Supporting Information

ZnWO₄/WO₃ Composite for Improving Photoelectrochemical Water Oxidation

Kevin C. Leonard, Ki Min Nam, Heung Chan Lee, Soon Hyung Kang, Hyun S. Park, Allen J. Bard⁎

Figure S1. SPECM image of a 3x6 spot array electrode of Zn/WO₃ composites under full UV irradiation. Here each column is the exact same composition of Zn/WO₃ in order to demonstrate the reproducibility of the composites. The color represents the measured photocurrent given by the scale bar below the SPECM image. The photocurrent shown is for sulfite oxidation (0.1 M Na₂SO₄ + 0.1 M Na₂SO₃ at pH 7) measured at an applied potential of +0.2 V vs. Ag/AgCl.
Figure S2. The photoelectrochemical response of bulk film electrodes characterized by linear sweep voltammetry with chopped light at 20 mV/s for sulfite oxidation (0.1 M Na$_2$SO$_4$ + 0.1 M Na$_2$SO$_3$ at pH 7). (A) 0.95 µm thick WO$_3$ and 0.97 µm thick 9% Zn/WO$_3$ under full UV irradiation; (B) 0.64 µm thick WO$_3$ and 0.66 µm thick 9% Zn/WO$_3$ under full UV irradiation; (C) 0.64 µm thick WO$_3$ and 0.66 µm thick 9% Zn/WO$_3$ under visible (>420 nm) irradiation.
Figure S3. Structural diagrams showing the structure of the monoclinic WO$_3$ and monoclinic ZnWO$_4$.

(A) WO$_3$
Figure S4. UV-Vis absorbance as a function of wavelength for a variety of film thicknesses for (A) WO$_3$, (B) 9% Zn/WO$_3$, and (C) ZnWO$_4$. 
Figure S5  (A) Scanning electron microscope image of a drop-cast 9% ZnWO₄/WO₃ composite sample. (B) Energy dispersive X-Ray spectroscopy images showing the SEM image along with elemental maps of Zn, W, and combined Zn + W for the same 9% ZnWO₄/WO₃ composite sample.
Figure S6. The photoelectrochemical response of bulk film electrodes characterized by linear sweep voltammetry with chopped light under full UV irradiation at 20 mV/s for water oxidation (0.1 M Na$_2$SO$_4$ at pH 7) for WO$_3$ and four ZnWO$_4$/WO$_3$ samples showing the order of deposition. Two sequential annealed samples one where the WO$_3$ was deposited annealed first, followed by the ZnWO$_4$ (WO$_3$/ZnWO$_4$) and one where the ZnWO$_4$ was deposited annealed first, followed by the WO$_3$ (ZnWO$_4$/WO$_3$). Also shown are two simultaneously annealed samples showing the drop-casted order (WO$_3$/ZnWO$_4$ vs ZnWO$_4$/WO$_3$).