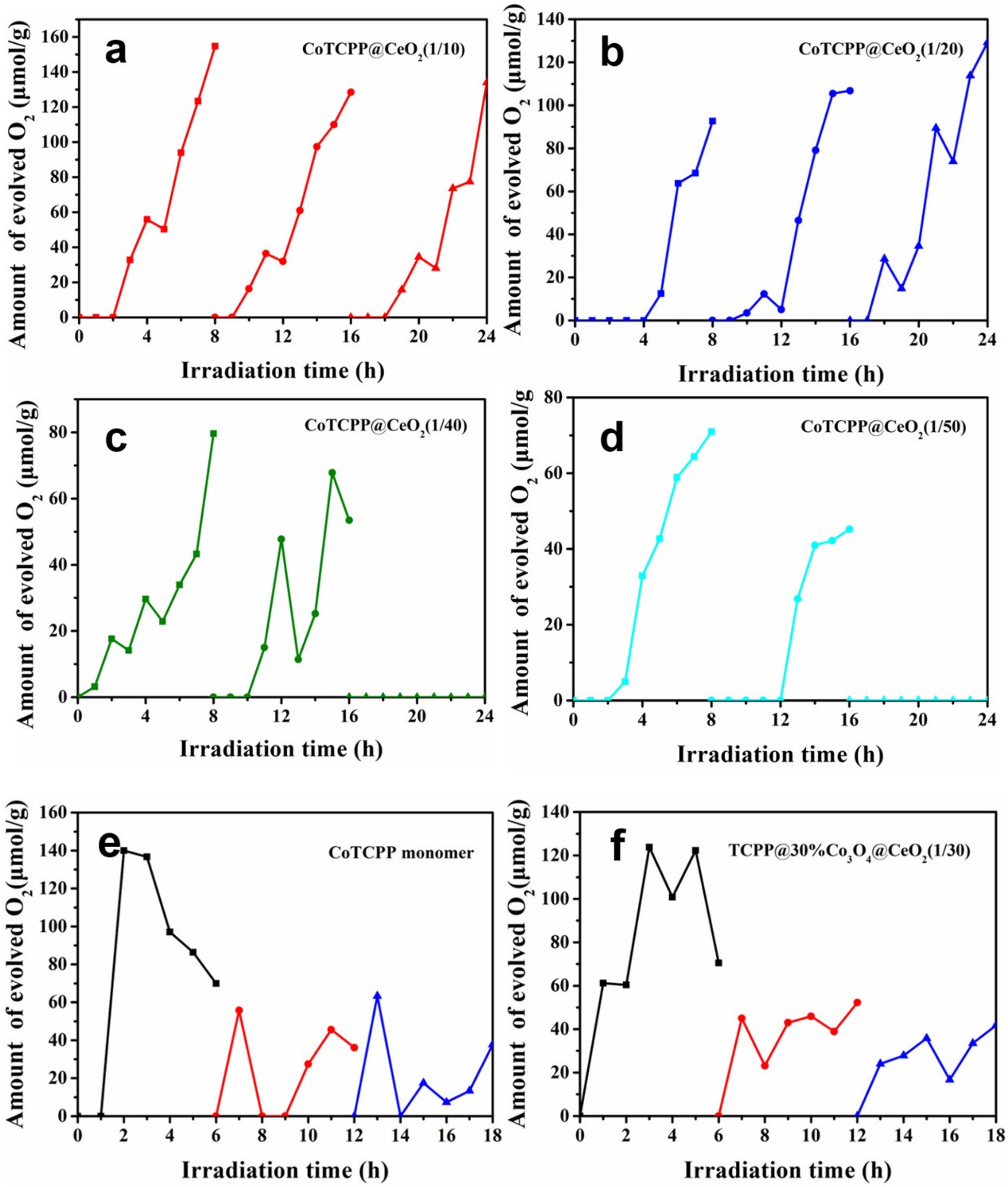


Fig. S7 Cyclic oxygen production of the (a) **CoTCPP@CeO$_2$ (1/10)**, (b) **CoTCPP@CeO$_2$ (1/20)**, (c) **CoTCPP@CeO$_2$ (1/40)**, (d) **CoTCPP@CeO$_2$ (1/50)**, (e) CoTCPP monomer and (f) TCPP@30%Co$_3$O$_4$@CeO$_2$ (1/30).

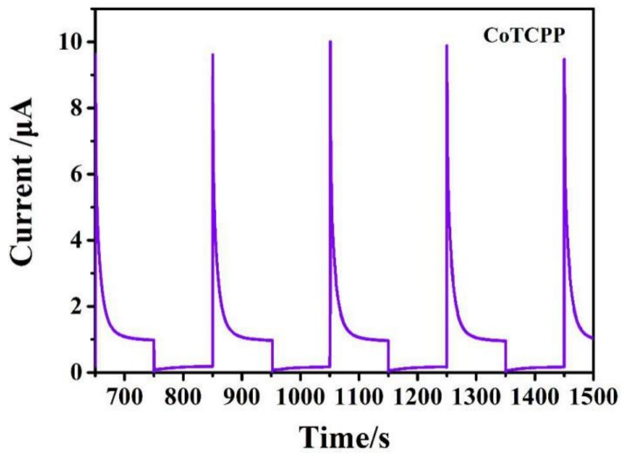


Fig. S8 Transient photocurrent response of the CoTCPP monomer.

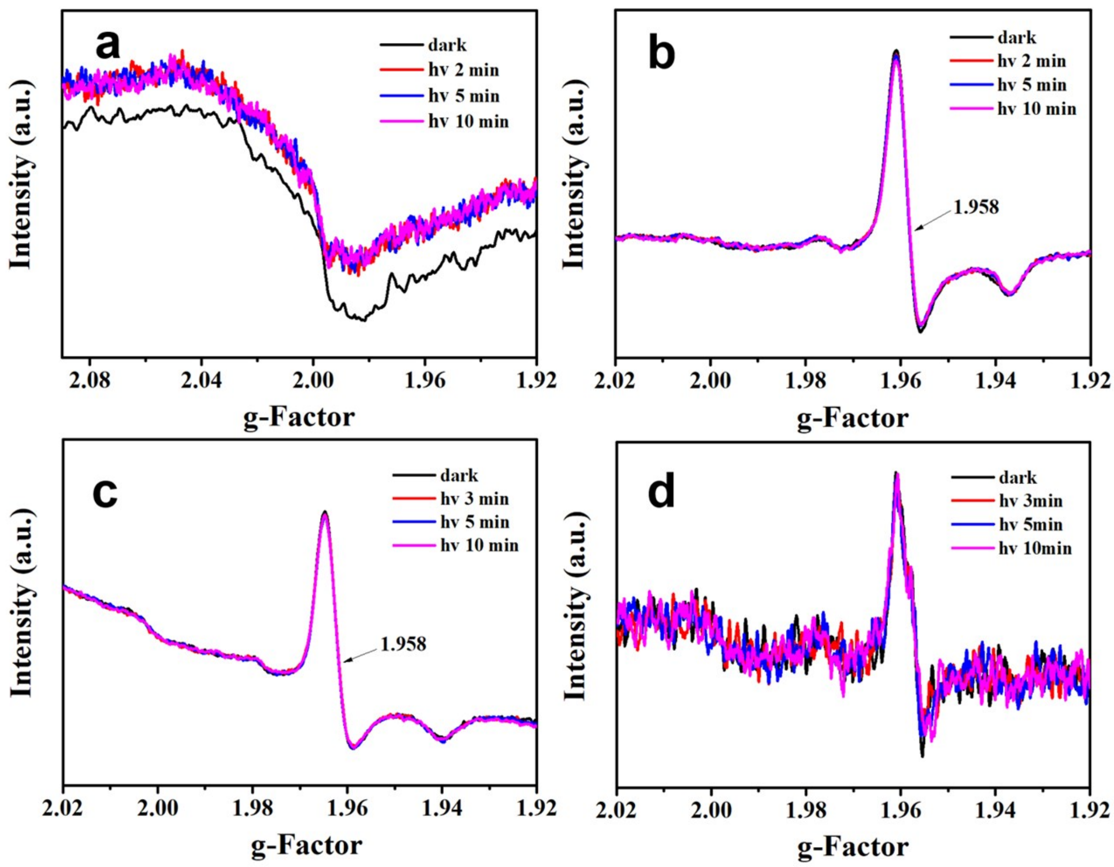
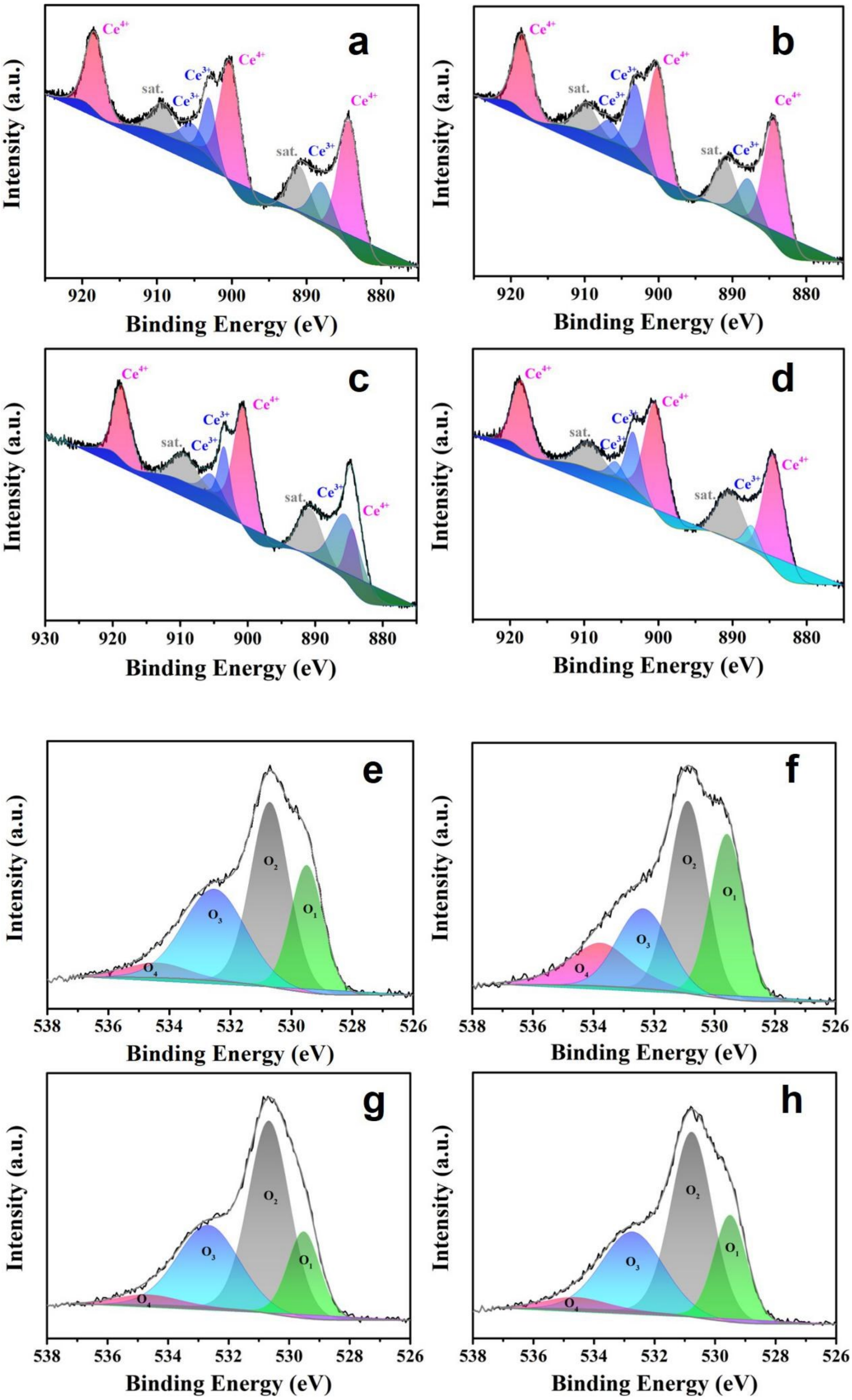


Fig. S9 EPR signal of the (a) CoTCPP monomer, (b) CeO_2, (c) TCPP@30%Co_3O_4@CeO_2 (1/30) and (d) 30%Co_3O_4@CeO_2.


a
b
c
d
e
f
g
h
Ce4+
Ce3+
sat.
O1
O2
O3
O4
Intensity (a.u.)
Binding Energy (eV)
930
920
910
900
890
880
538
536
534
532
530
528
526

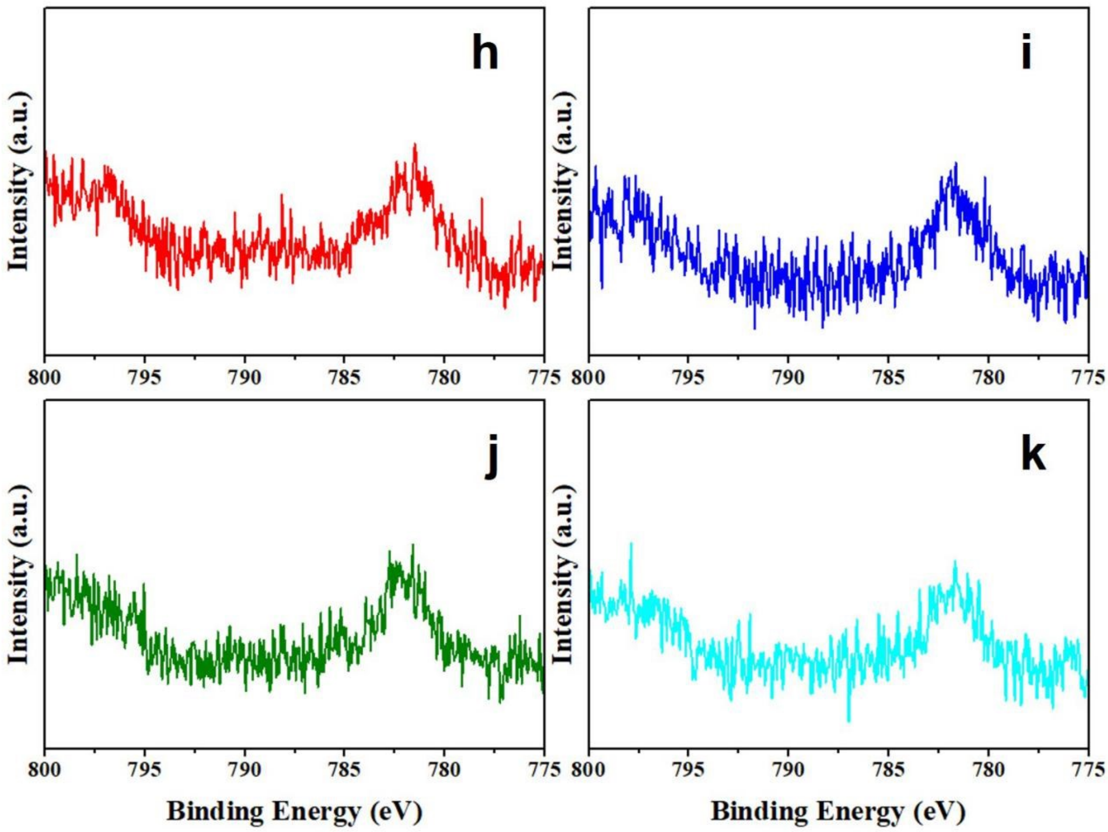


Fig. S10 Ce 3d XPS spectra (a, b, c, d), O 1s XPS spectra (e, f, g, h)and Co 2p XPS spectra (h, i, j, k)of **CoTCPP@CeO$_2$ (1/10)** (a, e, h), **CoTCPP@CeO$_2$ (1/20)** (b, f, i), **CoTCPP@CeO$_2$ (1/40)** (c, g, j) **and CoTCPP@CeO$_2$ (1/50)** (d, h, k), respectively.

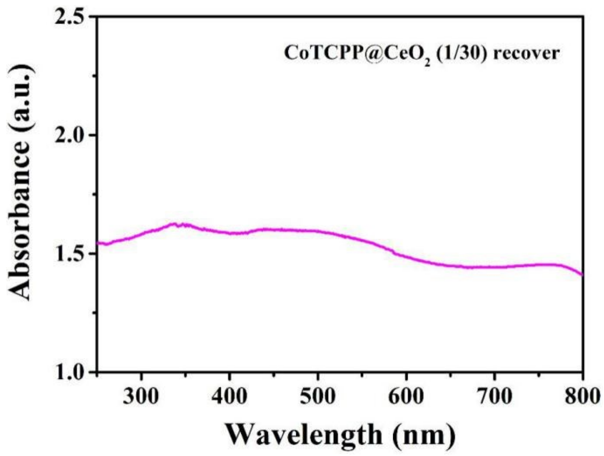


Fig. S11 Absorption spectra of the **CoTCPP@CeO$_2$ (1/30)** after the OER.

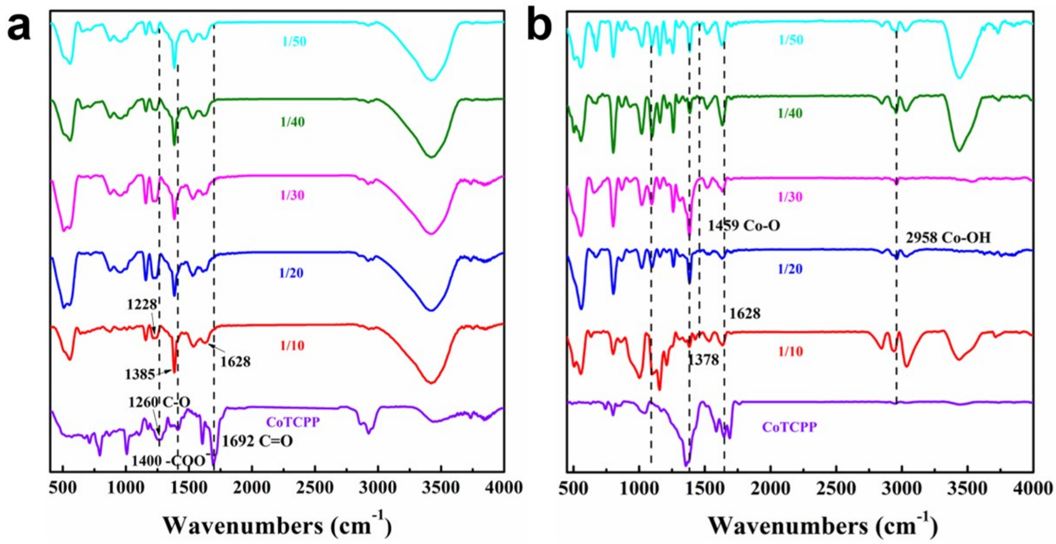


Fig. S12 Fourier transform infrared spectroscopy (FTIR) of a series of **CoTCPP@CeO$_2$**.

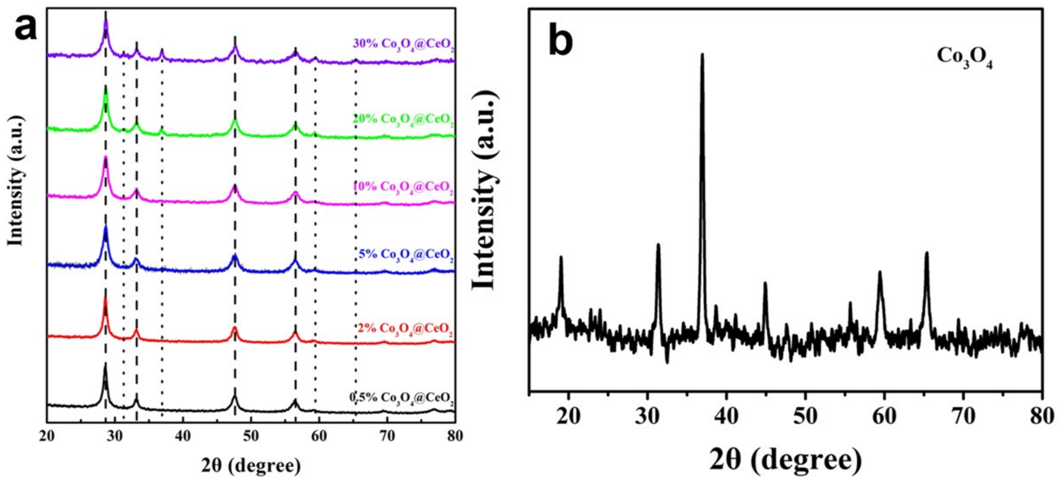


Fig. S13 XRD patterns of the Co_3O_4@CeO_2 NTs and the pure Co_3O_4. (The characteristic peaks of CeO_2 are marked by dash line and Co_3O_4 by dot line.) CeO_2（1 1 1）（2 0 0）（2 2 0）（3 1 1）; Co_3O_4（2 2 0）（3 1 1）（5 1 1）（4 4 0）

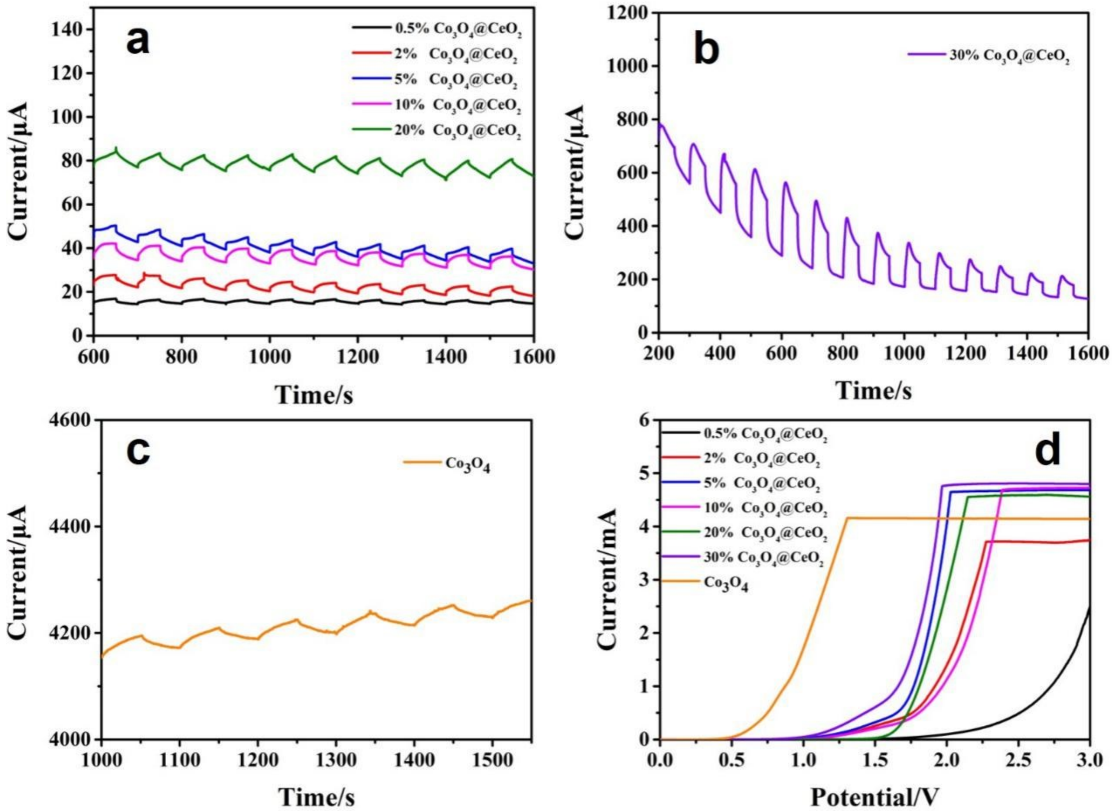


Fig. S14 (a) (b) Transient photocurrent response of the Co_3O_4@CeO_2 in different cobalt oxide content and (c) the pure Co_3O_4; (d) overpotential test of a series of Co_3O_4@CeO_2.

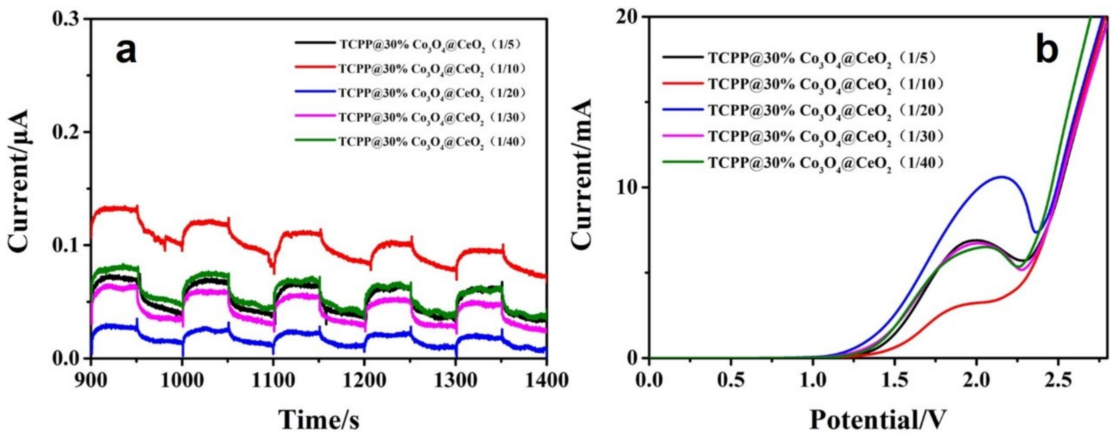


Fig. S15 (a) Transient photocurrent response of the TCPP@30%Co_3O_4@CeO_2 in different TCPP content and (d) overpotential test of a series of TCPP@30%Co_3O_4@CeO_2.

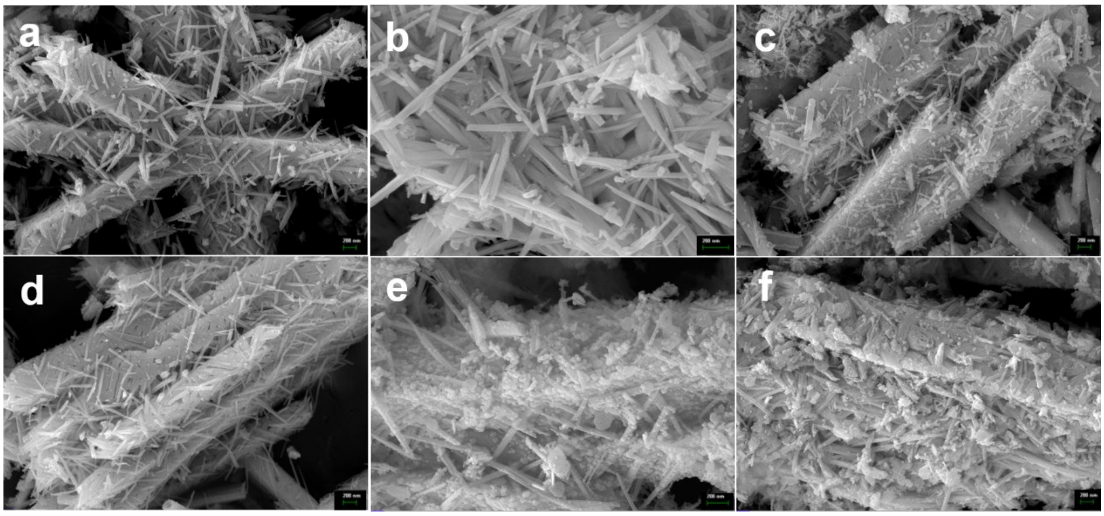


Fig. S16 SEM images of the Co_3O_4@CeO_2, composite materials with different Co_3O_4 content (a) 0.5%, (b) 10%, (c) 20%, (d) 30%, (e) 40%, (f) 50%.

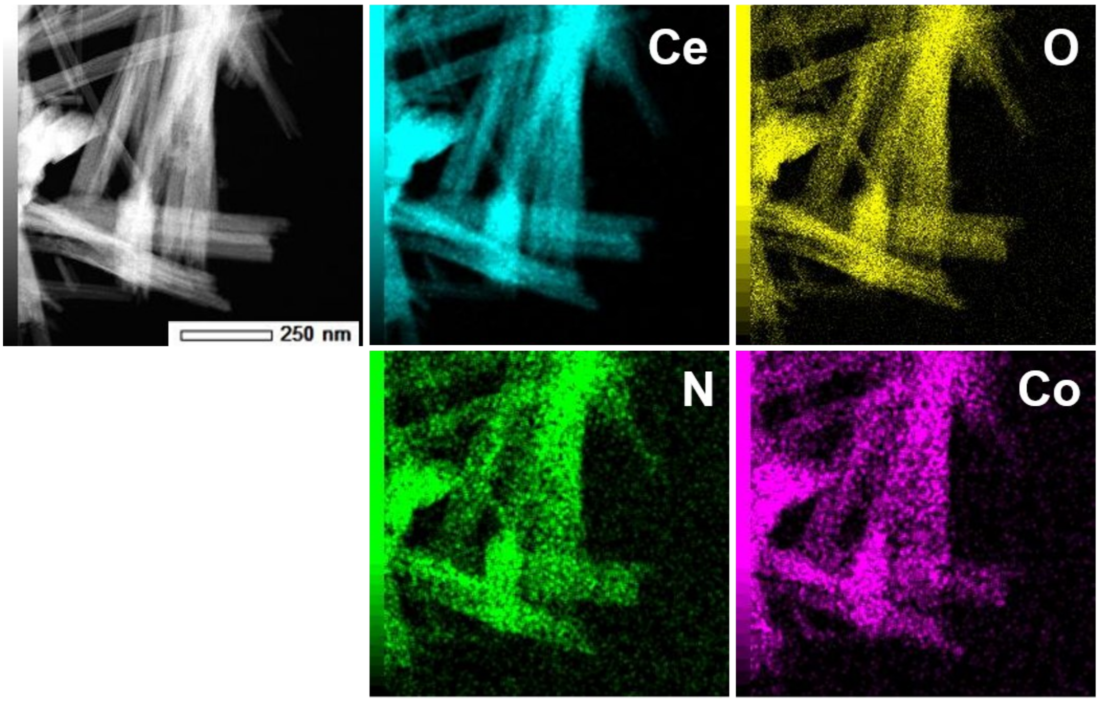


Fig. S17 TEM-EDX mapping images of the TCPP@30%Co_3O_4@CeO_2 (1/30).

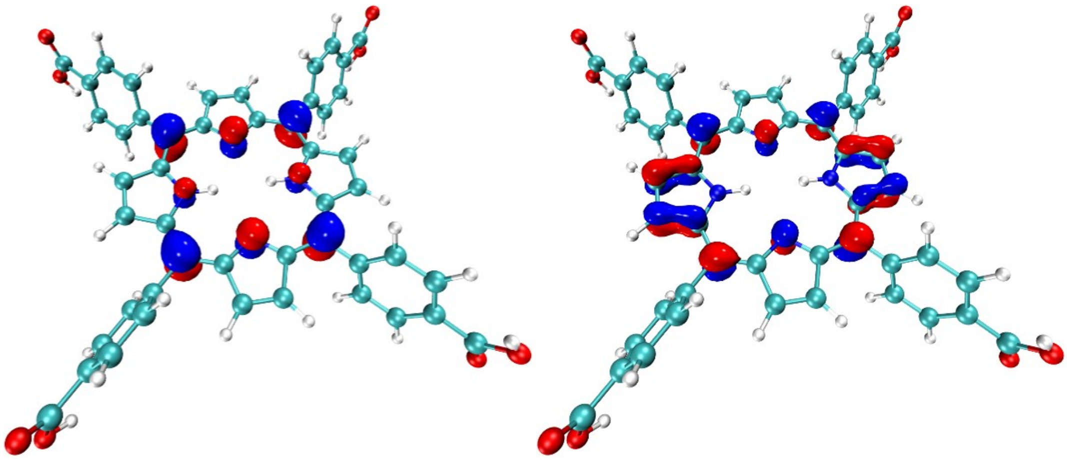


Fig. S18 Melecular orbital (MO) of the H_2TCPP, HOMO (left) and LUMO (right).

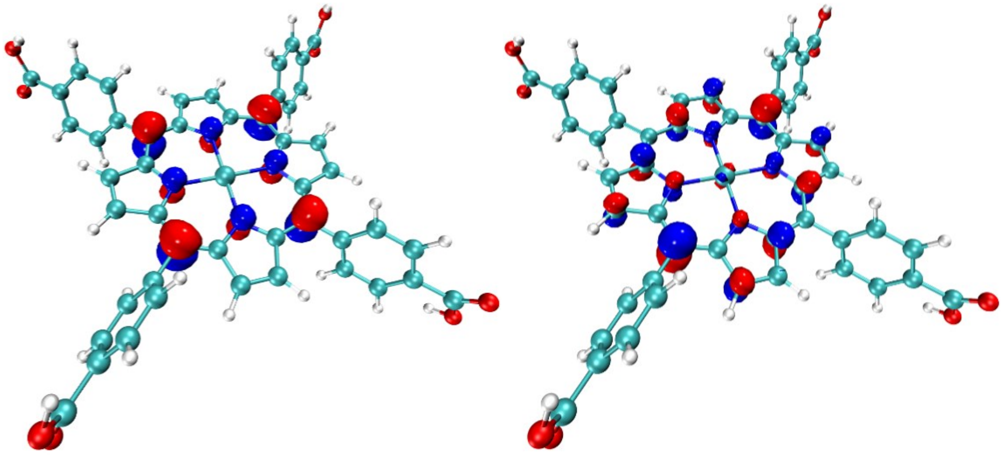


Fig. S19 MO of the CoTCPP, α HOMO (left) and α LUMO (right).

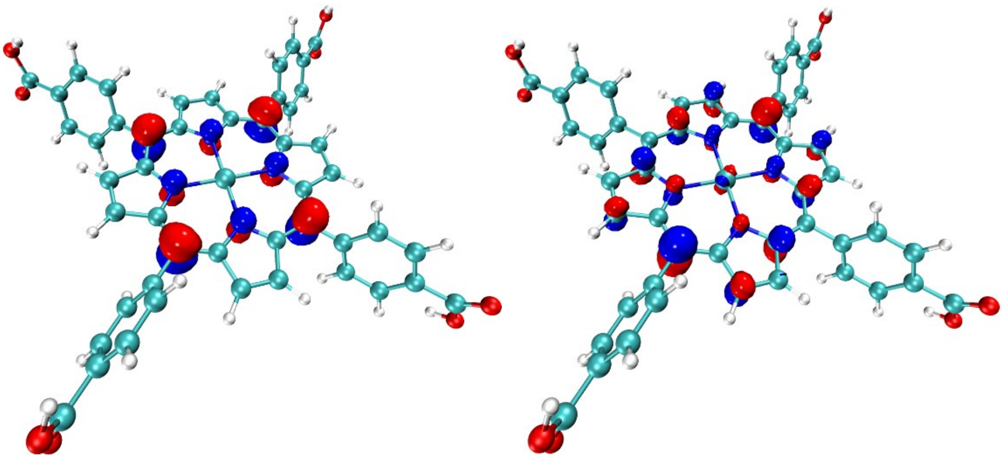


Fig. S20 MO of the CoTCPP, β HOMO (left) and β LUMO (right).

Table

	Chemical	Peak (eV)	AC%
O_1	Ce (IV)-O	529.57	27.05
O_2	Ce (III)-O	530.80	39.39
O_3	C=O	532.54	26.73
O_4	C-OH	534.14	6.83

Table S1 Fine peaks of O1s XPS before oxygen production test of the **CoTCPP@CeO2=1:30**.

	Chemical	Peak (eV)	AC%
O_1	Ce (IV)-O	529.7	38.53
O_2	Ce (III)-O	530.59	14.58
O_3	C=O	532.1	37.24
O_4	C-OH	533.33	9.65

Table S2 Fine peaks of O1s XPS after oxygen production test of the **CoTCPP@CeO2=1:30**.

	1:10	1:20	1:30	1:40	1:50
Oxygen vacancies (%)	**39.77**	**35.9**	**39.39**	**48.25**	**45.70**
Ce^{3+}(%)	**20.79**	**24.37**	**25.35**	**31.58**	**14.59**

Table S3 Oxygen vacancies percentage composition of the **CoTCPP@CeO_2**.

	HOMO	LUMO
TCPP	**-5.883938 eV**	**-3.198660 eV**
CoTCPP (α)	**-5.933958 eV**	**-3.029727 eV**
CoTCPP (β)	**-5.934171 eV**	**-3.021372 eV**

Table S4 Specific HOMO and LUMO level positions of TCPP and CoTCPP relative to vacuum levels.