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Supporting Information

Synergetic Effect of Hollowlization and Sulfonation on Improving Photocatalytic performance of Covalent Porphyrin Polymers in the reduction of CO_2

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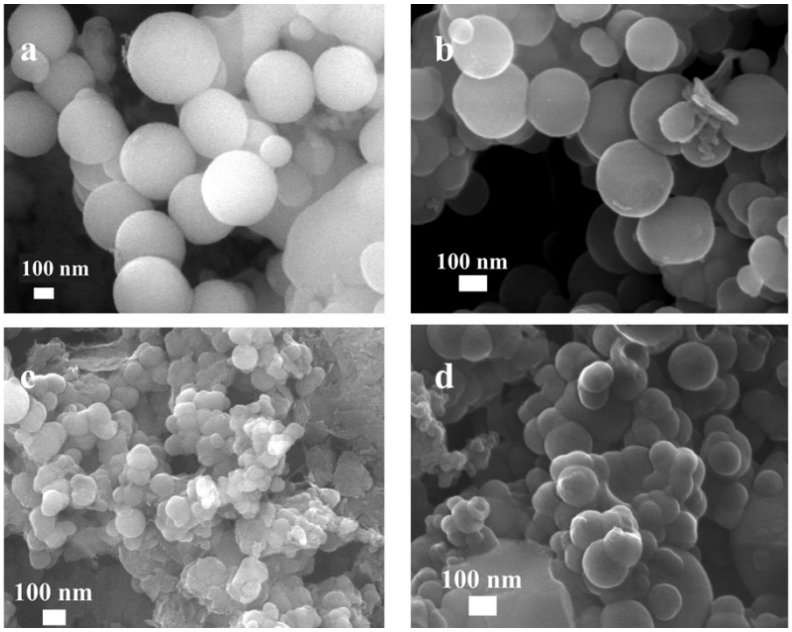


Figure S1. SEM of (a) COP-P, (b) h-COP-P, (c) s-COP-P and (d) sh-COP-P.

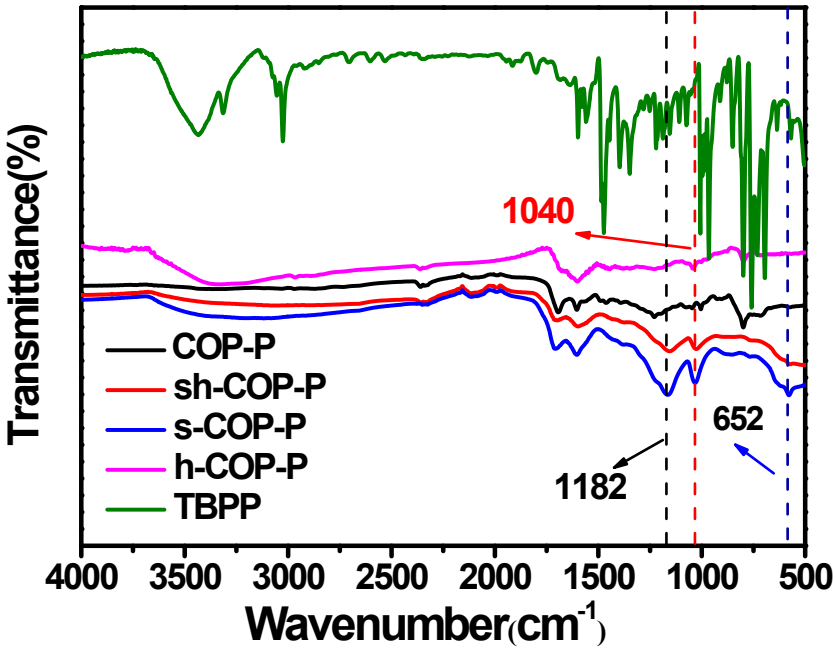


Figure S2. FT-IR spectra of TBPP, COP-P, h-COP-P, s-COP-P and sh-COP-P.

Table S1. ICP analyses of the sulphur and aluminum content for COP-P, h-COP-P, s-COP-P, and sh-COP-P.

samples	S (wt %)	Al (wt %)
COP-P	undetectable	0.153
h-COP-P	undetectable	0.036
s-COP-P	5.81	0.066
sh-COP-P	6.12	0.050

Table S2. The elemental analysis of COP-P, h-COP-P, s-COP-P, and sh-COP-P.

samples	C (atomic %)	N (atomic %)	H (atomic %)
COP-P	51.90	3.37	4.51
h-COP-P	65.64	2.97	5.27
s-COP-P	54.79	2.71	4.28
sh-COP-P	48.31	2.66	4.09

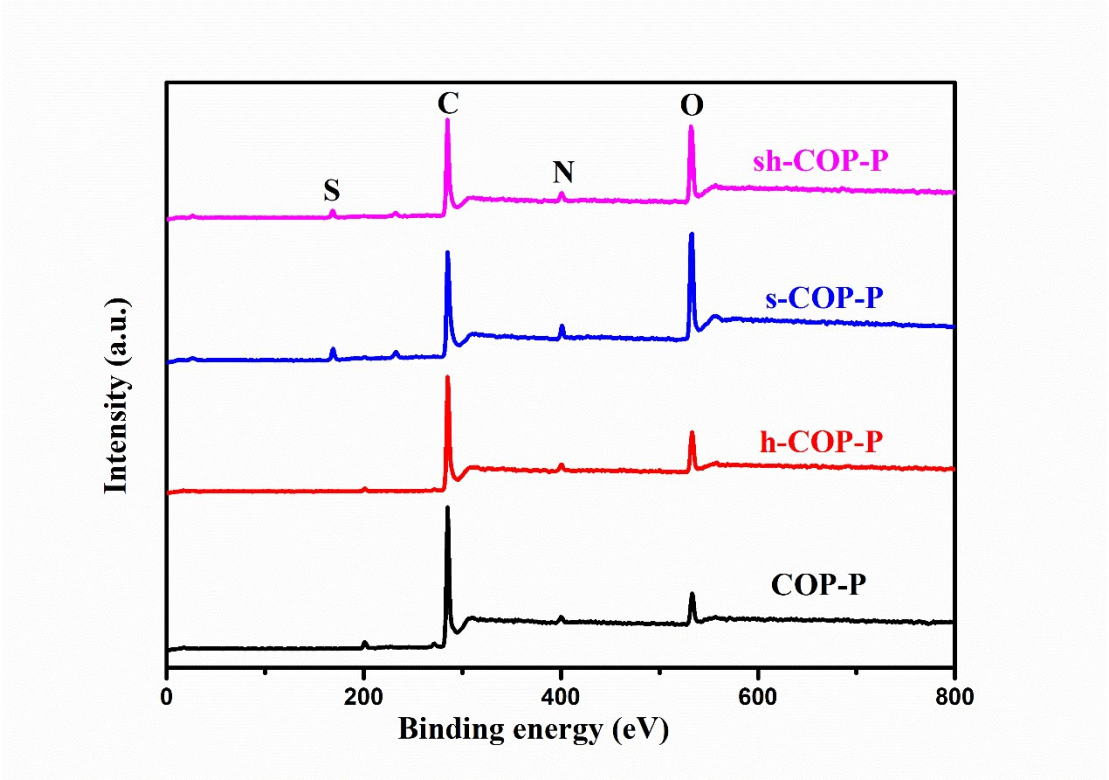


Figure S3. XPS survey spectra of COP-P, h-COP-P, s-COP-P, and sh-COP-P.

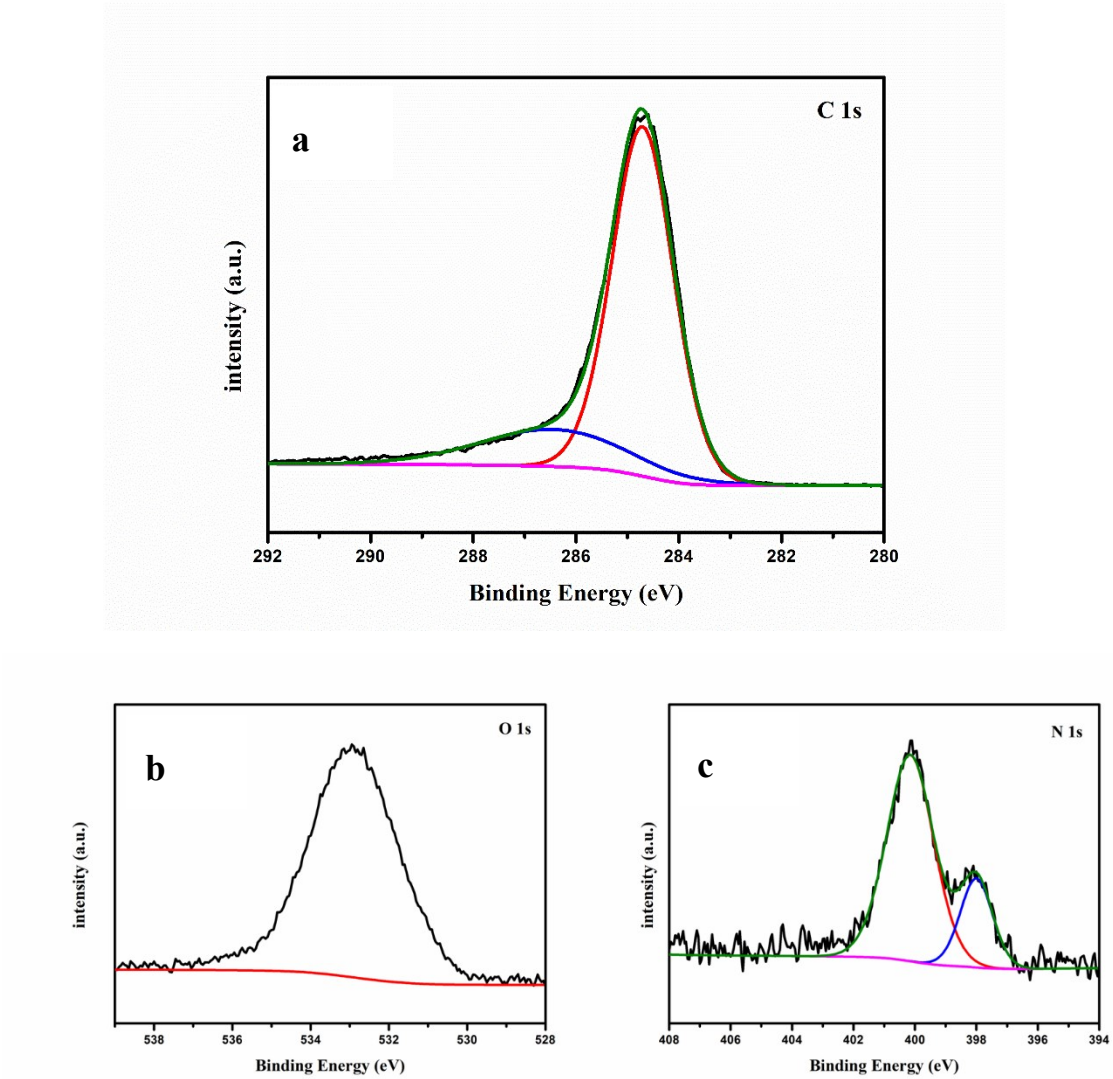


Figure S4. High resolution XPS spectra of the C1s (a), O1s (b), and N1s (c) recorded for the COP-P.

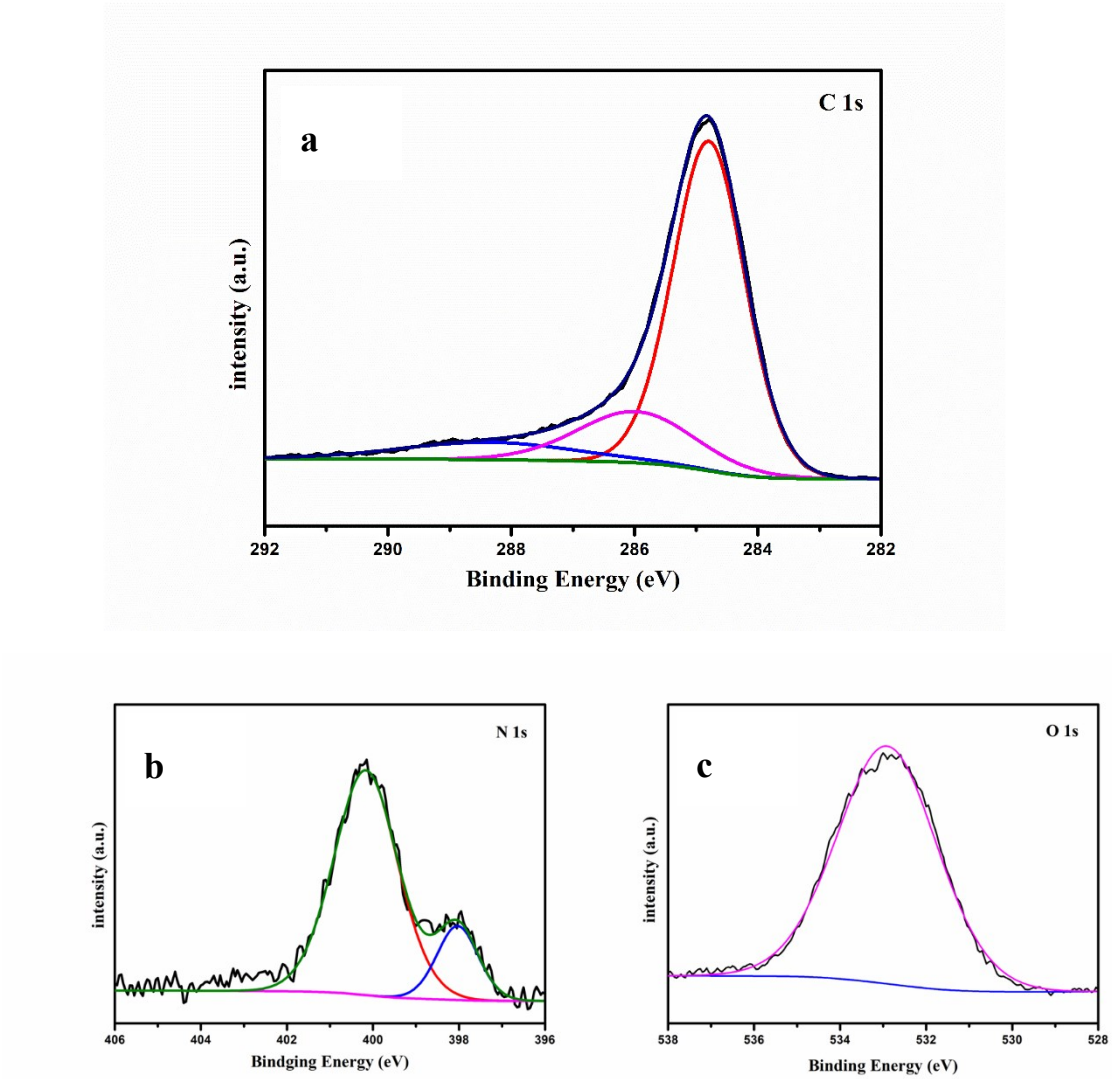


Figure S5. High resolution XPS spectra of the C1s (a), N1s (b), and O1s (c) recorded for the h-COP-P.

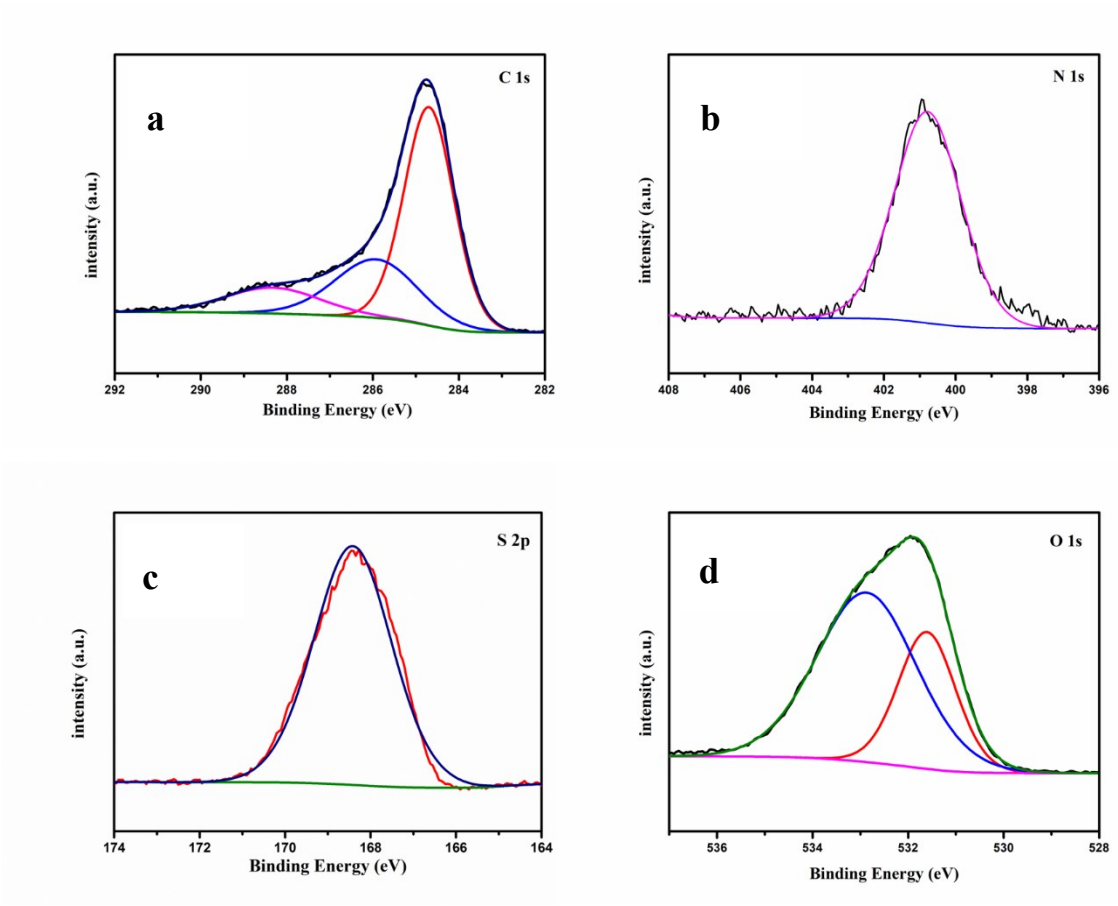


Figure S6. High resolution XPS spectra of the C1s (a), N1s (b), S2p (c), and O1s (d) recorded for the s-COP-P.

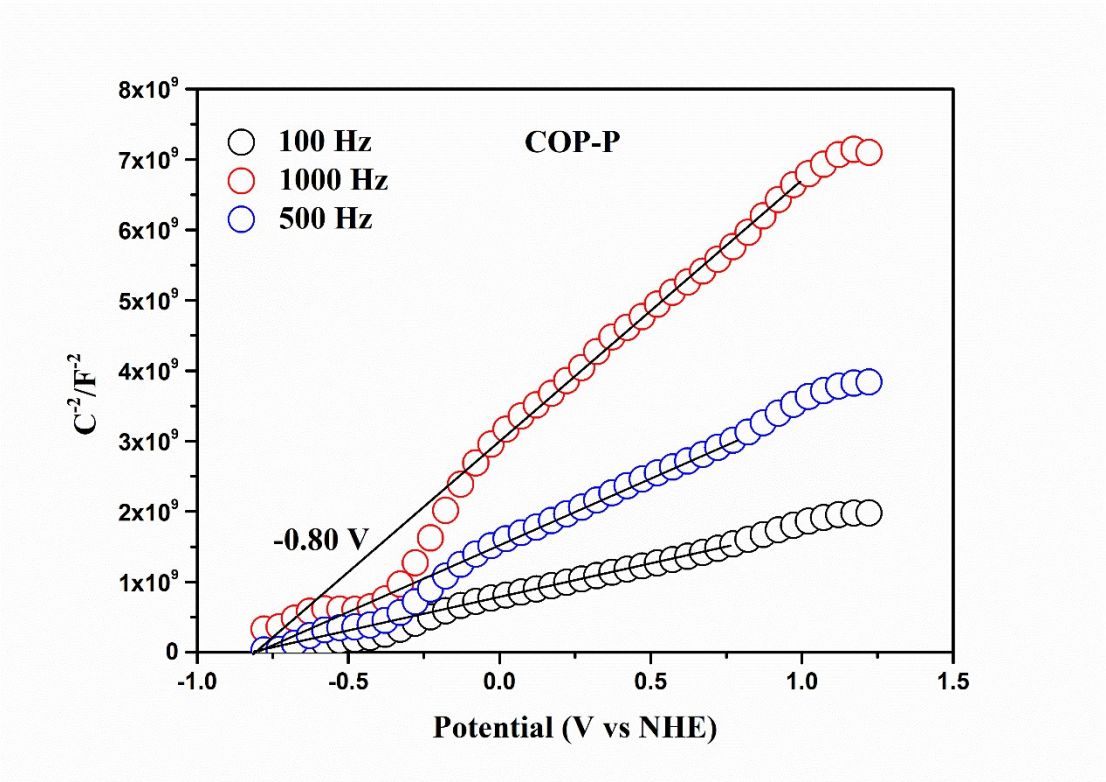


Figure S7. Mott−Schottky plots of COP-P collected at various frequencies (V *vs* NHE).

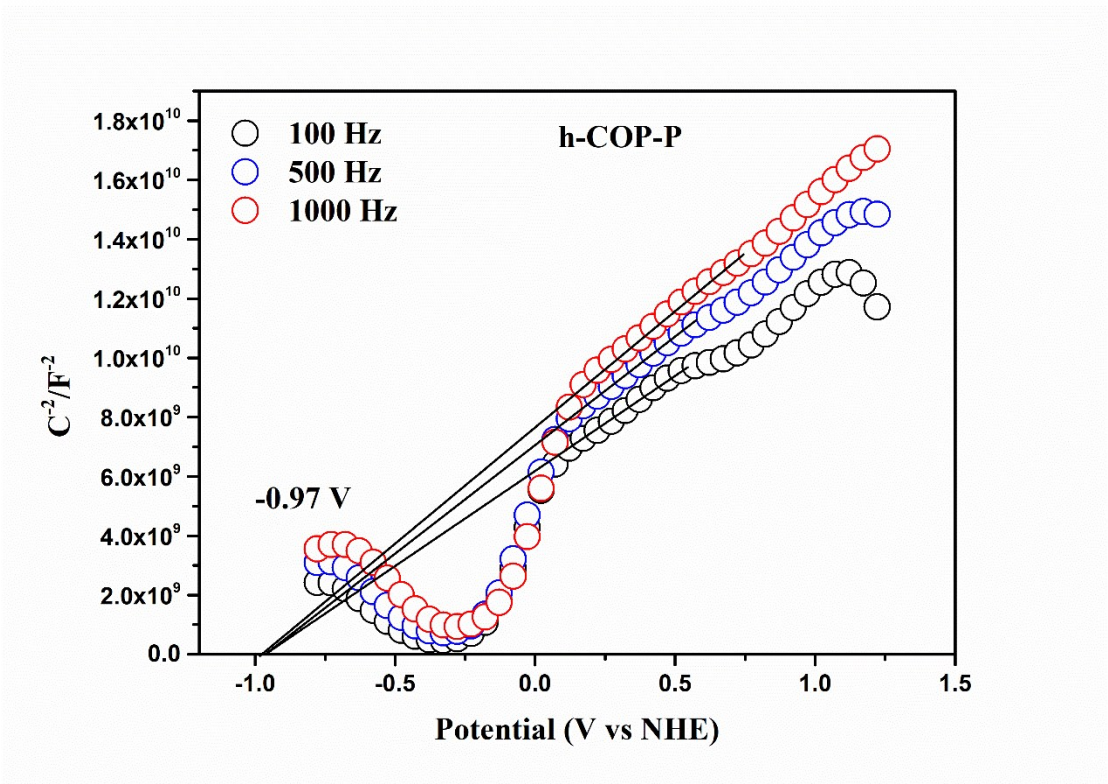


Figure S8. Mott−Schottky plots of h-COP-P collected at various frequencies (V *vs* NHE).

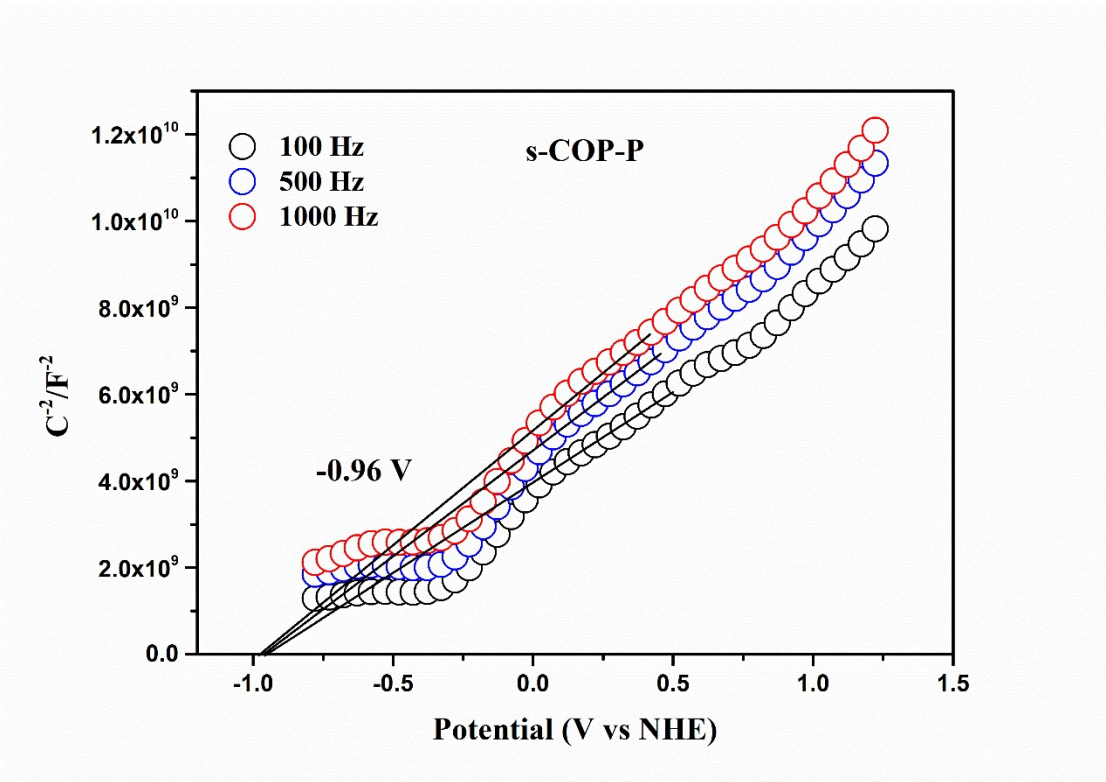


Figure S9. Mott−Schottky of s-COP-P plots collected at various frequencies (V *vs* NHE).

Table S3. The energy band data of COP-P, h-COP-P, s-COP-P, and sh-COP-P (in eV *vs* NHE).

samples	E_{VB}[a]	E_{CB}	E_{Gap}
COP-P	1.05	-0.80	1.85
h-COP-P	0.86	-0.97	1.83
s-COP-P	0.83	-0.96	1.79
sh-COP-P	1.13	-0.67	1.80

[a] deduced from eq: $E_{VB}= E_{Gap}+E_{CB}$

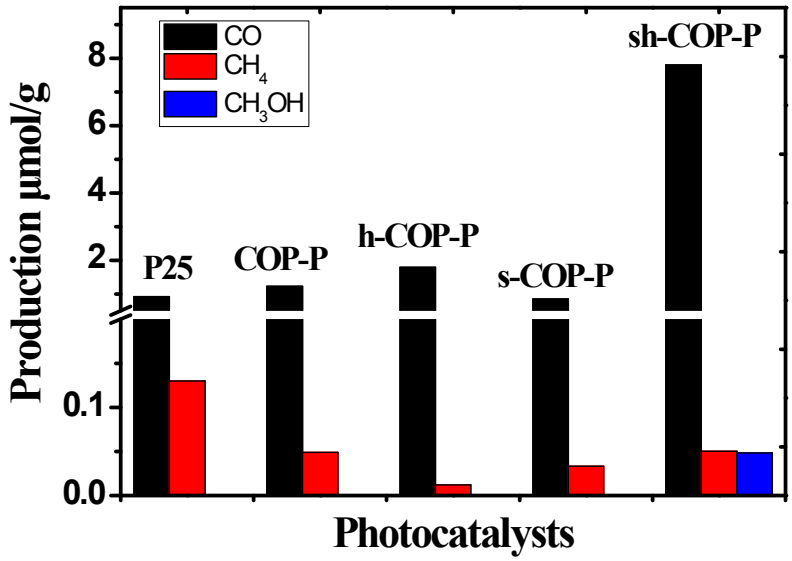
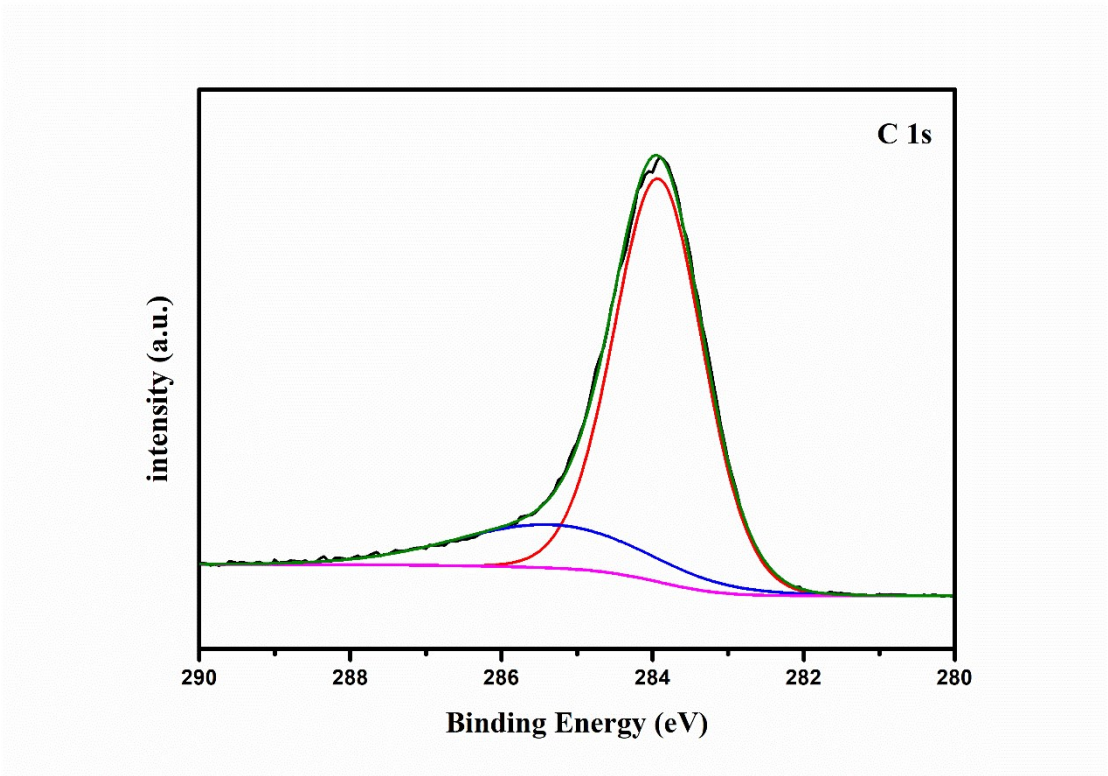


Figure S10. The output of CO CH_3OH and CH_4 under the photocatalyzation of P25 and four COPs within 1 h (the output of CH_3OH was undetectable for P25, COP-P, s-COP-P and sh-COP-P).

Table S4. The photocatalytic production of CO, CH_3OH and CH_4 measured for four COPs and commercial P25 (μmol/g) within 1 h.

	CO[a]	CH_4	CH_3OH
P25	0.918 (87.6%)	0.130	undetectable
COP-P	1.229 (96.2%)	0.049	undetectable
h-COP-P	1.795 (99.3)	0.012	undetectable
s-COP-P	0.855 (96.3)	0.033	undetectable
sh-COP-P	7.798 (98.7%)	0.050	0.048

[a]The percentage in the bracket is the selectivity of CO production



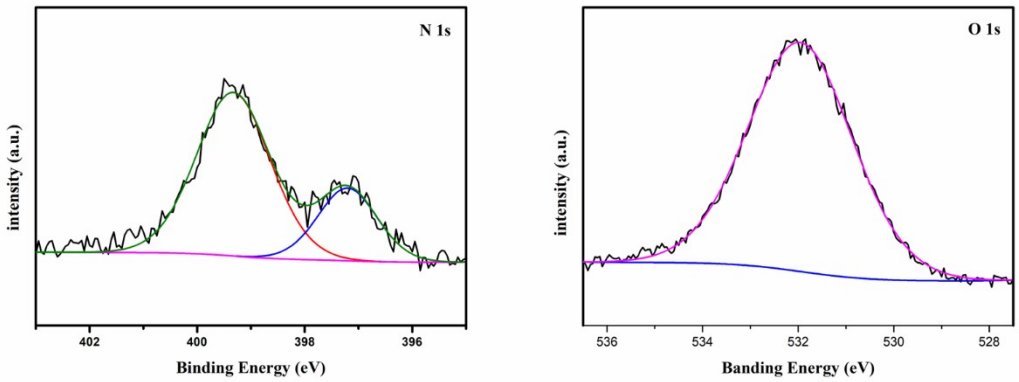


Figure S11 High resolution XPS spectra of the C1s (a), N1s (b), and O1s (c) recorded for the COP-P after photocatalysis.

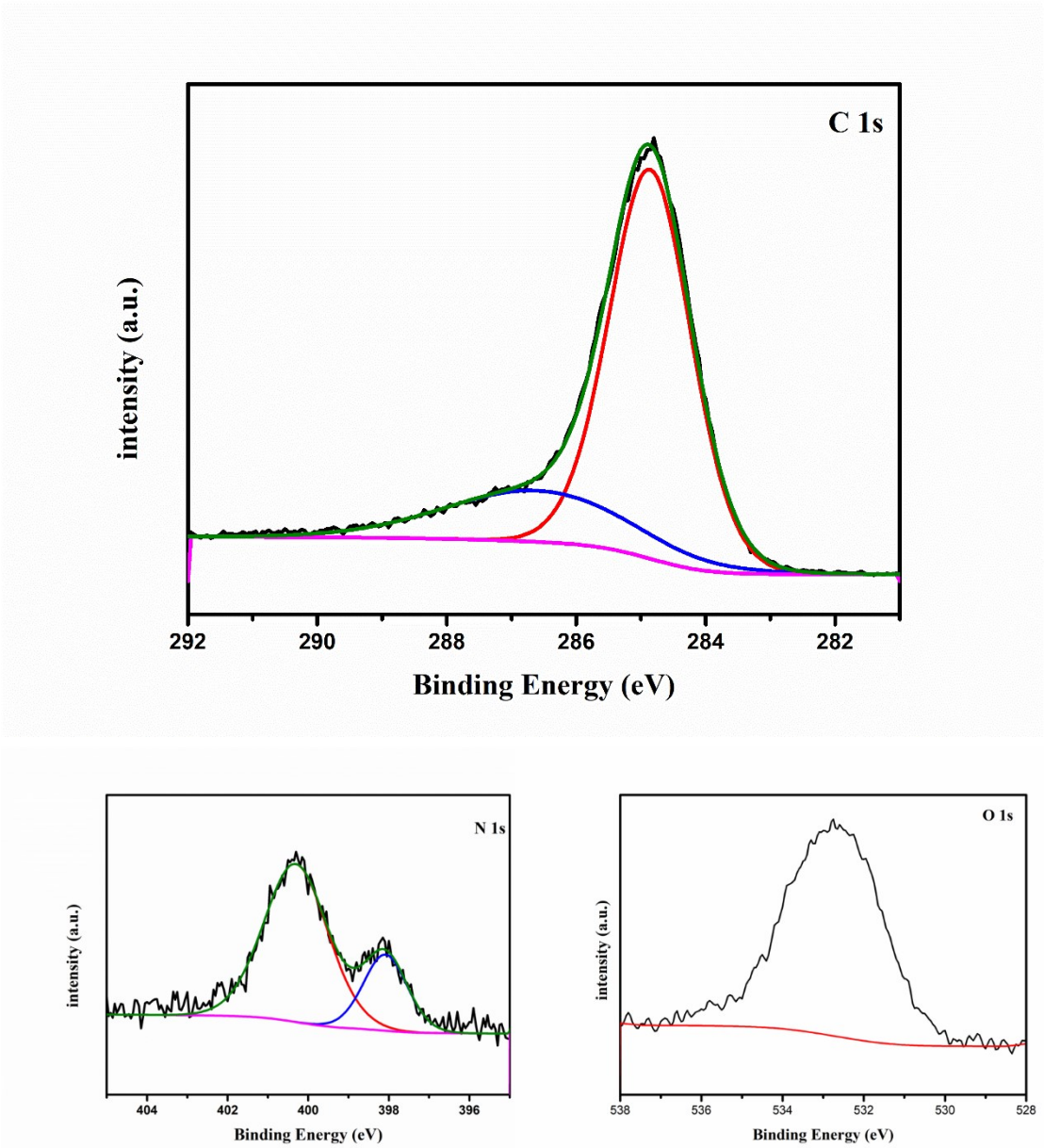


Figure S12. High resolution XPS spectra of the C1s (a), N1s (b), and O1s (c) recorded for the h-COP-P after photocatalysis.

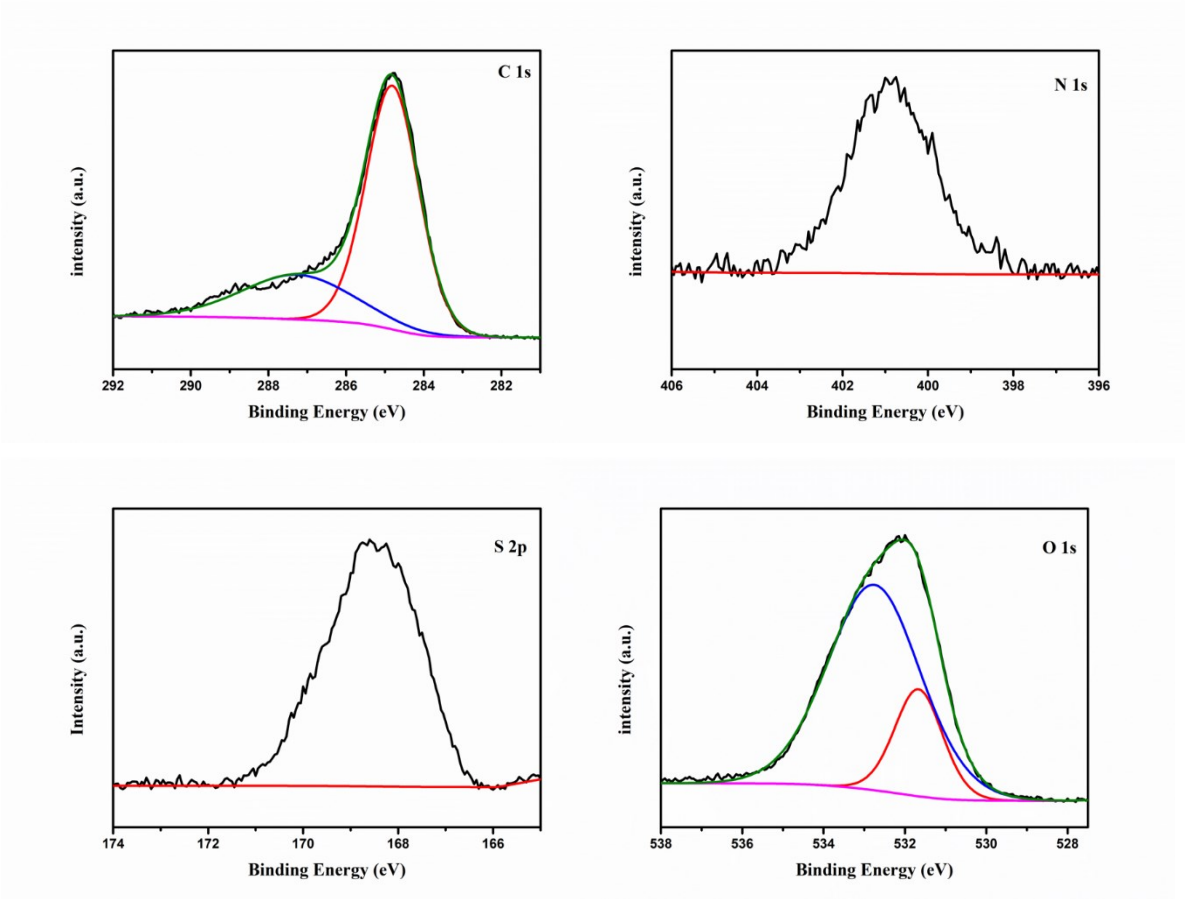


Figure S13. High resolution XPS spectra of the C1s (a), N1s (b), S2p (c) and O1s (d) recorded for the s-COP-P after photocatalysis.

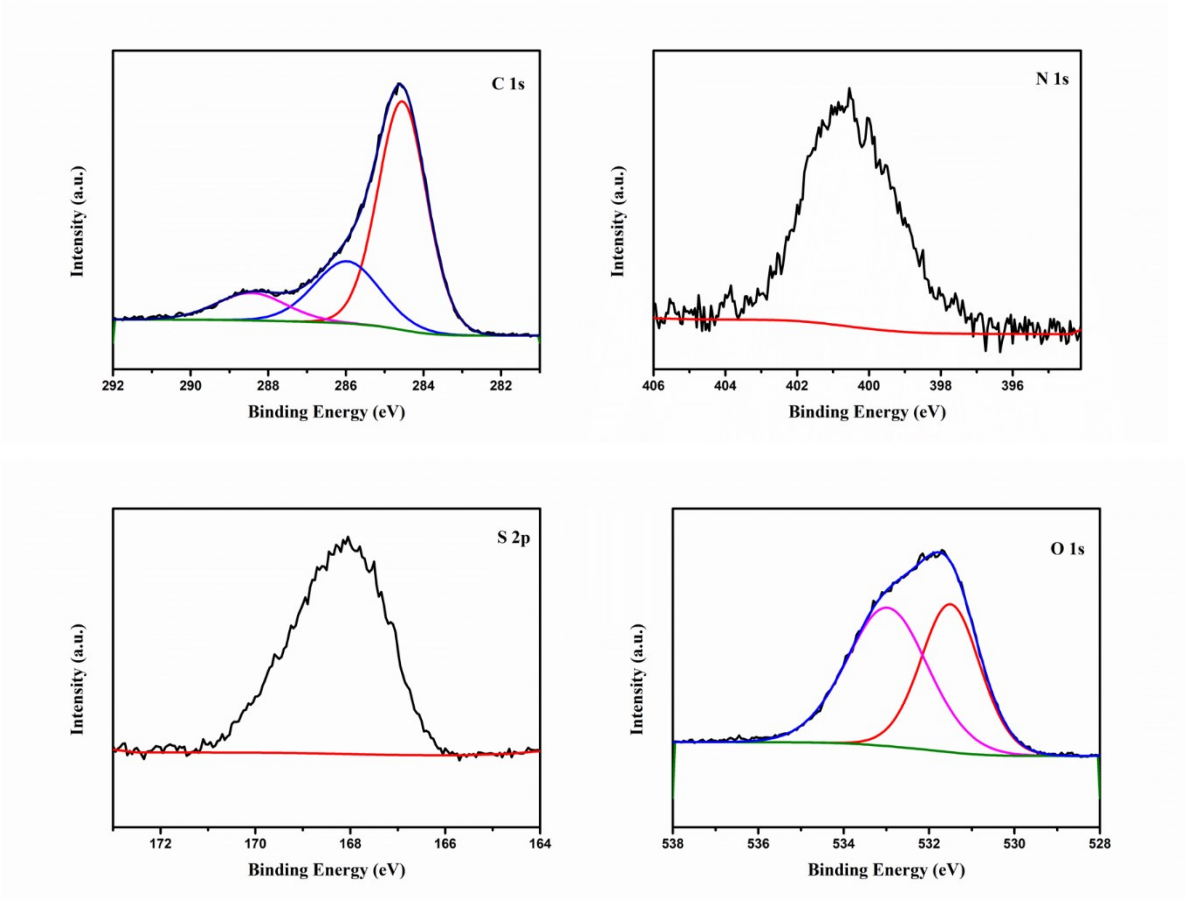


Figure S14. High resolution XPS spectra of the C1s (a), N1s (b), S2p (c) and O1s (d) recorded for the sh-COP-P after photocatalysis.

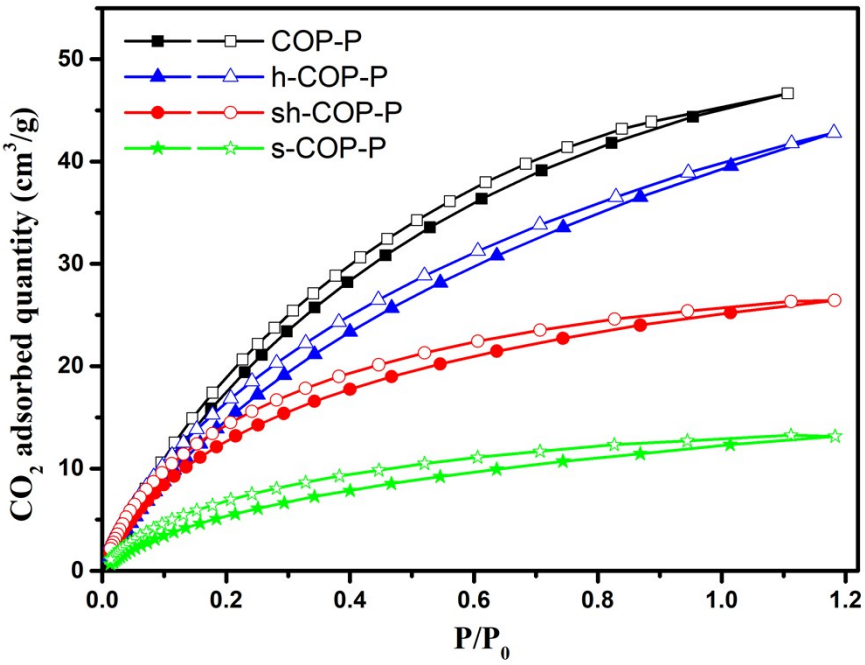


Figure S15. CO_2 adsorption of COPs at 298K.

Table S5. The variation of sulfur contents in sh-COP-P and the corresponding photocatalytic activity with the sulfonation conditions

samples	Sulfonation Condition (temp. and time)	Sulfur Content（%）[a]	CO production (μmol/g within 1h)
s1	50 °C, 15 min	2.56	0.92
s2	50 °C, 30 min	3.26	1.13
s3	50 °C, 60min	3.51	4.01
s4	100 °C, 60 min	6.09	7.54

[a] determined from ICP measurement.

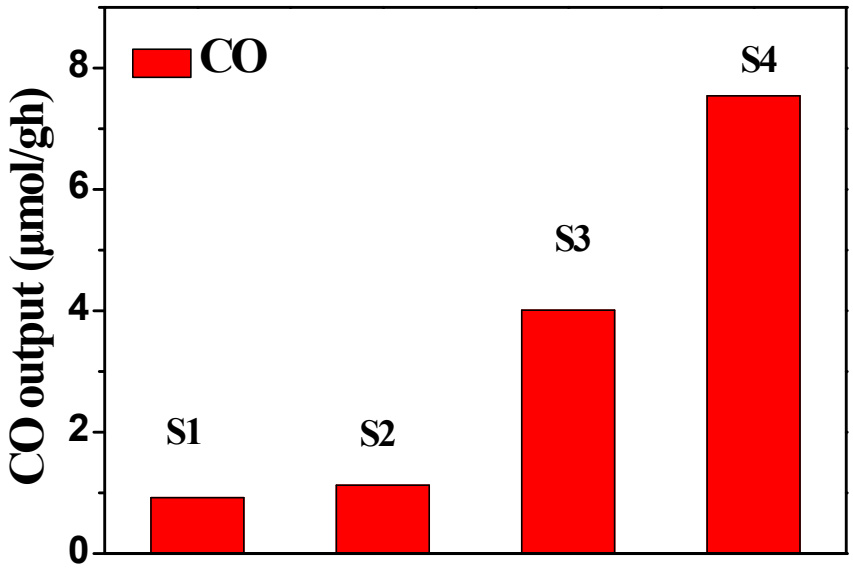


Figure S16. CO output within 1 h photocatalysed by different sh-COP-Ps.