Supporting Information:

A direct Z-scheme ZnS/Co_9S_8 heterojunction-based photoelectrochemical sensor for the highly sensitive and selective detection of chlorpyrifos

Shi-Hua Chen,[†,‡,§] Xiang-Yu Xiao,[†,‡,§] Pei-Hua Li,[†,‡,§] Yi-Xiang Li,[†,‡] Meng Yang, *[,†] Zheng Guo,*[, ‖] and Xing-Jiu Huang*[,†,‡]

[†] Key Laboratory of Environmental Optics and Technology, And Institute of Intelligent Machines, Chinese Academy of Sciences, Hefei 230031, PR China

[‡]Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, PR China

[‖]Institutes of Physical Science and Information Technology, Anhui University, Hefei 230601, P. R. China

[§]S.H.C., X.Y.X. and P.H.L. contributed equally to this work.

*Corresponding author should be addressed to X.J.Huang, Z.Guo and M. Yang.

E-mail addresses: xingjiuhuang@iim.ac.cn (X.J.H.), zhguo@ahu.edu.cn (Z.G) and myang@iim.ac.cn (M.Y.)

Tel.: +86-551-65591142; fax: +86-551-65592420.

Contents

1. Experimental Section

1.1 Synthesis of Cu_2O Cubes. Typically, 30 mL of 0.1 M NaOH aqueous solution was added into 300 mL of 0.01 M $CuCl_2 \cdot 2H_2O$ aqueous solution. Half an hour later, 30 mL of 0.6 M ascorbic acid solution was added dropwise and the mixture was aged for 3 hours. The whole reaction was carried out under magnetic stirring in a water bath at 55℃. The brick-red precipitate was collected by centrifugation and washed with deionized water thrice and ethanol twice, and finally dried in vacuum at 60℃ overnight.

1.2 Synthesis of $Co(OH)_2$ hollow cages. Briefly, 200 mg Cu_2O powder was firstly dispersed in 200 mL ethanol and 200 mL aqueous solution under ultrasound for an hour. Then, 6 g PVP K30 was added into the above solution. After stirring for half an hour, 68 mg $CoCl_2 \cdot 6H_2O$ was added in the mixture under stirring in 15 min. After that, pre-configured $Na_2S_2O_3 \cdot 5H_2O$ aqueous (160 mL, 1 M) was added dropwise and the reaction continues until the solution changed from brick-red to light green. The precipitate was collected by centrifugation and washed with deionized water and ethanol trice, and finally dried in vacuum at 60℃ overnight.

2. Figures

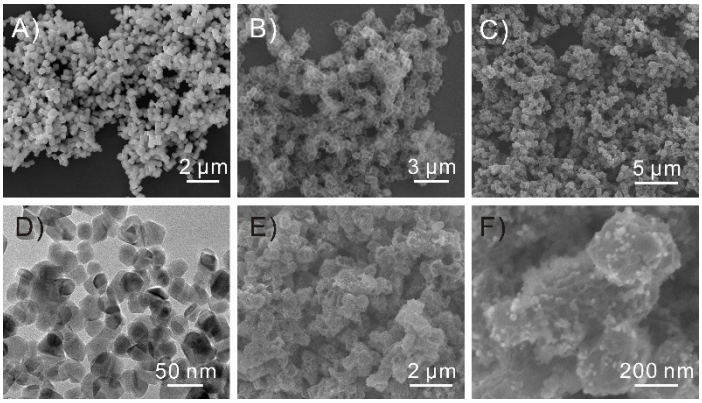

Fig. S1. FE-SEM images of A) Cu_2O cubes; B) $Co(OH)_2$ hollow cages; C) Co_9S_8 hollow cages; D)TEM image of ZnS NPs and E, F)FE-SEM images of ZnS/Co_9S_8.

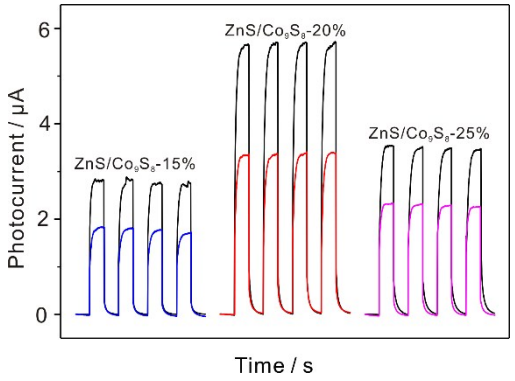

Fig. S2. Photoresponses of ZnS/Co_9S_8-x/ITO in 0.1 M PBS (pH=7) at a bias potential of 0.2 V(x=15, 20, 25 wt%) in the absence and presence of 0.2 ppb chlorpyrifos.

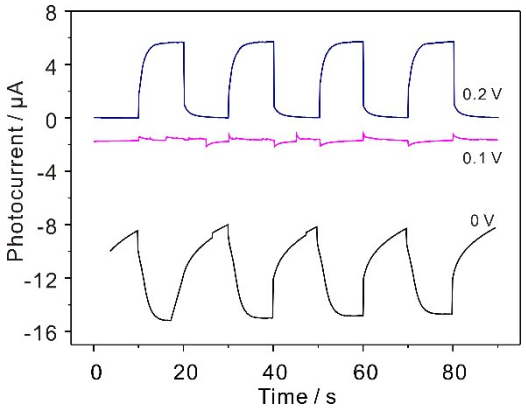

Fig. S3. Photoresponses of ZnS/Co_9S_8-based PEC sensor under different bias potentials (0 V, 0.1 V and 0.2 V).

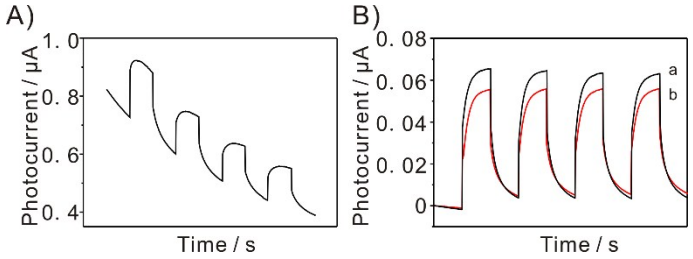

Fig. S4 A) Unstable photoresponse of the mixture of the ZnS and Co_9S_8 (20 wt%) modified ITO B) Stable photocurrents of the mixture of the ZnS and Co_9S_8 (20 wt%) modified ITO in the absence (a) and presence (b) of 0.2 ppb chlorpyrifos. in 0.1 M PBS (pH=7) at a bias potential of 0.2 V.

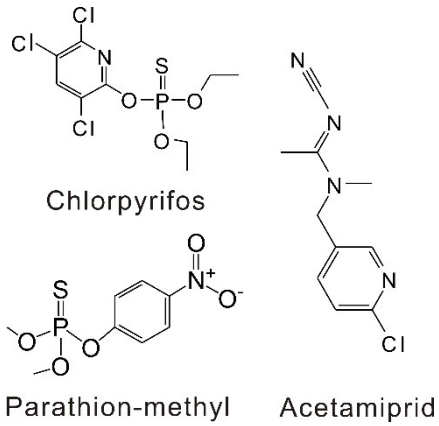

Fig. S5. Chemical structural formulas of Chlorpyrifos, parathion-methyl and acetamiprid.

3. Table

Table S1. Energy band levels of Co_9S_8 and ZnS (E vs. NHE).

Samples	**E_g(eV)**	**E_{fb}(eV)**	**E_{CB}(eV)**	**E_{VB} (eV)**
Co_9S_8	0.80	-0.853	-1.053	-0.253
ZnS	3.33	-0.323	-0.523	2.807