Supporting Information

ZnWO₄/WO₃ Composite for Improving Photoelectrochemical Water Oxidation



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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 Na₂SO₄ + 0.1 M Na₂SO₃ at pH 7). (A) 0.95 μ m thick WO₃ and 0.97 μ m thick 9% Zn/WO₃ under full UV irradiation; (B) 0.64 μ m thick WO₃ and 0.66 μ m thick 9% Zn/WO₃ under full UV irradiation; (C) 0.64 μ m thick WO₃ and 0.66 μ m thick 9% Zn/WO₃ under full UV irradiation; (C) 0.64 μ m thick WO₃ and 0.66 μ m thick 9% Zn/WO₃ under full UV irradiation; (C) 0.64 μ m thick WO₃ and 0.66 μ m thick 9% Zn/WO₃ under full UV irradiation; (C) 0.64 μ m thick WO₃ and 0.66 μ m thick 9% Zn/WO₃ under full UV irradiation; (C) 0.64 μ m thick WO₃ and 0.66 μ m thick 9% Zn/WO₃ under full UV irradiation; (C) 0.64 μ m thick WO₃ and 0.66 μ m thick 9% Zn/WO₃ under visible (>420 nm) irradiation.



Figure S3. Structural diagrams showing the structure of the monoclinic WO₃ and monoclinic ZnWO₄.





Figure S4. UV-Vis absorbance as a function of wavelength for a variety of film thicknesses for (A) WO₃, (B) 9% Zn/WO₃, and (C) ZnWO₄.



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 Na₂SO₄ at pH 7) for WO₃ and four ZnWO₄/WO₃ samples showing the order of deposition. Two sequential annealed samples one where the WO₃ was deposited annealed first, followed by the ZnWO₄ (WO₃/ZnWO₄) and one where the ZnWO₄ was deposited annealed first, followed by the WO₃ (ZnWO₄/WO₃). Also shown are two simultaneously annealed samples showing the drop-casted order (WO₃/ZnWO₄ vs ZnWO₄/WO₃).