

## Bifunctional black phosphorus: Coupling with hematite for Z-scheme photocatalytic overall water splitting

### Supporting Information

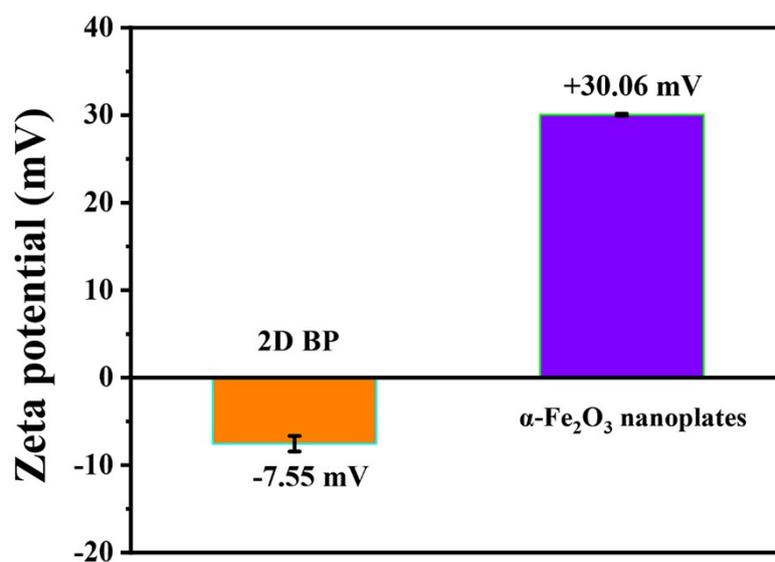


Figure S1. Zeta potential measurements of BP nanosheets and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoplates.

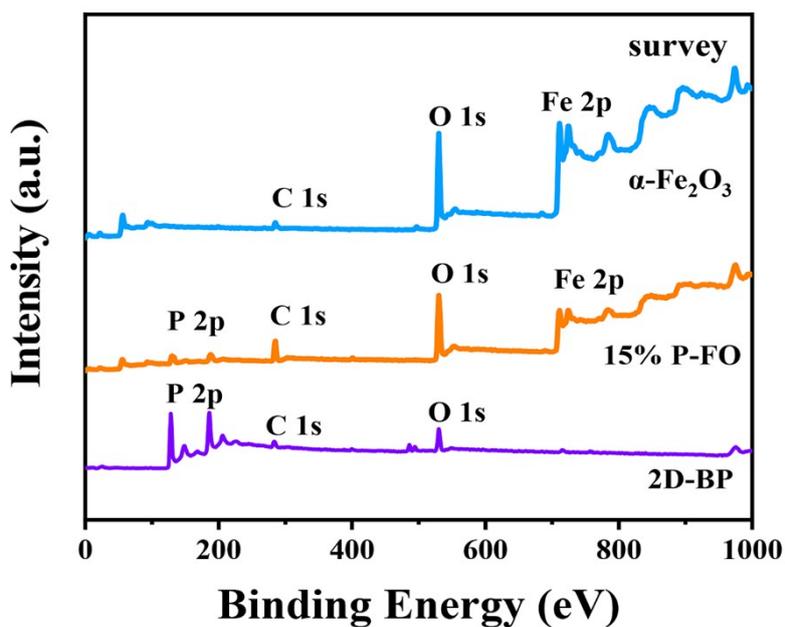


Figure S2. Full XPS spectra of BP, Fe<sub>2</sub>O<sub>3</sub> and 15% P-FO heterostructure.

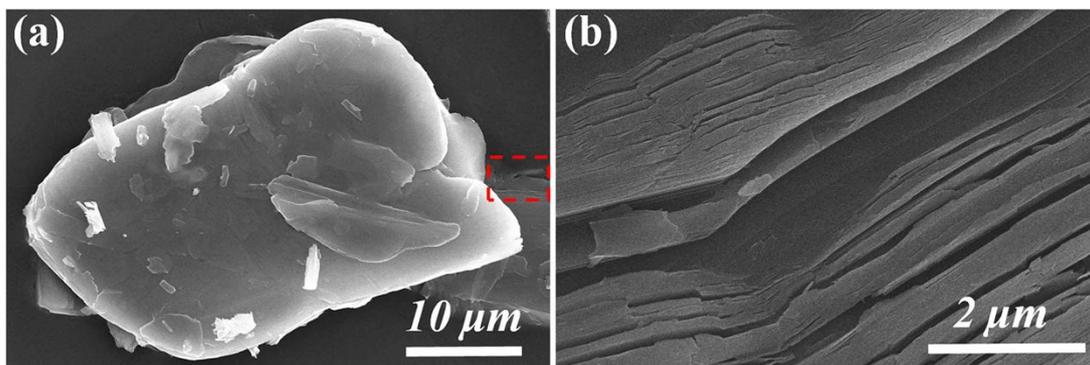


Figure S3. (a) SEM image of bulk BP, (b) enlarged SEM image of bulk BP.

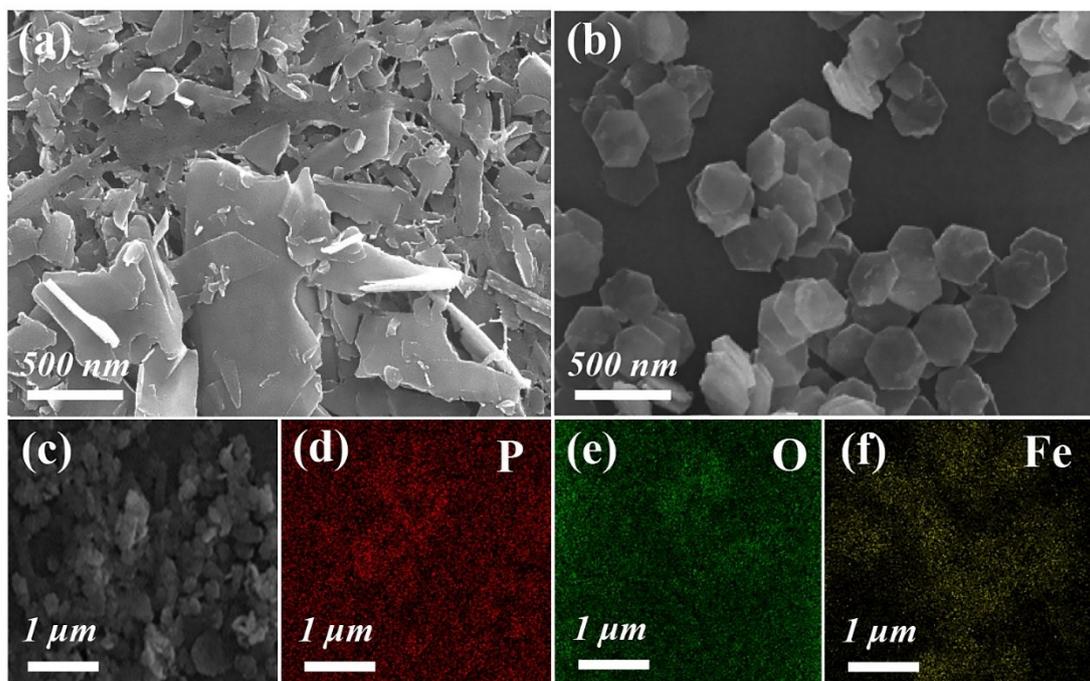


Figure S4. SEM images of (a) BP nanosheets, (b)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoplates, (c) 15% P-FO heterostructure and corresponding EDX elemental mapping of (d) P, (e) Fe, (f) O elements of the 15% P-FO heterostructure.

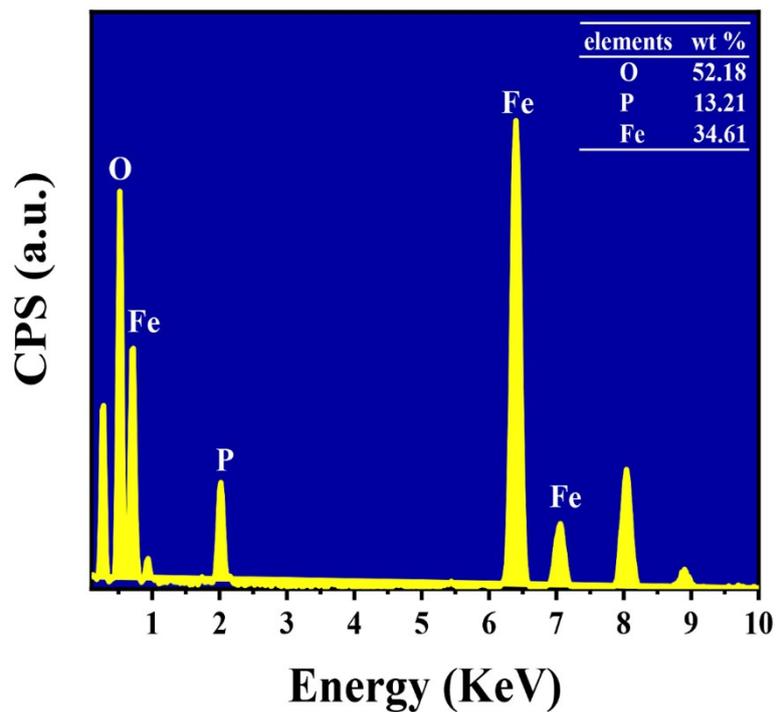


Figure S5. TEM EDX spectra of 15% P-FO heterostructure. The peaks at 8.0 to 9.0 eV were attributed to Cu signals, which are coming from the substrate for supporting samples.

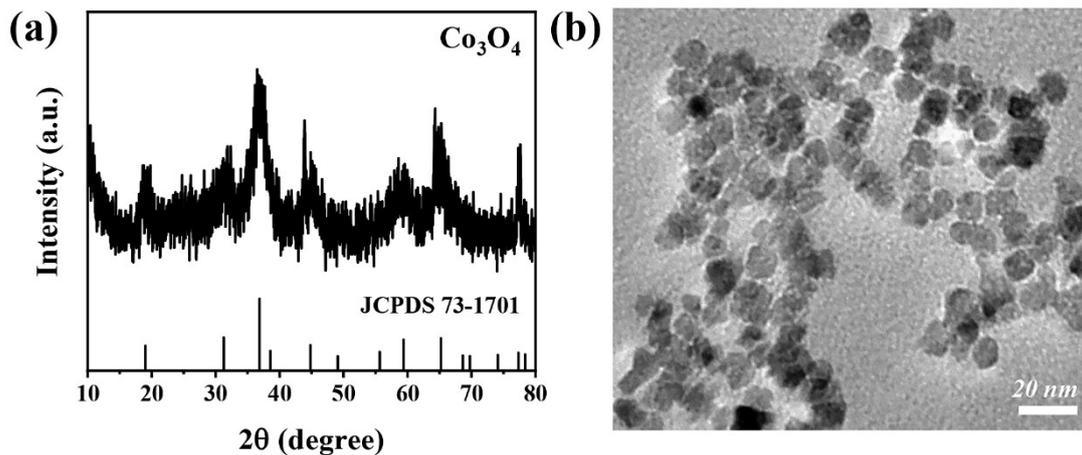


Figure S6. (a) XRD pattern and (b) TEM image of as-prepared  $\text{Co}_3\text{O}_4$  nanoparticles.

### Synthesis of $\text{Co}_3\text{O}_4$ nanoparticles

Typically, 0.58 g  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was dissolved into 100 mL of deionized water under magnetic stirring in a 250 mL three-necked flask for ten minutes, then 1.62 mL ammonia aqueous solution ( $\text{NH}_3 \cdot \text{H}_2\text{O}$ , 25 wt %) was added, subsequently, 120  $\mu\text{L}$   $\text{H}_2\text{O}_2$  (30 wt %) was injected to this solution. The three-necked flask was heated to 60 °C by oil bath for 15 minutes to ensure that  $\text{Co}^{2+}$  was completely oxidized to  $\text{Co}^{3+}$ . After that, another 0.3 g  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was dissolved into 40 mL deionized water, this solution was added to the reactor. After 3 hours reaction, the black products were collected by centrifugation and washed repeatedly with absolute ethanol and deionized water for several times, and dried at 60 °C for further use.

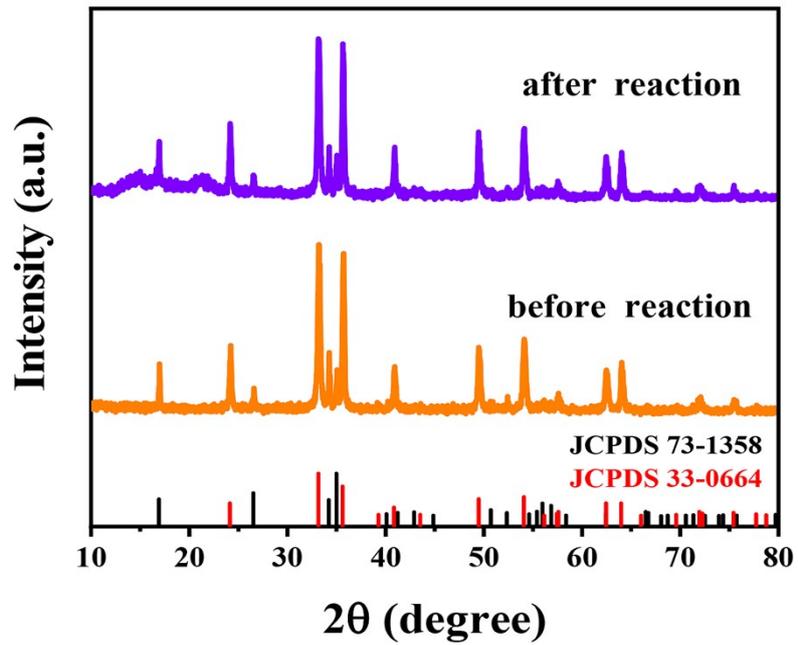


Figure S7 XRD spectra of 15 % P-FO heterostructure before and after photocatalytic reaction.

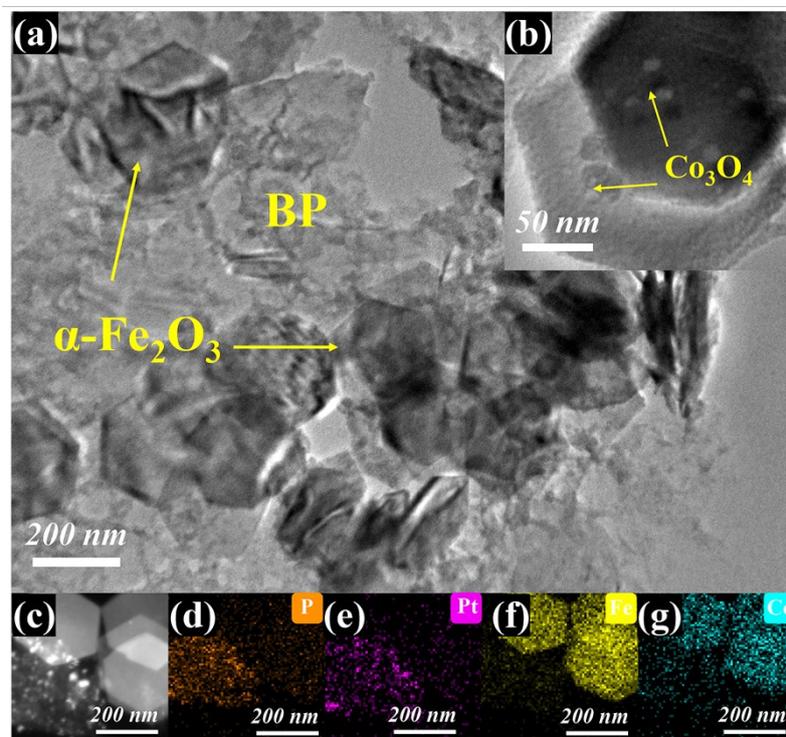


Figure S8. (a) TEM image, (b) enlarged TEM image, (c) STEM image and (d) corresponding EDX elemental mapping of (d) P, (e) Pt, (f) Fe and (g) Co of the 15% P-FO heterostructure after 5 h photocatalytic reaction.

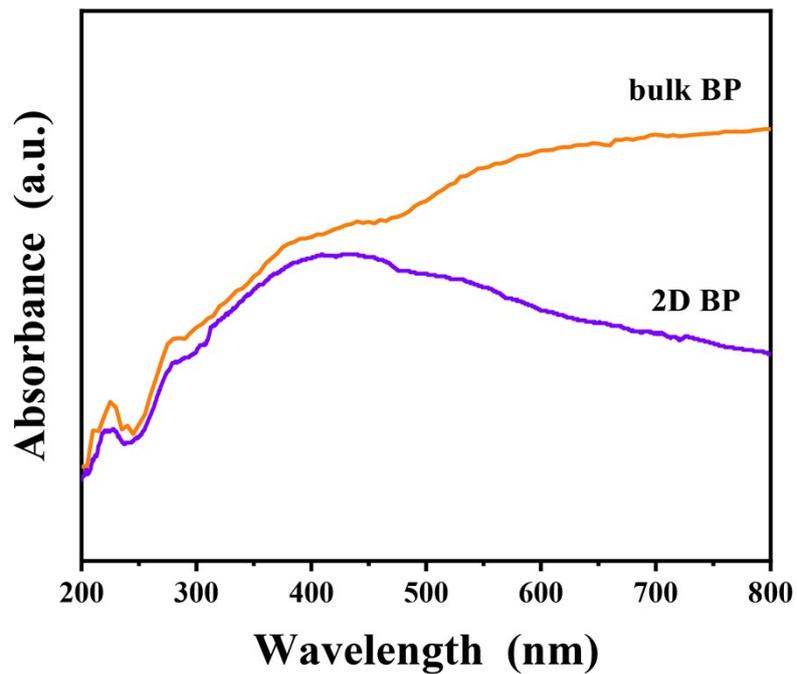


Figure S9. UV-vis diffuse reflectance spectra of bulk BP and 2D BP.

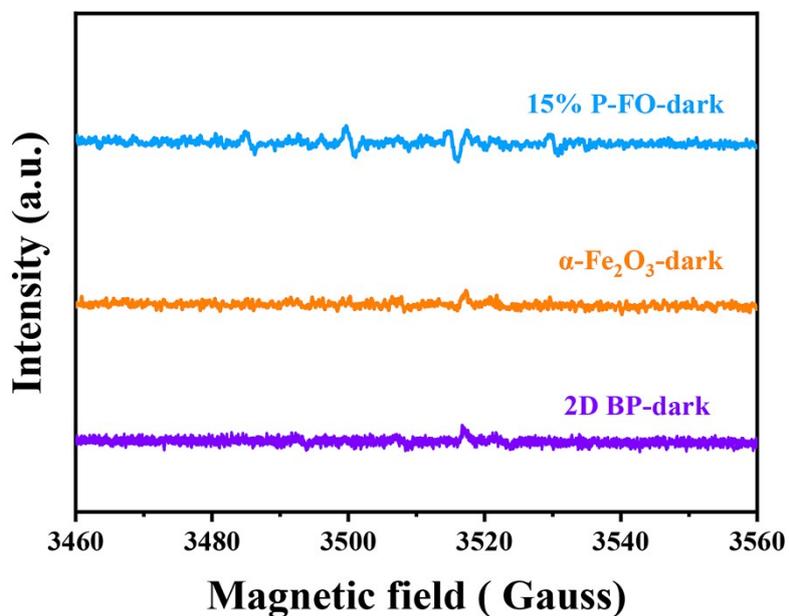


Figure S10. DMPO spin-trapping ESR spectra recorded for  $\bullet$ OH under dark condition of 2D BP,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, and 15% P-FO heterostructure.

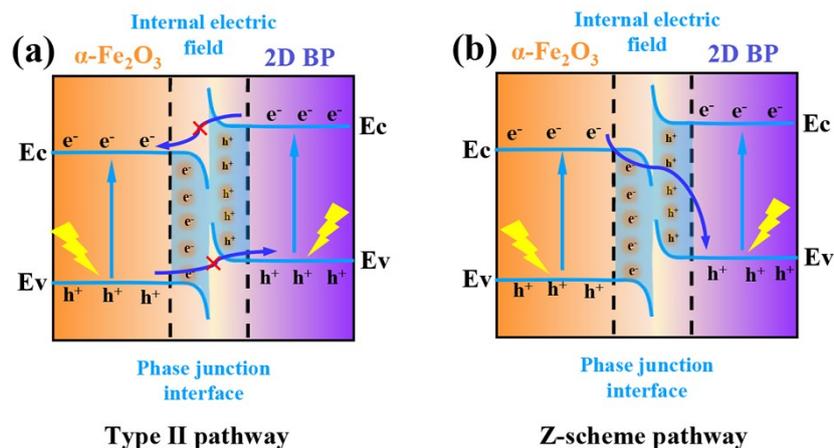


Figure S11. Schematic illustration of (a) Type II charge transfer pathway and (b) Z-scheme charge transfer pathway.

Table S1: Gas production by using different samples with and without sacrificial agent or co-catalyst under visible light irradiation.

| HPP    | OPP  | Sacrificial agent   | $\text{H}_2$ [ $\mu\text{mol h}^{-1}$ ] | $\text{O}_2$ [ $\mu\text{mol}^{-1}$ ] |
|--------|--|---------------------|---|---------------------------------------|
| BP     | —  | —                   | none                                    | 0                                     |
| BP     | —  | 10% TEOA            | 0.05                                    | 0                                     |
| BP/ Pt | —  | 10% TEOA            | 0.14                                    | 0                                     |
| —      | $\alpha\text{-Fe}_2\text{O}_3$                       | —                   | 0                                       | none                                  |
| —      | $\alpha\text{-Fe}_2\text{O}_3$                       | 10% $\text{AgNO}_3$ | 0                                       | 0.17                                  |
| —      | $\alpha\text{-Fe}_2\text{O}_3/\text{Co}_3\text{O}_4$ | 10% $\text{AgNO}_3$ | 0                                       | 0.45                                  |
| BP/Pt  | $\alpha\text{-Fe}_2\text{O}_3$                       | 10% TEOA            | 1.32                                    | 0                                     |
| BP/Pt  | $\alpha\text{-Fe}_2\text{O}_3/\text{Co}_3\text{O}_4$ | —                   | 0.59                                    | 0.29                                  |