## CoP Decorated 2D/2D Red Phosphorus/B Doped g-C<sub>3</sub>N<sub>4</sub> Type II Heterojunction for Boosted Pure Water Splitting Activity via Two-Electron Pathway

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## The leak ratios of Co and P atoms (wt%)

ICP-MS and ion chromatography were used to detect the concentration of  $\text{Co}^{2+}$  and  $\text{PO}_4^{3-}$  in the solution after the reaction to confirm the stability of CoP/RP/BCN. The concentration of  $\text{Co}^{2+}$ and  $\text{PO}_4^{3-}$  were 19.1 µg L<sup>-1</sup> and 0.99 mg L<sup>-1</sup> by ICP-MS and ion chromatography analysis, respectively. The leak ratios of Co and P atoms (wt%) are calculated as as follows:

$$R_{P} = \frac{C_{PQ_{4}^{3}} \times V_{H_{2}O}}{M \times W_{P}} = \frac{0.99 \times 0.03}{6 \times 49.81\%} \times 100\% = 0.99\% \ R_{Co} = \frac{C_{Co^{2+}} \times V_{H_{2}O}}{M \times W_{Co}} = \frac{0.019 \times 0.03}{6 \times 0.64\%} \times 100\% = 1.48\%$$

where R is the leak ratio. C is the concentration of  $\text{Co}^{2+}$  or  $\text{PO}_4^{3-}$  in the solution after the reaction. V is the volume of the reaction solution. M is the mass of catalyst. W is the concentration of Co or P in CoP/RP/BCN.

Sample	τ <sub>1</sub> (ns)	$\mathbf{A}_{1}$	τ <sub>2</sub> (ns)	$A_2$	τ <sub>3</sub> (ns)	<b>A</b> <sub>3</sub>	$\tau_{Ave}(ns)$
CN	0.61	1696.87	2.46	535.08	11.56	29.144	2.89
BCN	0.55	1545.56	2.46	604.51	12.99	27.79	3.26
RP/BCN	0.50	3294.12	2.60	813.35	10.39	99.89	3.57
CoP/RP/BCN	1.06	5751.70	4.85	695.11	34.59	29.85	5.58

 Table S1 The radiative fluorescence lifetimes and their relative percentages of photo-excited

 charge carriers in the different samples.

Group	Sample	Hydrogen evolution rate /μmol h <sup>-1</sup> g <sup>-1</sup>	Multiple	
1 -	BCN <sup>a</sup>	1.3	1.6	
	$CN^b$	0.8		
	COP/RP/BCN <sup>a</sup>	166.2	2.8	
	COP/RP/CN <sup>b</sup>	44.0	3.8	
2 -	RP/BCN <sup>a</sup>	5.4	1.6	
	BCN <sup>b</sup>	1.3	1.0	
	COP/RP/BCN <sup>a</sup>	166.2	50.4	
	COP/BCN <sup>b</sup>	3.3	30.4	
3 -	COP/BCN <sup>a</sup>	3.3	2.5	
	BCN <sup>b</sup>	1.3		
	COP/RP/BCN <sup>a</sup>	166.2	20.8	
	RP/CN <sup>b</sup>	5.4	30.8	

 Table S2
 The effect of B, RP, and CoP on sample photocatalytic activity.

a, the numerator of multiple; b, the denominator of multiple

Sample	B (wt%)	P (wt%)	Co (wt%)
CoP <sub>3</sub> /RP <sub>8</sub> /B <sub>0.5</sub> CN	0.40	33.81	0.26
CoP <sub>3</sub> /RP <sub>8</sub> /B <sub>1</sub> CN	0.64	49.81	0.64
CoP <sub>3</sub> /RP <sub>8</sub> /B <sub>1.5</sub> CN	1.10	58.77	0.95

Table S3 The elemental contents of different samples based on the ICP-MS analysis



Fig. S1 SEM images of (a) CN, (b) BCN, (c) RP/BCN, and (d) CoP/RP/BCN.



Fig. S2 TEM images of (a) CN, (b) BCN, and (c) CoP/RP/BCN. (d) HRTEM image of CoP/RP/BCN.



Fig. S3 HRTEM image of CoP/RP/BCN.



Fig. S4 XRD patterns of CoP, RP, RP/BCN, and CoP/RP/BCN.



Fig. S5 TEM images of (a) RP and (b) CoP.



Fig. S6 SADE pattern of CoP loaded on the CoP/RP/BCN.



**Fig. S7** The XPS spectra of (a) B 1s for CN and BCN, (b) Co 2p for CoP/RP/BCN, P 2p for (c) CoP/RP/BCN and (d) RP/BCN and CoP/BCN.



Fig. S8 The XPS spectra of B 1s for (a) CoP/ BCN and (b) CoP/RP/BCN



Fig. S9 The water contact angles of (a) RP/BCN and (b) CoP/RP/BCN.



Fig. S10 PL spectra of (a)  $B_xCN$ , (b)  $CoP_x/RP_8/CN$ , and (c)  $CoP_3/RP_x/B_1CN$ .



Fig. S11 Photocatalytic H<sub>2</sub> evolution rates of CoP/RP/BCN under light irradiation ( $\lambda > 420$  nm).



Fig. S12 Wavelength-dependent AQYs for CoP/RP/BCN at different wavelengths.



Fig. S13 (a) SEM and (b) TEM images of CoP/RP/BCN after cycling hydrogen generation under visible light irradiation ( $\lambda$ >420nm).



Fig. S14 The HRTEM image of CoP for CoP/RP/BCN after cycling hydrogen generation under visible light irradiation ( $\lambda$ >420nm).



Fig. S15 The XPS spectra of (a, b) C 1s and (c, d) N 1s for sonicated CoP/RP/BCN after cycling hydrogen generation under visible light irradiation ( $\lambda$ >420nm) compared with that of before.



**Fig. S16** The XPS spectra of (a, b) P 2p and (c, d) Co 2p for sonicated CoP/RP/BCN after cycling hydrogen generation under visible light irradiation ( $\lambda$ >420nm) compared with that of before.



Fig. S17 UV-vis absorption spectra of CoP/RP/BCN system with light irradiation by iodometry.



Fig. S18 (a) Standard curve of different concentration of  $H_2O_2$  by iodometry. (b) Photocatalytic  $H_2O_2$  evolution rates of CoP/RP/BCN under light irradiation ( $\lambda > 420$  nm) and dark.