## Nanostructured Bi<sub>2</sub>S<sub>3</sub>/WO<sub>3</sub> Heterojunction Films Exhibiting Enhanced Photoelectrochemical Performance

Huichao He,<sup>a, b</sup> Sean P. Berglund,<sup>a</sup> Peng Xiao,<sup>b, c</sup> William D. Chemelewski,<sup>a</sup> Yunhuai Zhang,<sup>\*b</sup> and C. Buddie Mullins<sup>\*a</sup>

<sup>a</sup> McKetta Department of Chemical Engineering and Department of Chemistry and Biochemistry, University of Texas at Austin, 1 University Station C0400, Austin, Texas 78712-0231, United States Fax: (512) 471-7060; Tel: (512) 471-5817; E-mail: mullins@che.utexas.edu

<sup>b</sup> College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400030, China.

<sup>c</sup> College of Physics, Chongqing University, Chongqing 400030, China.

\* To whom correspondence should be addressed: <u>mullins@che.utexas.edu</u> and <u>xp2031@163.com</u>



**Fig.S1** Top-view SEM images of nanostructure WO<sub>3</sub>.  $0.33H_2O$  film synthesized at a  $V_{water}$ :  $V_{ethanol}$  of (a) 6:0, (b) 5:1, (c) 4:2, (d) 3:3, (e) 2:4, (f) 1:5 and (g) 0:6. (h) Cross-view SEM image of WO<sub>3</sub>.0.33H<sub>2</sub>O nanoprism arrays on FTO-glass substrate synthesized at a  $V_{water}$ :  $V_{ethanol}$  of 3:3.



**Fig.S2** LSV scans for the as synthesized WO<sub>3</sub> films in  $0.1M \text{ Na}_2\text{SO}_4$  under backside illumination (100 mW/cm<sup>2</sup>) employing different ratios of water and ethanol volume for film growth (as indicated in the figure) and without illumination (dark). The scan rate was 50mV/s. Equal volumes of water and ethanol proved best.



Fig.S3 High resolution XPS spectrum of (a)  $O_{1s}$  and (b)  $S_{2s}$  for  $Bi_2S_3/WO_3$  heterojunction film.



**Fig.S4** Chopped LSV scans for single layer  $Bi_2S_3$  film,  $WO_3$  film and 1 layer  $Bi_2S_3/WO_3$  heterojunction film in a non-aqueous solution containing the iodide/triiodide redox couple under illumination with 100 mW/cm<sup>2</sup> white light. The solution was prepared by dissolving 10 mM I<sub>2</sub> and 50 mM NaI in ethanol. The scan rate was 50mV/s.



**Fig.S5** SEM images of an urchin-like  $Bi_2S_3$  sphere before (a) and after (b and c) the amperometric i-t measurement that was conducted in 0.1 M Na<sub>2</sub>SO<sub>4</sub> at a constant applied potential of 1.0 V *vs.* Ag/AgCl under 3600 seconds illumination with 100 mW/cm<sup>2</sup> white light.



**Fig.S6** Amperometric i-t curve for single layer  $Bi_2S_3$  film,  $WO_3$  film and 1 layer  $Bi_2S_3/WO_3$  heterojunction film in a non-aqueous solution containing the iodide/triiodide redox couple at a constant applied potential of 0.4 V vs. Ag/AgCl.



**Fig.S7** Chopped LSV scans for (a) a WO<sub>3</sub> film and (b) a one layer  $Bi_2S_3/WO_3$  heterojunction film before and after the amperometric i-t measurements that were conducted in 0.2 M NaCl mixed water-ethanol solution at a constant applied potential of 1.0 V *vs.* Ag/AgCl under illumination with 100 mW/cm<sup>2</sup> white light. The scan rate was 50mV/s.

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**Fig.S8** A typical incident light power density spectrum (from 340 - 620 nm) used for the IPCE measurements.



**Fig.S9** LSV scans for (a) single  $Bi_2S_3$  layer film and (b) 1 layer  $Bi_2S_3/WO_3$  heterojunction film in 0.2 M NaCl mixed water-ethanol solution without irradiation (dark) and under illumination with different white light intensities. The scan rate was 50mV/s. (c) The photocurrent of single  $Bi_2S_3$  layer film and 1 layer  $Bi_2S_3/WO_3$  heterojunction film in 0.2 M NaCl mixed water-ethanol solution under illumination with different white light intensities at a constant applied potential of 1.0 V vs. Ag/AgCl.



**Fig.S10** LSV scans for  $Bi_2S_3$  (only) films synthesized with different numbers of  $Bi_2S_3$  layers on FTO glass substrate in (a) 0.1M  $Na_2SO_4$  and (c) 0.2 M NaCl mixed water-ethanol solution under illumination with white light. The scan rate was 50 mV/s. IPCE spectra for  $Bi_2S_3$  films synthesized with different numbers of  $Bi_2S_3$  layers coated on FTO glass substrate in (b) 0.1M  $Na_2SO_4$  and (d) 0.2 M NaCl mixed water-ethanol solution at a constant applied potential of 1.0 V vs. Ag/AgCl.