Supporting Information

Surface Interrogation Scanning Electrochemical Microscopy (SI-SECM) of Photoelectrochemistry at a W/Mo-$BiVO_4$ Semiconductor Electrode – Quantification of Hydroxyl Radicals During Water Oxidation

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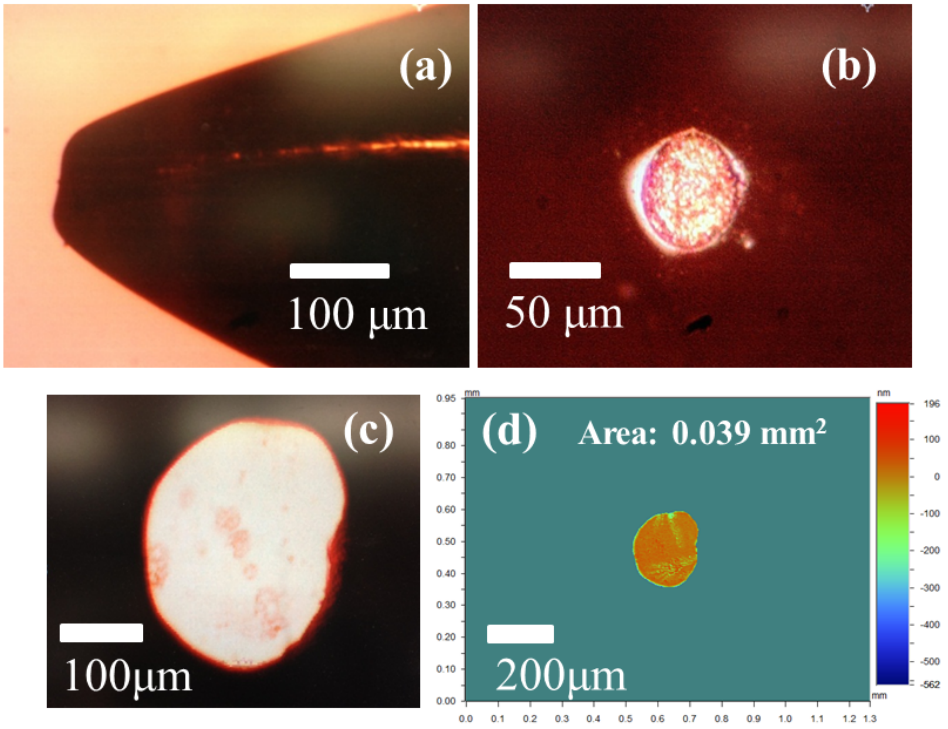

Figure S1. Optical microscopic images of Au UME from side (a) and top (b), and the image of the W/Mo-$BiVO_4$ photoanode covered by the insulating layer (c). Optical surface profiler images of the photoanode (d) that is identical W/Mo-$BiVO_4$ shown in (c). The optical profiler was used to measure the exposed area of the photoanode (0.039 mm^2) and to measure the thickness of the insulating Teflon layer on the photoanode (~ 20 µm).

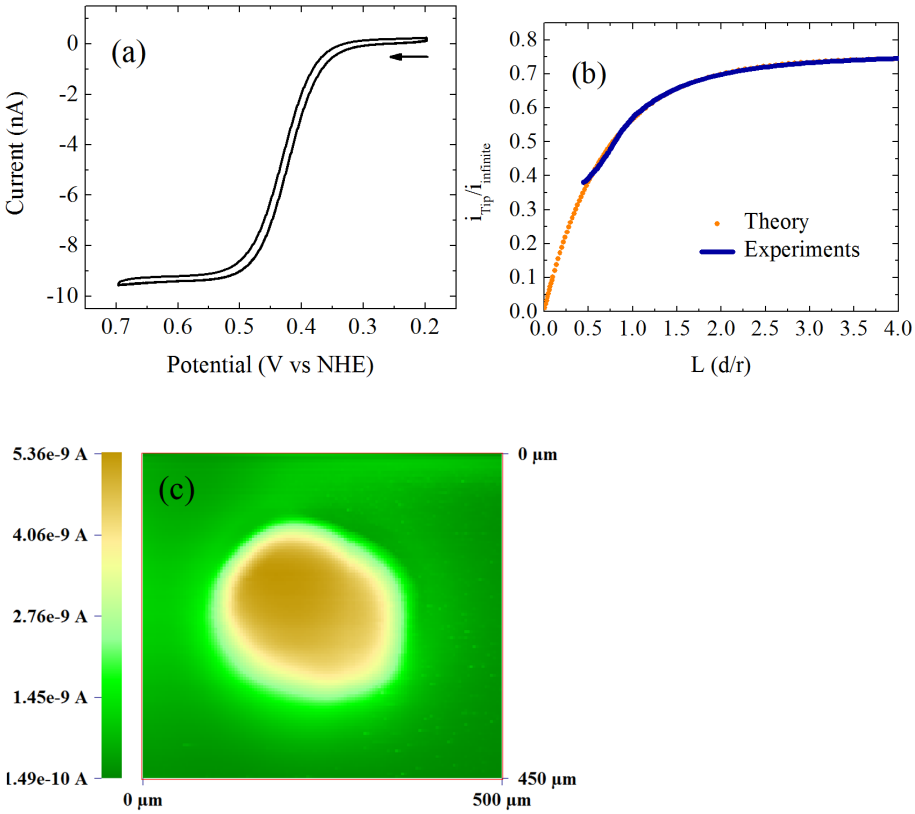

Figure S2. Cyclic voltammogram (CV) (a), approach curve (b, blue solid line) of Au UME, and SECM image of TC-SG experiments on W/Mo-$BiVO_4$ (c) in a 1 mM ferrocenemethanol (FcMeOH) and 0.1 M KCl aqueous solution. CV was measured in bulk solution with a scan rate of 20 mV s^{-1} in (a). For the approach curve in (b), the tip moved toward the insulating substrate with the increment distance of 1 µm per 0.2 s. The tip potential was 0.7 V (vs NHE). The theoretical curve (yellow dots) in (b) was obtained with R_g=2. (Sun, P.; Laforge, F. O.; Mirkin, M. V. *Phys. Chem. Chem. Phys.* **2007,** *9,* 802–823.) *d* is the distance between the tip and the substrate, and *r* is the radius of the tip, i.e. 25 µm. For TC/SG-SECM in (c), tip potential was held at 0.3 V and the substrate was at 0.4 V under UV-Visible irradiation. Scan rate was 20 µm

s^{-1} with the increment distance of 4 μm and the increment time was 0.2 s. The tip was placed about 12 μm above the substrate.

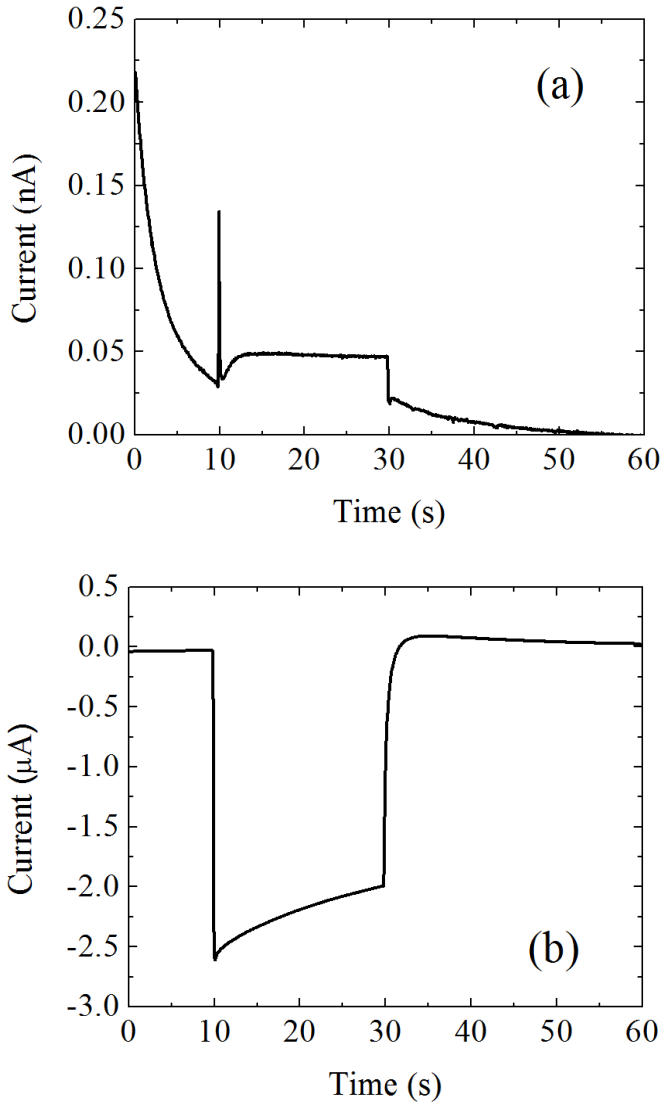

Figure S3. Tip collection for oxygen reduction at Au UME (a) and substrate generation for water oxidation at W/Mo-$BiVO_4$ (b) in 0.1 M Na_2SO_4 aqueous solution (0.2 M phosphate buffer, pH 7). The potential of tip was at 0.5 V (vs NHE) and W/Mo-$BiVO_4$ was held at 0.6 V. The irradiation was switched on from 10 to 30 s with an ELH lamp (300 W) through the light guide (diameter of 3 mm) in the experimental configurations shown in Figure 1. Au UME tip with a diameter of 50 μm was used and the area of W/Mo-doped $BiVO_4$ was larger than that used in Figure 8 to increase the generation current.

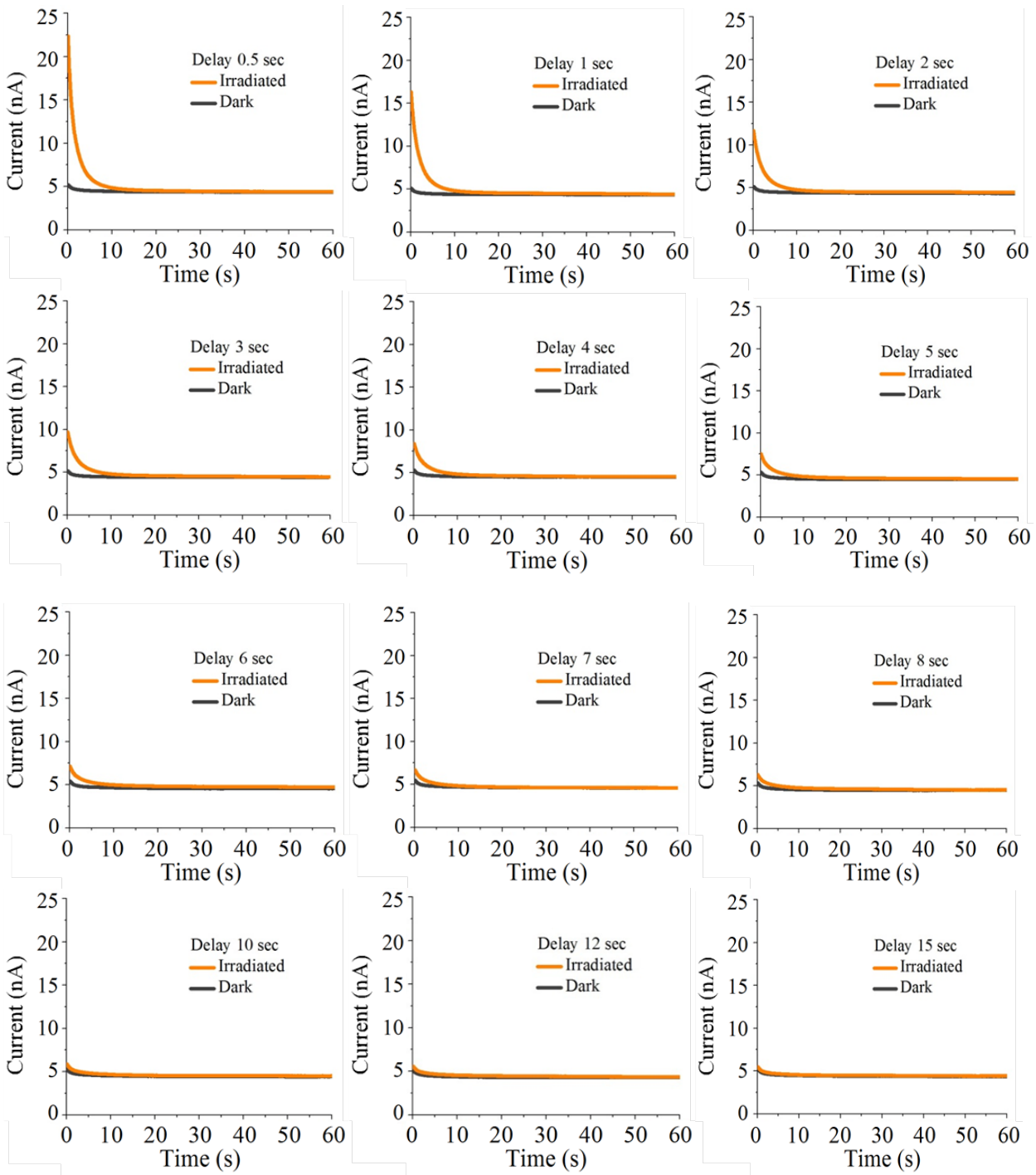

Figure S4. Chronoamperograms (CAs) of surface interrogation using Au UME on the W/Mo-$BiVO_4$ electrode with different decay times from 0.5 s to 15 s after UV-Visible irradiation for 5 s (yellow). CA of that without the irradiation is shown as a grey solid line. The potential of Au

UME was 0.5 V (vs NHE) and the W/Mo-$BiVO_4$ was held at 0.6 V during the irradiation. The potential and experimental configurations for the measurements was set as shown in Figure 1. Measurements were done in 1 mM K_2IrCl_6 and 0.1 M Na_2SO_4 aqueous solution. Au UME was placed about 12 μm above W/Mo-$BiVO_4$.

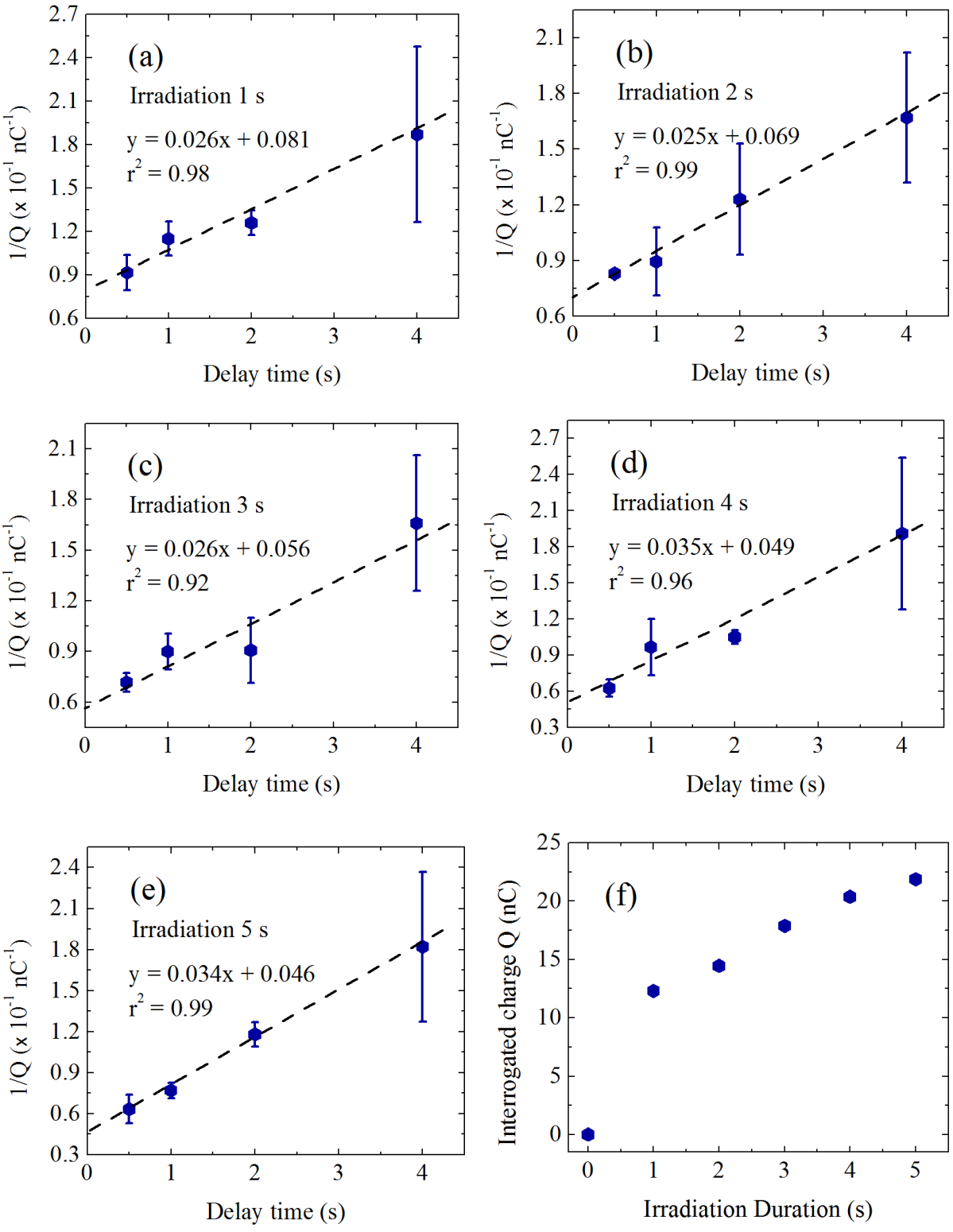

Figure S5. Interrogated charges of OH• at W/Mo-$BiVO_4$ with various irradiation durations of (a) 1, (b) 2, (c) 3, (d) 4, and (e) 5 s. For each measurement, four different decay times were allowed

from 0.5 to 4 s. Experimental configurations were identical with that shown in Figure 1 and Figure 6 except the duration of UV-Visible irradiation. The interrogated charge of the OH• was summarized in (f) for the different irradiation time. Electrode area of W/Mo-$BiVO_4$ or the collection factor of the interrogation experiments were not considered in the results shown in (f).

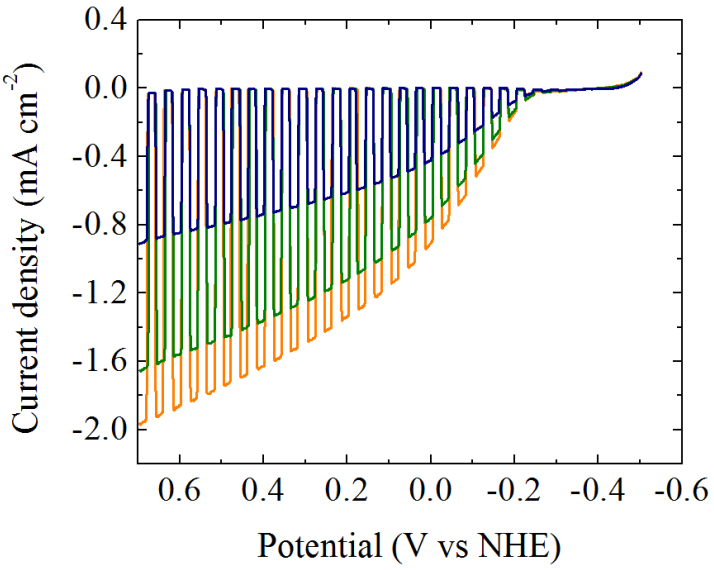

Figure S6. Linear sweep voltammogram of W/Mo-$BiVO_4$ with chopped light under UV-Visible irradiation in 0.1 M Na_2SO_4 and 0.1 M Na_2SO_4 aqueous solution (pH 7). Beam intensity was gradually increased from 100 (blue), 300 (green) to 400 mW cm^{-2} (yellow) with full output from a xenon lamp. Scan rate was 20 mV s^{-1}.