

## Electronic Supplementary Information (ESI)

### Phosphorus-doping $\text{In}_2\text{S}_3$ with rich sulfur vacancy toward efficient photocatalytic hydrogen production from formaldehyde solution

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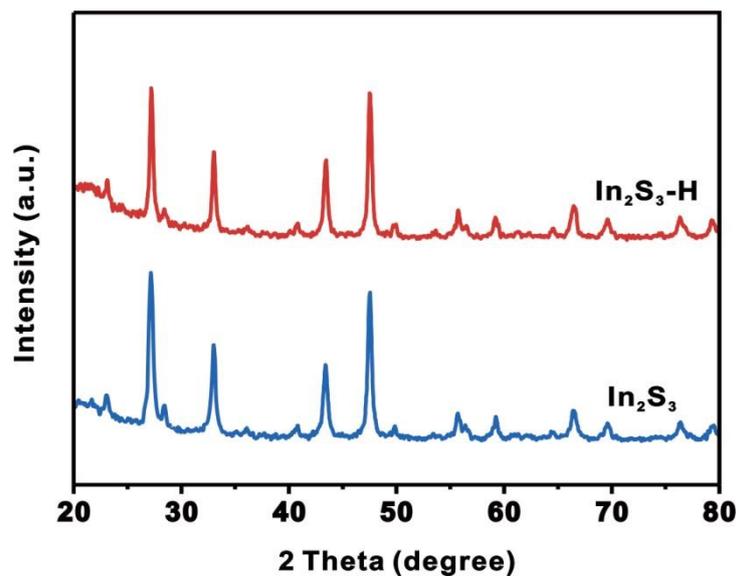
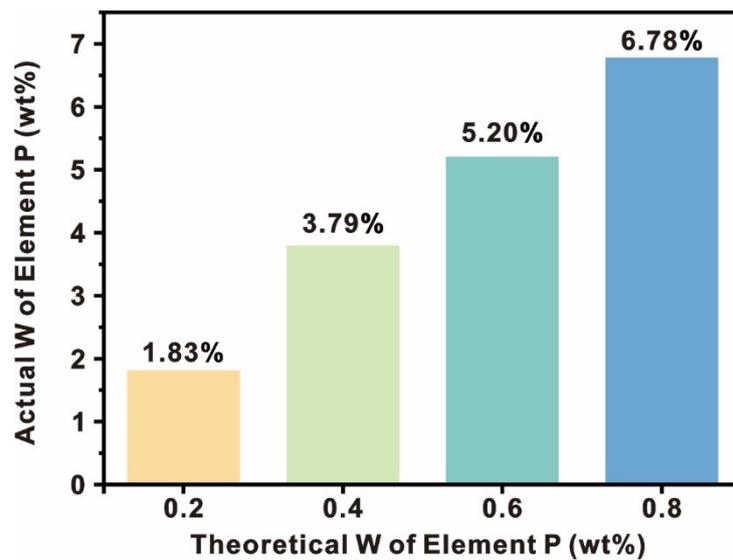
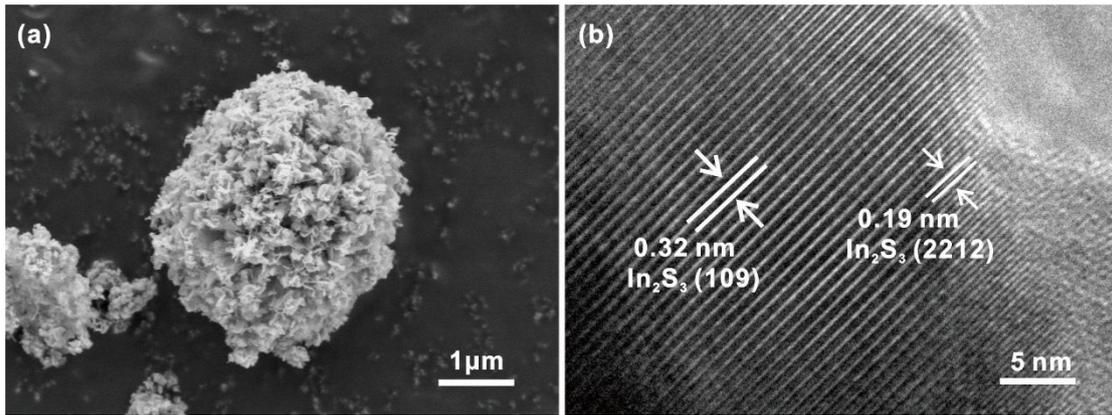


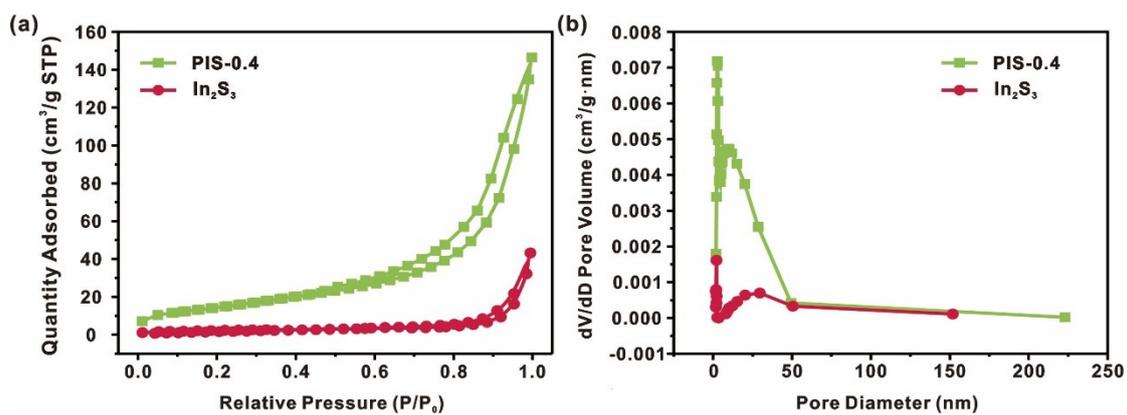
Figure S1. XRD patterns of In<sub>2</sub>S<sub>3</sub> and In<sub>2</sub>S<sub>3</sub>-H.



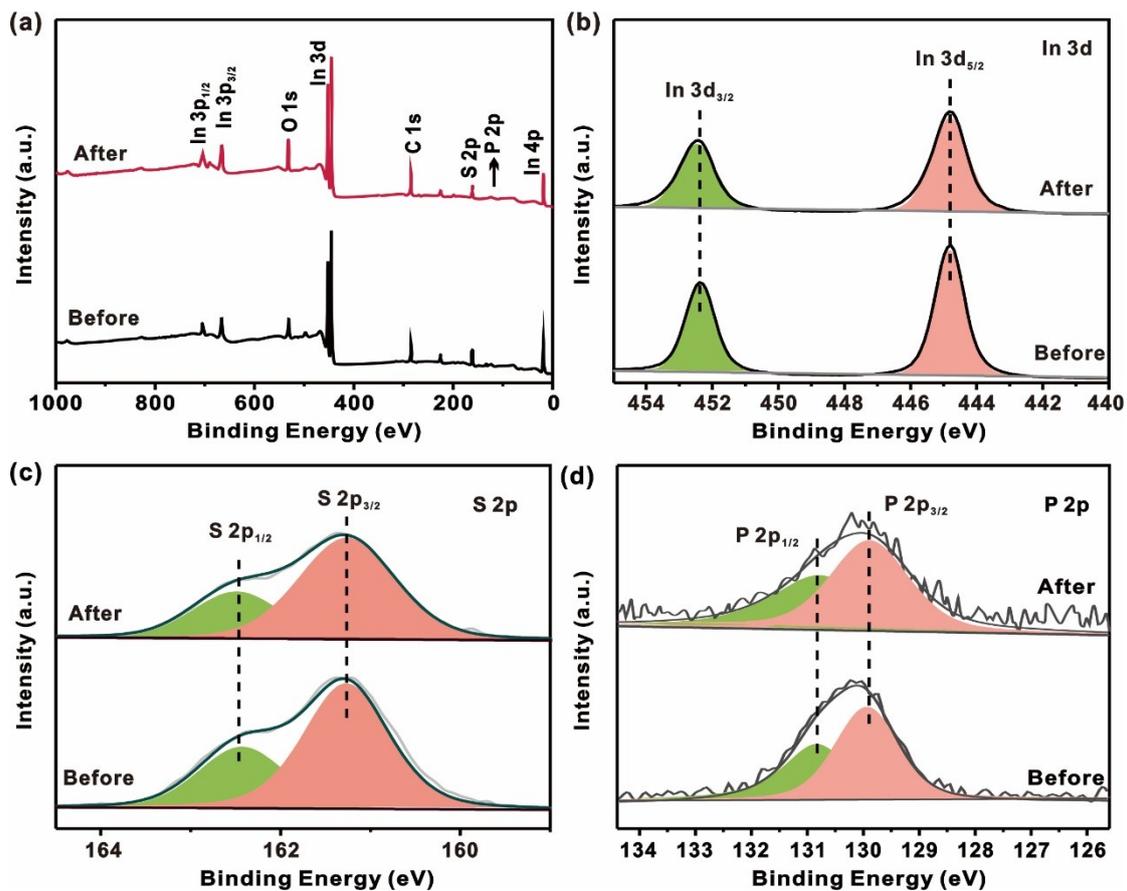
**Figure S2.** Mass fraction of phosphorus in P-In<sub>2</sub>S<sub>3</sub>.



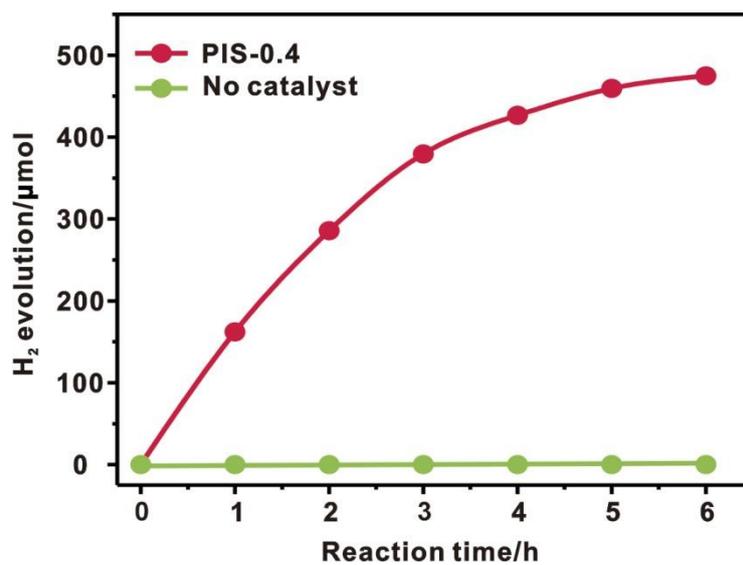
**Figure S3.** (a) SEM and (b) HRTEM of  $\text{In}_2\text{S}_3$ .



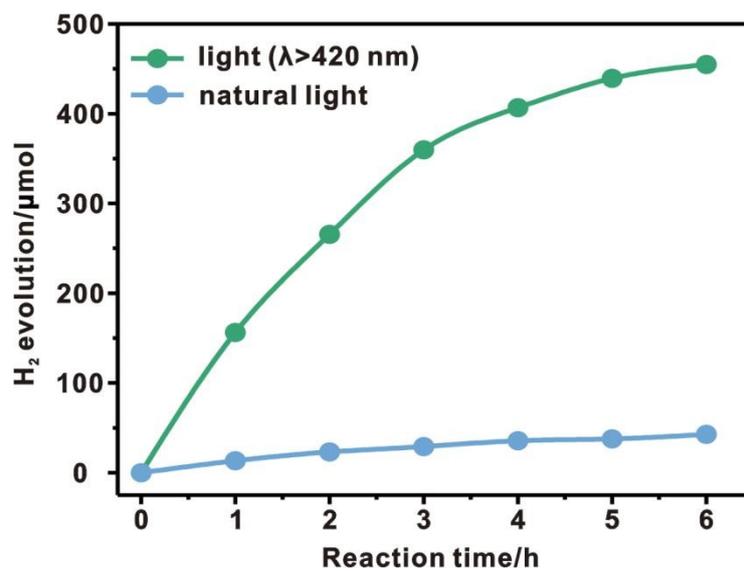
**Figure S4.** (a)  $N_2$  adsorption-desorption isotherms and (b) the pore size distribution plots of PIS-0.4 and  $In_2S_3$ .



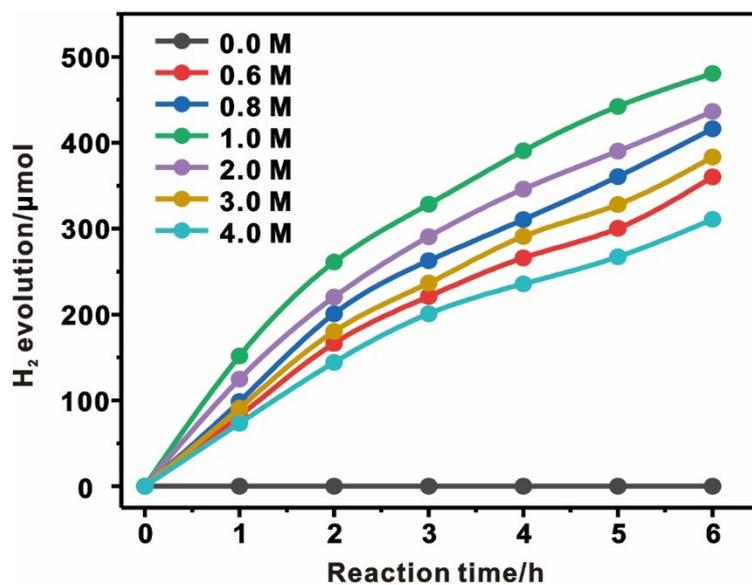
**Figure S5.** The XPS (a) survey, (b) In 3d, (c) S 2p, and (d) P 2p core levels spectra of PIS-0.4 before and after photocatalytic HCHO oxidation reaction.



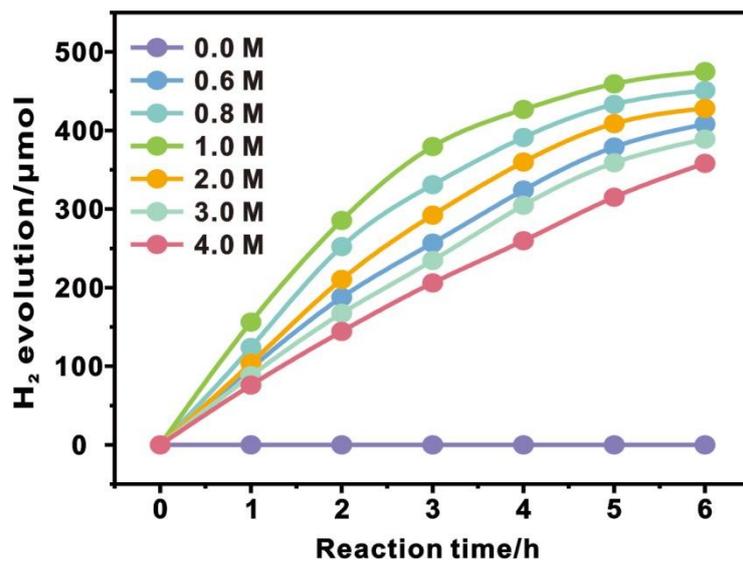
**Figure S6.** The time profiles of hydrogen production from PIS-0.4 and no catalyst suspending in an aqueous solution containing equimolar amounts (1M) of HCHO and NaOH at 0.21 O<sub>2</sub> atm under light conditions.



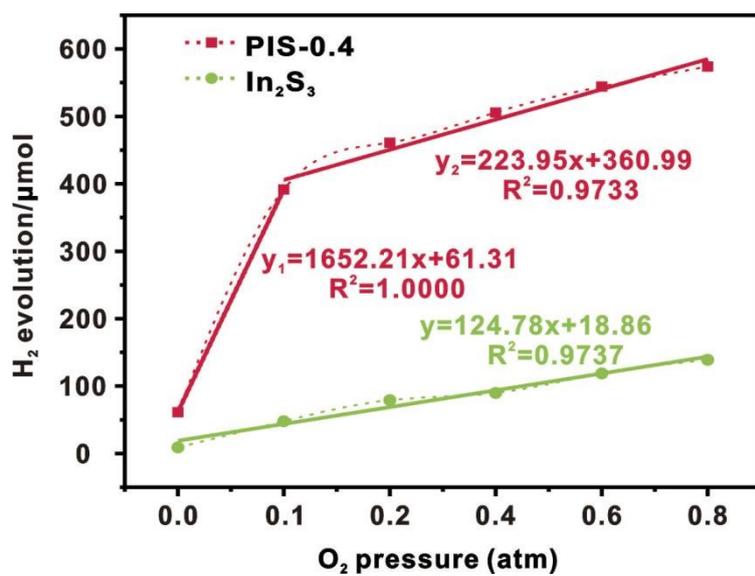
**Figure S7.** The time profiles of hydrogen production from PIS-0.4 suspending in an aqueous solution containing 1 M HCHO and 1 M NaOH at 0.21 O<sub>2</sub> atm, under natural light and light conditions ( $\lambda > 420$  nm).



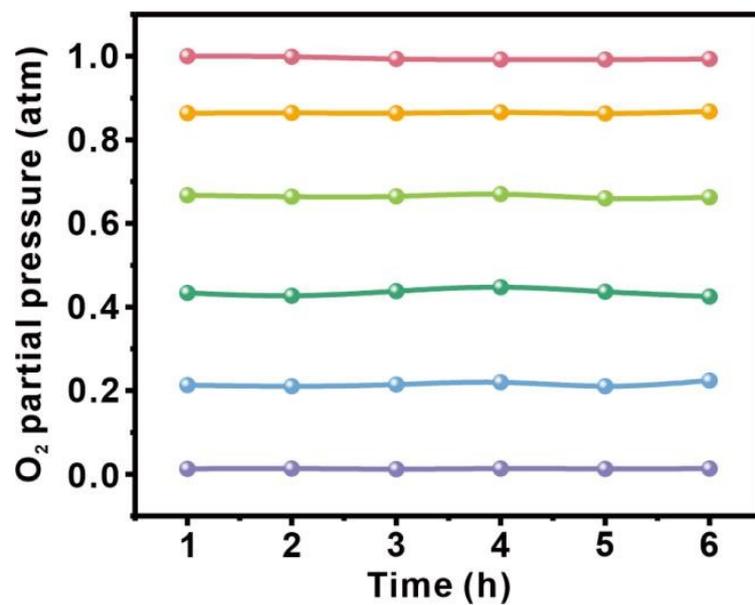
**Figure S8.** The time profiles of hydrogen production from PIS-0.4 suspending in an aqueous solution containing 1 M of NaOH and different concentrations of HCHO at 0.21 O<sub>2</sub> atm under visible-light irradiation ( $\lambda > 420$  nm).



**Figure S9.** The time profiles of hydrogen production from PIS-0.4 suspending in an aqueous solution containing 1 M of HCHO and different concentrations of NaOH at 0.21 O<sub>2</sub> atm under visible-light irradiation ( $\lambda > 420$  nm).



**Figure S10.** The amount of H<sub>2</sub> evolved after 6 h of photocatalytic reaction of PIS-0.4 and In<sub>2</sub>S<sub>3</sub> as a function of  $pO_2$ .



**Figure S11.** The temporal change of O<sub>2</sub> partial pressure within 6 h of reaction with different initial O<sub>2</sub> partial pressure ( $p_{O_2}$ ).