Electronic Supplementary Information

WO₃ nanosponge photoanodes with high applied bias photon-tocurrent efficiency for solar hydrogen and peroxydisulfate production

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Spectrum of illuminated solar simulator



Fig. S1: The spectra for 100 mW·cm⁻² AM1.5G (1 SUN) and simulated solar light from a 150 W Xe lamp (XES-40S2-CE, San-Ei Electric)

Determination quantity of $S_2O_8^{2-}$ in the solutions

The production of $S_2O_8^{2-}$ was evaluated by colorimetry by using the UV-VIS spectroscopy. The obtained solution specimen was mixed with equivalent amount of 0.01M FeSO₄ and 1M H₂SO₄ solution. The optical absorbance spectra was measured after the stirring of mixed solutions, and the $S_2O_8^{2-}$ quantity was evaluated from the absorption at 310

nm.

XPS spectra for the samples

The W 4f XPS for the W1, W2 and W3 are shown in Fig. S2. XPS peaks were confirmed at 35.9 and 38.0 eV in all samples without clear peak shift. These peaks can be assigned to $4f_{7/2}$ and $4f_{5/2}$ of W⁶⁺. The peaks corresponding to W⁵⁺ should be at 34.5 and 36.7 eV. These samples would contain slight W⁵⁺ due to the oxygen deficiency as predicted from the optical absorbance and Mott-Schottky plots, however, they could not be clearly detected probably by the overlapping with the strong W⁶⁺ signals.





Fig. S3: The J-V curve of WO₃ photoanodes under 1 Sun illumination from the back side of photoanode.

Stability of photoanode W3

Figure S4 shows the *J-t* curve for the PEC test of W3 under 1 Sun illumination at 1.5 V_{RHE} for 60 min. The test was repeated twice. The W3 photoanode was washed by distilled water and dried by N₂ stream after 1st run, and then reused for 2nd run.



Fig. S4: The *J*-*t* curve of W3 under 1 Sun illumination from the back side of photoanode.

Figure S5 shows the SEM images for the surface and cross-section of W3 photoanode after the PEC test under 1 Sun illumination at 1.5 V_{RHE} for 120 min.



Fig. S5: The SEM for the W3 after the PEC test for 120 min.

LHE, R and T spectra for the W3

The LHE was calculated by following equation: LHE (%) = 100 - R(%) - T(%). The *R* and *T* were reflectance and transmittance measured by UV-Vis spectrometer with the integrating sphere, respectively.

