Supporting Information

## Synthesis of $ZnTPyP/WO_3$ nanorod-on-nanorod heterojunctions direct Z-scheme with spatial charge separation ability for enhanced photocatalytic hydrogen generation

Shuanghong Liu,<sup>a</sup> Siyu Xia,<sup>a</sup> Jiefei Wang,<sup>b</sup> Xitong Ren,<sup>a</sup> Sudi Chen,<sup>a</sup> Yong Zhong,<sup>\*a</sup> Feng Bai<sup>\*a</sup>

<sup>a</sup> Key Laboratory for Special Functional Materials of Ministry of Education, National & Local Joint

Engineering Research Center for High-efficiency Display and Lighting Technology, School of

Materials Science and Engineering, Collaborative Innovation Center of Nano Functional Materials

and Applications, Henan University, Kaifeng 475004, P. R. China;

<sup>b</sup> International Joint Centre for Biomedical Innovation, School of Life Sciences, Henan University, Kaifeng 475004, P. R. China;

E-mail addresses: zhywy8521115@163.com (Y. Zhong), baifengsun@126.com (F. Bai).



**Figure S1.** SEM images of (a) pure ZnTPyP nanorods (pH = 8.6) and (b) WO<sub>3</sub> nanorods.



**Figure S2.** TEM of ZnTPyP/WO<sub>3</sub> were prepared under different pH: (a) pH=3.06, (b) pH=8.83, (c) pH=10.96, (d) pH=11.82.



**Figure S3.** TEM images of ZnTPyP/WO<sub>3</sub> nanorod-on-nanorod heterojunctions prepared in different surfactant type: (a) SDS and (b) MTAB.



**Figure S4.** Nitrogen adsorption-desorption isotherm curve of the ZnTPyP nanorod,  $WO_3$  nanorod and ZnTPyP/WO<sub>3</sub> nanorod-on-nanorod heterojunctions.



**Figure S5.** Thermogravimetric analysis (TGA) curve for the ZnTPyP nanorod,  $WO_3$  nanorod and ZnTPyP/WO<sub>3</sub> nanorod-on-nanorod heterojunctions.



Figure S6. UV-vis diffuse reflectance spectra (DRS) of pure  $WO_3$  nanorods, ZnTPyP nanorods, and ZnTPyP/WO<sub>3</sub> (26.1 wt %).



**Figure S7.** (a) Photograph of pure WO<sub>3</sub> nanorods, ZnTPyP nanorods, ZnTPyP/WO<sub>3</sub> (26 wt %), and ZnTPyP/WO<sub>3</sub> treated with HCl aqueous solution. (b) TEM of WO<sub>3</sub>@ZnTPyP core-shell treated with NaOH. (c) TEM of ZnTPyP/WO<sub>3</sub> treated with HCl. (d) XRD of ZnTPyP/WO<sub>3</sub> treated with HCl (red) and NaOH (black). (e) Corresponding FT-IR of ZnTPyP powder, ZnTPyP nanorods, and HCl-treated ZnTPyP/WO<sub>3</sub>.



**Figure S8.** Fluorescence spectra of pure  $WO_3$  nanorods, ZnTPyP nanorods, and ZnTPyP/ $WO_3$  (26.1 wt %),  $E_x$ : 420 nm.



**Figure S9.** Representative gas chromatograph (GC) results of 1 mg photocatalysis using 50 mL different sacrificial electron donor solution with 1 wt% Pt loading: (a) 10 vol% triethanolamine (TEOA) aqueous solution, (b) 10 vol% of CH<sub>3</sub>OH aqueous solution and (c) 0.35 M Na<sub>2</sub>S/0.25 M Na<sub>2</sub>SO<sub>3</sub> aqueous solution.



Figure S10. TEM of ZnTPyP/WO $_3$  nanorod-to-nanorod nanostructures with 1 wt.% Pt co-catalyst loading.



Figure S11. STEM of ZnTPyP/WO $_3$  nanorod-to-nanorod nanostructures with 5 wt.% Pt co-catalyst loading.