Supporting Information

Sunlight-Harnessing and Storing Heterojunction TiO₂/Al₂O₃/WO₃ Electrodes

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Figure S1. EDX analyses for the cross section of $TiO_2/Al_2O_3/WO_3$ (TAW). Distance refers to the location from top (i.e., from WO3 to TiO2).



Figure S2. SEM images of (a) TiO_2/Al_2O_3 (top view) and (b) magnification of inset in (a). 0.2 M aluminum-precursor solution treated and annealed.



Figure S3. EDX analyses of TiO₂/Al₂O₃ (TA) surface treated with 0.2 M aluminum precursor.



Figure S4. EDX analyses of TiO_2/Al_2O_3 (TA) surface treated with 0.2 M aluminum precursor.



Figure S5. XPS spectra of Ti2p bands for TiO_2 and TiO_2/Al_2O_3 samples. 0.2 M aluminum precursor treated.



Figure S6. Resolved XPS spectra of O1s band for TiO_2 sample. 0.2 M aluminum precursor treated.



Figure S7. UV-Vis diffuse reflectance absorption spectra of TW before and after light on/off.



Figure S8. XPS spectrum of TAW3 electrode immersed in Cr^{6+} solution after 10.5 h from light-off (irradiation time: 0.5 h). No Cr signal was found.



Figure S9. XPS spectra of TW and TAW3 electrodes immersed in Ag^+ solution after 1.5 h from light-off (irradiation time: 0.5 h). The binding energies of these bands correspond to Ag^0 . Atomic percentages of Ag^0 are 21% (TW) and 30% (TAW).



Figure S10. Chopped linear sweep voltammograms of T, W, TW, and TAW electrodes in airequilibrated 0.1 M Na₂SO₄ electrolyte.

In n-type oxide semiconductors, conduction band level (E_{cb}) is located at ca. 0.2 V negative of flat band potential (E_{fb}) and hence both potentials are often considered same.¹ Although there are several ways to estimate the flat band potentials, one of the commonly accepted is to measure the photocurrent onset potential (E_{on}) .¹ With this in mind, we obtained chopped linear sweep voltammograms of sample electrodes to estimate their flat band potentials (Figure S10). The onset potentials of TiO_2 and WO_3 are around -0.83 and +0.03 V vs. SCE, respectively. These values correspond to -0.235 and 0.625 V vs. RHE (reversible hydrogen electrode), which are similar to the literature values $(-0.1 \text{ and } +0.41 \text{ V vs. RHE})^2$ Accordingly, the 0.2 V-difference between E_{cb} and E_{fb} is also quite acceptable. When TiO₂ and WO₃ are layer-by-layer-coupled, the onset potential is around -0.3 V vs. SCE (+0.295 V vs. RHE), which is close to the mid-point of the two onset potentials. Under a photo-steady state, photogenerated electrons move from TiO₂ to WO₃, shifting the WO₃ conduction band upwardly and creating the mid-potential (potential mixing due to Fermi level equilibration). With the Al_2O_3 -treatment, the onset potential is insignificantly changed, indicating that Al_2O_3 hardly influences the energetics of the interfacial semiconductors. The electrons at the TiO₂ side can move to WO₃ through Al₂O₃ because of the energy difference ~ 0.8 V. Upon light-off, the mixed potentials of the electrodes (TW and TAW) will be -0.3 V vs. SCE. In this situation, TiO₂ has a limited number of carriers, while WO₃ retains a number of electrons of -0.3 V vs. SCE. The backward transfer of these electrons is possible yet very slow due to the Al_2O_3 .

- 1 H.O. Finklea, Semiconductor Electrodes. Elsevier: New York, 1988.
- 2 H. Park, Y. Park, W. Kim and W. Choi, J. Photochem. Photobiol. C, 2013, 15, 1-20.