Supporting Information

## Improving light absorption and photoelectrochemical performance of

## thin-film pho-toelectrode with a reflective substrate

Jingran Xiao<sup>a,\*</sup>, Lingling Peng<sup>a</sup>, Le Gao<sup>a</sup>, Jun Zhong<sup>a</sup>, Zhongliang Huang<sup>a</sup>, Enxian Yuan<sup>b</sup>, Vijayan Srinivasapriyan<sup>c</sup>, Shu-Feng Zhou<sup>a</sup>, Guowu Zhan<sup>a,\*</sup>

a College of Chemical Engineering, Huaqiao University, 668 Jimei Blvd, Xiamen, Fujian, 361021, P.R. China b School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou

b School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou, Jiangsu 225002, P.R. China.

c. Key Laboratory of Nanosystem and Hierarchical Fabrication, CAS Center for Excellence in Nanoscience, National Center for Nanoscience and Technology, Beijing 100190, China.

\* E-mail: xjr@hqu.edu.cn (J. Xiao), gwzhan@hqu.edu.cn (G. Zhan)



Fig. S1. Film thickness vs. hydrothermal reaction time of the hematite electrodes.



Fig. S2. (a-e) Cyclic voltammetry test of the  $Fe_2O_3$ :Ti electrodes, (f) Plots of the capacity current differences and the calculated electrochemical specific surface area ECSA values of the  $Fe_2O_3$ :Ti electrodes.



Fig. S3. (a) The LHE of bare FTO, (b) The solar irradiance spectrum of AM 1.5G (ASTM G173-03) and those weighted by the LHE spectra of  $Fe_2O_3$ :Ti electrodes.



Fig. S4. The reflectance of the Cu foil, CM and Ag foil, insert are the photographs of the three reflective substrates. (b-e) Comparison of the LHE of the  $Fe_2O_3$ :Ti electrodes with and without overlay of the Ag reflective substrate. (f) A comparison of the LHE of  $Fe_2O_3$ :Ti electrodes supported by Ag reflective substrate.



Fig. S5. Comparison of the polarization curves of the  $Fe_2O_3$ : Ti electrodes with and without overlay of the Ag reflective substrate.



Fig. S6. Comparison of the polarization curves of the  $Fe_2O_3$ :Ti180 electrode with and without Au back-layer deposition. Inset is the photograph of Au deposited  $Fe_2O_3$ :Ti180.



Fig. S7. Comparison of the incident photon-to-electron conversion efficiency (IPCE) of the  $Fe_2O_3$ : Ti electrodes with and without overlay of the Ag reflective substrate.



Fig. S8. SEM vertical and cross-section view of the (a,d)  $BiVO_4$ , (b,e)  $TiO_2$ , (c,f)  $CuBi_2O_4$  electrodes. Scale bars are 500 nm. Insets in (a-c) are corresponding photographs of the as-prepared electrode.



Fig. S9. Comparison of the LHE of (a)  $BiVO_4$ , (b)  $TiO_2$ , (c)  $CuBi_2O_4$  and (d)  $TiO_2$ +  $CuBi_2O_4$  photoelectrodes with and without overlay of the Ag reflective substrate.



Fig. S10. Schematic of the tandem cell constructed by  $TiO_2$  photoanode and the rear  $CuBi_2O_4$  photocathode with the integration of Ag reflective substrate.