Supporting Information

Sunlight-Harnessing and Storing Heterojunction TiO$_2$/Al$_2$O$_3$/WO$_3$ Electrodes

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Figure S1. EDX analyses for the cross section of TiO$_2$/Al$_2$O$_3$/WO$_3$ (TAW). Distance refers to the location from top (i.e., from WO$_3$ to TiO$_2$).
Figure S2. SEM images of (a) TiO$_2$/Al$_2$O$_3$ (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$_2$O$_3$ (TA) surface treated with 0.2 M aluminum precursor.
Figure S5. XPS spectra of Ti2p bands for TiO$_2$ and TiO$_2$/Al$_2$O$_3$ 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).
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.\textsuperscript{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}).\textsuperscript{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\textsubscript{2} and WO\textsubscript{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 and +0.41 V vs. RHE).\textsuperscript{2} Accordingly, the 0.2 V-difference between E_{cb} and E_{fb} is also quite acceptable. When TiO\textsubscript{2} and WO\textsubscript{3} 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 TiO\textsubscript{2} to WO\textsubscript{3}, shifting the WO\textsubscript{3} conduction band upwardly and creating the mid-potential (potential mixing due to Fermi level equilibration). With the Al\textsubscript{2}O\textsubscript{3}-treatment, the onset potential is insignificantly changed, indicating that Al\textsubscript{2}O\textsubscript{3} hardly influences the energetics of the interfacial semiconductors. The electrons at the TiO\textsubscript{2} side can move to WO\textsubscript{3} through Al\textsubscript{2}O\textsubscript{3} 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, TiO\textsubscript{2} has a limited number of carriers, while WO\textsubscript{3} 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\textsubscript{2}O\textsubscript{3}.