

# Elemental S/P photocatalyst for hydrogen evolution from water under visible to near-infrared light irradiation

Qiuyan Cao,<sup>a</sup> Minna Guo,<sup>a</sup> Jing Cao,<sup>\*a</sup> Haili Lin,<sup>a</sup> Yong Chen<sup>\*b</sup> and Shifu Chen<sup>\*a</sup>

<sup>a</sup> College of Chemistry and Materials Science, Huaibei Normal University, Huaibei, 235000, Anhui, PR China.

E-mail: caojing@chnu.edu.cn, chshifu@chnu.edu.cn.

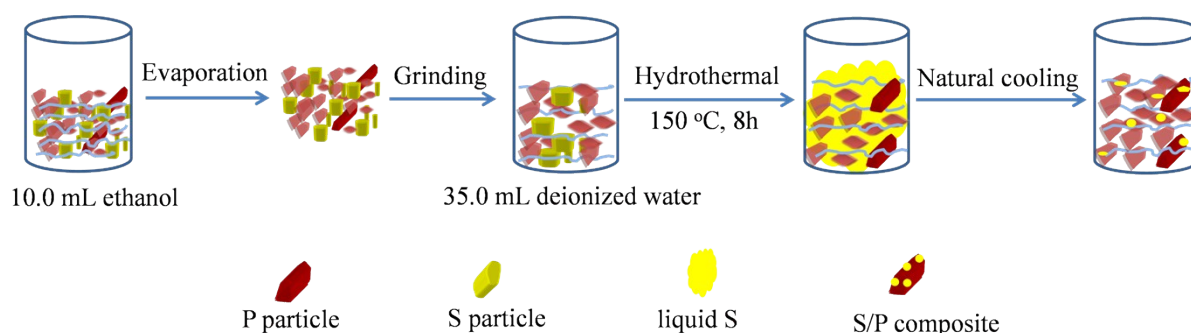
<sup>b</sup> Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing, 100190, PR China. E-mail: chen Yong@mail.ipc.ac.cn

## 1. Preparation of photocatalyst

Analytical purity sublimed sulfur (S), commercial red phosphorus (P) were purchased by Sinopharm Chemical Reagent Co. Ltd. Deionized water was applied in all experiments.

Commercial P was treated by hydrothermal method at 200 °C for 10 h to eliminate most of the surface phosphorus oxide. Commercial S was recrystallized using CS<sub>2</sub> as solvent at room temperature.

S/P composite was synthesized by physically hydrothermal process. First, 0.50 g P and 0.005 g S (1 wt%) were homogeneously dispersed in 10.0 mL ethanol and stirred until liquid evaporates. Then the mixture dispersed in 35.0 mL deionized water was transferred to 50 mL Teflon-lined stainless steel autoclave and kept at 150 °C for 8 h. After centrifuging, washing and drying, the 1% S/P composite was finally prepared. Similarly, 3-9% S/P composites were also obtained.



**Scheme S1** Schematic diagram of the synthetic route of S/P composite.

## 2. Characterization

BRUKER D8 ADVANCE X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) was used to study the crystalline structures of the as-obtained samples with the scanning speed of 4°/min. The morphologies of different catalysts were tested with an FEI Sirion 200 field emission scanning electron microscope (FESEM) at the scanning voltages of 5.0 kV. Transmission electron microscope (TEM) and high resolution transmission electron microscopy (HRTEM) and selected area energy dispersive X-ray spectroscopy (EDS) of samples were analyzed by Tecnai G2 F20 transmission electron microscope with the accelerating voltage of 200 kV. The spectral absorption properties of catalysts were conducted by a UV-Vis diffuse

reflectance spectroscopy (Hitachi UV-3600). The X-ray photoelectron spectroscopy spectra (XPS) was carried out on Thermo ESCALAB 250 with Al K $\alpha$  (1486.6 eV) line at 150 W. Specific surface area values of powders were acquired from Micromeritics ASAP2020.

### 3. Photoelectrochemical measurements

Transient photocurrent (TPC) and electrochemical impedance spectroscopy (EIS) experiments were examined by an electrochemical analyzer (CHI660E, Shanghai Chenhua Instruments Co., Ltd.) accompanied with a working electrode, a Pt counter electrode and an Ag/AgCl (3.0 M KCl) reference electrode. A 300 W Xe lamp equipped with a 420 nm cut-off filter was used as the light source. Generally, 0.05 g catalysts mixed with 1.0 mL chitosan were dispersed under sonication until forming homogeneous slurry and then the homogeneous slurry was smeared evenly on the conductive surface of ITO glass, and dried at 75 °C. The size and thickness of all smeared samples were kept similar. TPC was measured with the Xe lamp irradiation on all the time using phosphate buffered saline solution (0.1 M Na<sub>2</sub>HPO<sub>4</sub> and 0.1 M NaH<sub>2</sub>PO<sub>4</sub>) as electrolytes. EIS experiment was accomplished with 0.2 M KCl solution as the electrolytes.

### 4. Photocatalytic activity measurement

The H<sub>2</sub> production measurements of different samples were conducted on photocatalytic hydrogen system with a closed gas circulatory (CEL-SPH2N, Beijing China Education Au-light co., Ltd.). In a typical process, 0.05 g photocatalyst was added to a 100 mL photocatalytic reactor containing 45 mL deionized water as solvent and 5 mL triethanolamine (TEOA) as sacrificial agent. Then, the temperature of reaction system was cooled down and kept 6 °C by a circular cooling water system and gases within circular system were pulled out by a vacuum-pumping system. After that, the reactor was irradiated for 3 h by a 300 W Xenon lamp with UV-cutoff filter ( $\lambda > 420$  nm and  $\lambda > 800$  nm) and monochromatic light filter at  $\lambda = 420, 500, 600, 700$  nm, used as light source. The produced H<sub>2</sub> was detected by a gas chromatograph (GC-7920) with a 5 A molecular sieve column and a thermal conductivity detector (TCD).

### 5. Apparent quantum efficiency calculation

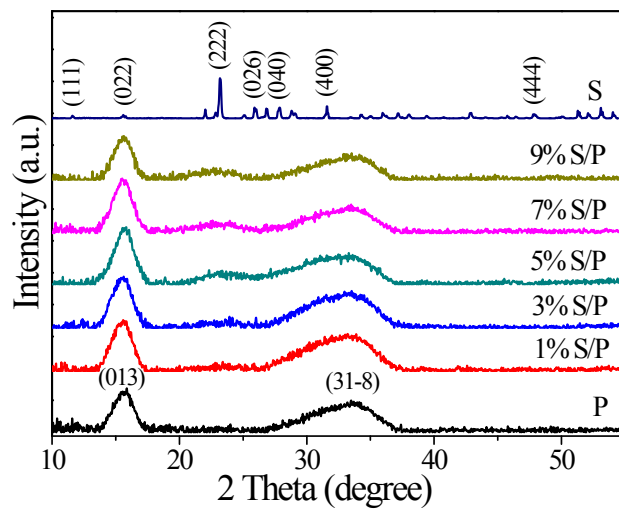
Apparent quantum efficiency (AQE) is a significant factor applied for reflecting the photon utilization in the photocatalytic process, so the AQE value<sup>1</sup> for 7% S/P sample was calculated as follows.

$$\phi_{H_2} = \frac{2 \times n(H_2) \times N_0}{N(\text{photon})} \times 100\% \quad (1)$$

$$N(\text{photon}) = F \times S \times t \quad (2)$$

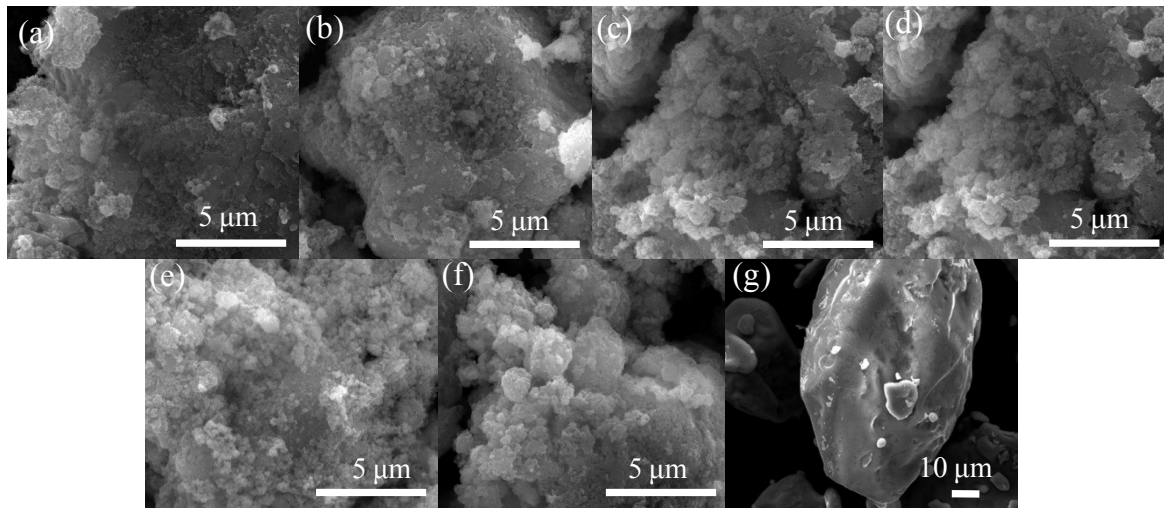
Where,  $n(H_2)$ ,  $N_0$  and  $N(\text{photon})$  refer to mole number of evolved H<sub>2</sub>, Avogadro constant and number of incident photons, respectively. Moreover,  $F$ ,  $S$  and  $t$  represent the power of light, light radiation area and illumination time, respectively. In our experiment,  $n(H_2) = 101.75 \mu\text{mol}\cdot\text{g}^{-1}$ ,  $N_0 = 6.022 \times 10^{23}$ ,  $F = 3.16 \times 10^{20} \text{ Photon}\cdot\text{m}^{-2}\cdot\text{s}$ ,  $S = 2.12 \times 10^3 \text{ m}^2$  and  $t = 14400 \text{ s}$ . Hence, the AQE value of 7% S/P composite at 420 nm monochromatic light was calculated to be 1.24%.

## 6. XRD measurement



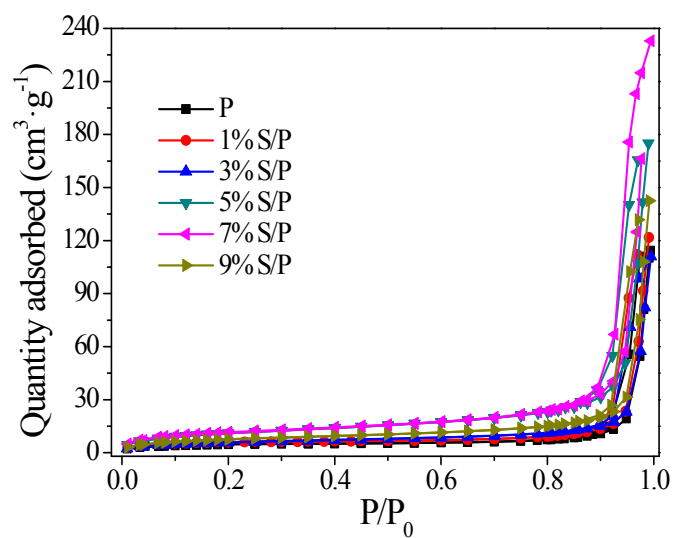
**Fig. S1.** XRD patterns of P, S and S/P composites with different S loading contents.

## 7. SEM analysis



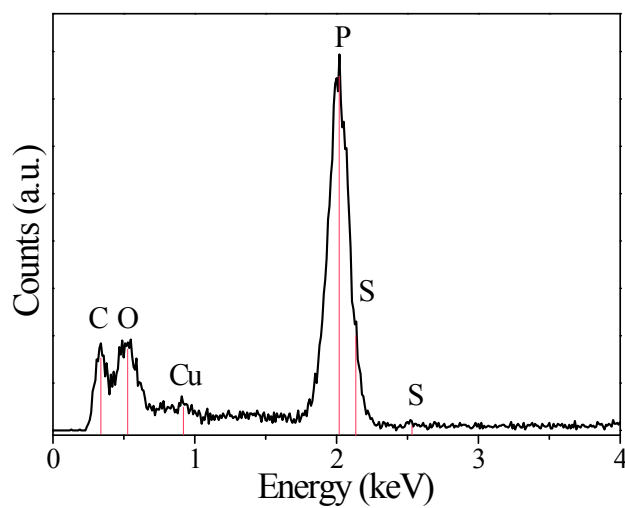
**Fig. S2.** SEM images of (a) P, (b) 1% S/P, (c) 3% S/P, (d) 5% S/P, (e) 7% S/P, (f) 9% S/P and (g) S.

## 8. BET analysis



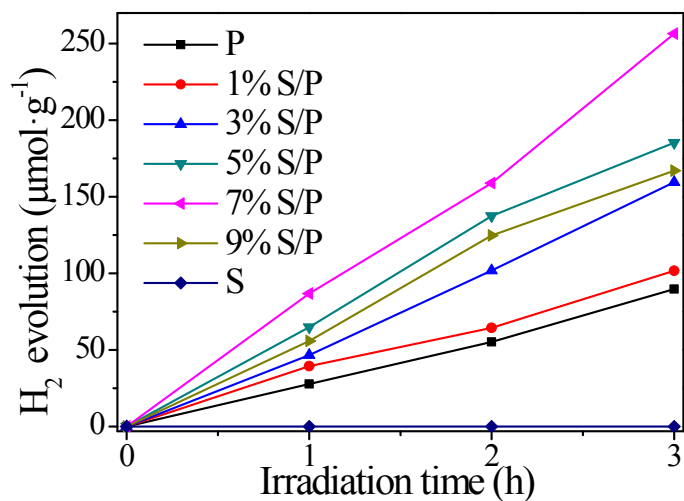
**Fig. S3.** N<sub>2</sub> adsorption-desorption isotherms of P and S/P composites.

## 9. EDS surface element analysis

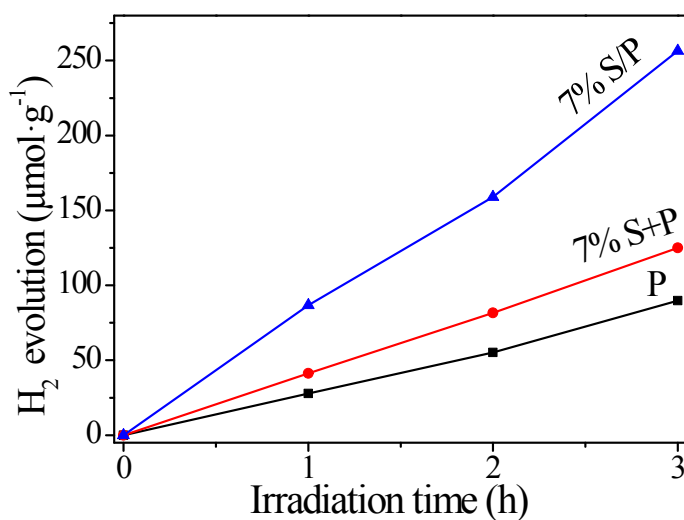


**Fig. S4.** EDS element analysis of 7% S/P composite.

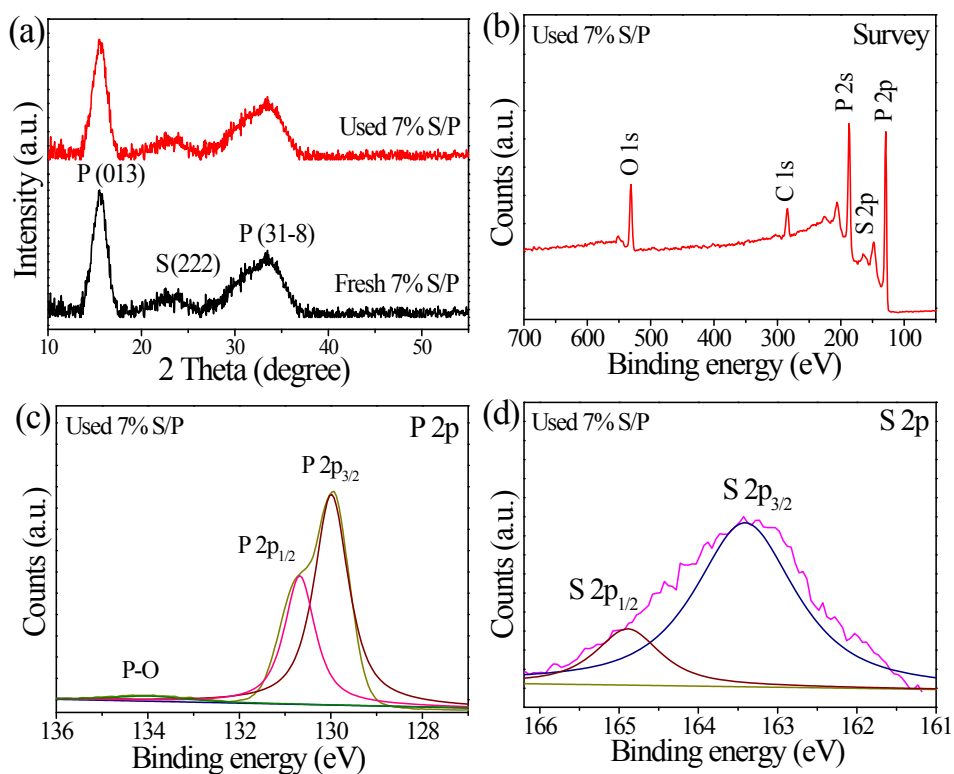
10. H<sub>2</sub> evolution analysis



**Fig. S5.** The amount of H<sub>2</sub> evolution from water splitting over P, S and S/P composites under visible light (300 W,  $\lambda > 420$  nm) in a mixture of 45.0 mL H<sub>2</sub>O and 5.0 mL TEOA as sacrificial agent.

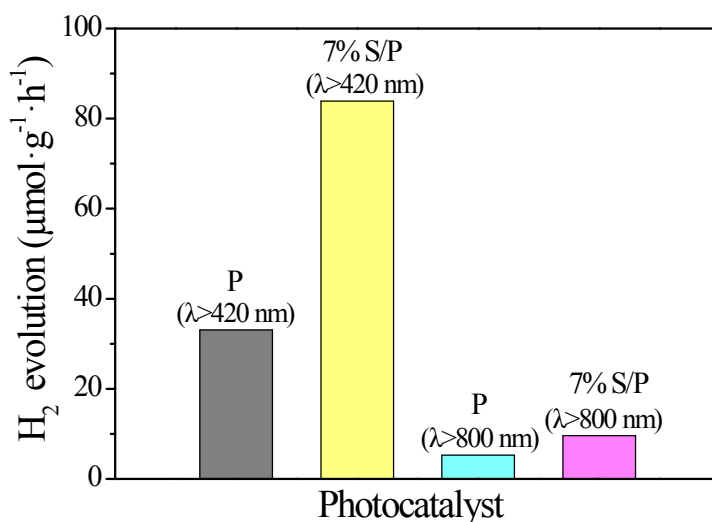


**Fig. S6.** The amount of H<sub>2</sub> evolution from water splitting of P, S/P composite and physical mixture of S+P prepared at room temperature without hydrothermal treatment (300 W,  $\lambda > 420$  nm) in a mixture of 45.0 mL H<sub>2</sub>O and 5.0 mL TEOA as sacrificial agent.



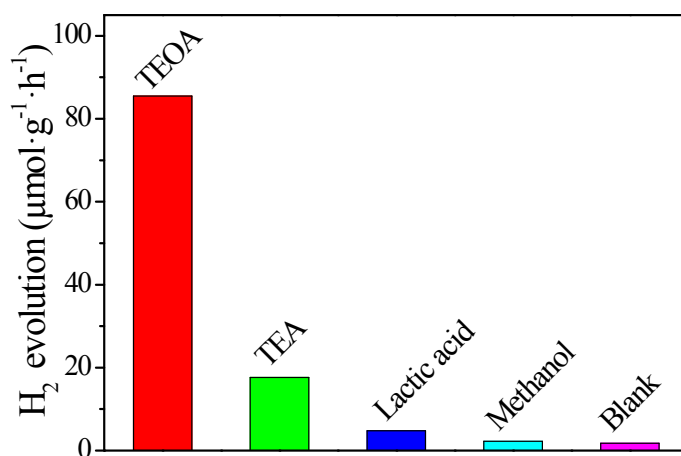
**Fig. S7.** (a) The XRD patterns of fresh and used 7% S/P composite and XPS spectra of used 7% S/P composite: (b) survey spectra, (c) P 2p and (d) S 2p.

### 11. Near-infrared light activity



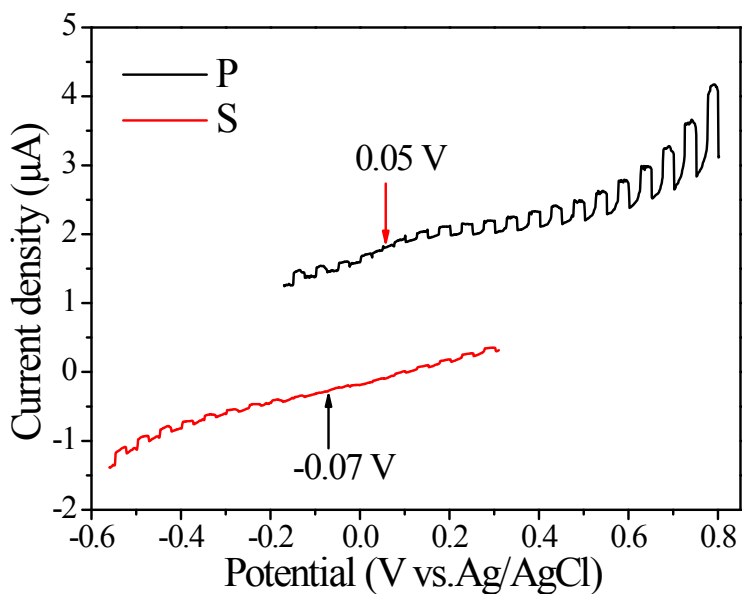
**Fig. S8.** The H<sub>2</sub> evolution rate from water splitting over 7% S/P composite under visible light (300 W, λ > 420 nm) and near-infrared light (300 W, λ > 800 nm).

## 12. Different sacrificial agent analysis



**Fig. S9.** The H<sub>2</sub> evolution rate from water splitting over 7% S/P composite under visible light (300 W,  $\lambda > 420$  nm) in a mixture of 45.0 mL H<sub>2</sub>O and 5.0 mL different sacrificial agents.

## 13. Current–potential analysis



**Fig. S10.** Current–potential curves of red P and S under visible light irradiation (300 W,  $\lambda > 420$  nm).  
Electrolyte: 0.1 M Na<sub>2</sub>HPO<sub>4</sub> and 0.1 M NaH<sub>2</sub>PO<sub>4</sub> (pH =6.8).

Red P and S demonstrate anodic and cathodic photocurrents, respectively. The onset potentials of red P and S are determined to be 0.05 and -0.07 V vs Ag/AgCl at pH 6.8. No overlap of the photocurrent can be found. Therefore, the photogenerated electrons of red P should transfer to S via type II heterostructure mechanism.

#### 14. Red P-based composites for H<sub>2</sub> generation under visible light

Table S1 The reported red P-based composites for H<sub>2</sub> generation under visible light in literatures

Photocatalyst	Sacrificial reagent	Pt	Light source	Rates for H <sub>2</sub> ( $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ )	Ref.
red phosphorus (P)	5 vol% methanol	no	300 W Xe ( $\lambda > 400 \text{ nm}$ )	1.6	[2]
P/g-C <sub>3</sub> N <sub>4</sub>	0.1M ascorbic acid	0.5 wt%	300 W Xe ( $\lambda > 420 \text{ nm}$ )	1000	[3]
P/YPO <sub>4</sub>	5 vol% methanol	1 wt%	300 W Xe ( $\lambda > 400 \text{ nm}$ )	65	[4]
Ni(OH) <sub>2</sub> /P	5 vol% methanol	no	300 W Xe ( $\lambda > 400 \text{ nm}$ )	33	[5]
S/P	10 vol% triethanolamine	no	300 W Xe ( $\lambda > 420 \text{ nm}$ )	83.86	This work

#### Reference

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