Electronic Supplementary Information for: "Water Photolysis with a Cross-linked Titanium Dioxide Nanowire Anode"

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1. Energy dispersive X-ray spectroscopy (EDS)

The EDS measurement was performed on a Zeiss Ultra55 field emission scanning electron microscope (10 kV electron beam) equipped with an energy dispersive spectrometer. The sample was a 20-μm thick TiO_2 nanowire film that was thermally annealed in forming gas at 600°C for 2 minutes. The EDS spectrum and the corresponding elemental analysis are shown in Figure S1. Quantitative analysis of the EDS spectrum shows that the atomic ratio of titanium to oxygen is close to the stoichiometric 1:2 with slightly lower oxygen content, suggesting the presence of oxygen vacancies. The spectrum taken with a 15 second collection time (Figure S1(a)) shows the absence of carbon and nitrogen in the sample, whereas the spectrum with a 30 second collection time (Figure S1(b)) illustrates the presence of trace amounts of carbon (~1 wt%) and no nitrogen. These data suggest that the trace carbon comes from the breakdown of organic contaminants due to electron irradiation and that PVP used during the synthesis is completely removed via calcination in air.

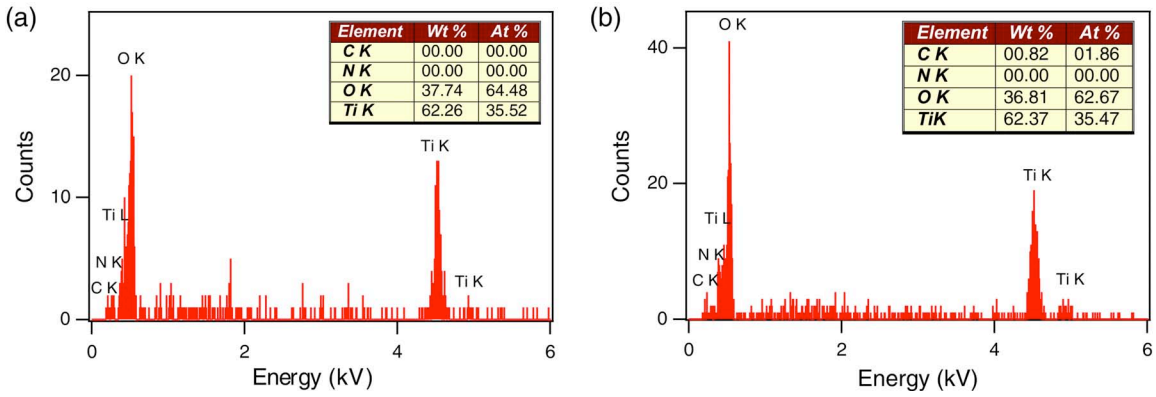

Figure S1. EDS spectra of a cross-linked TiO_2 nanowire film after thermal annealing, with data collection times of (a) 15 seconds and (b) 30 seconds.

2. Water photolysis in 1 M and 10 mM NaOH.

Figure S2(a) shows current-potential curves for a 22-μm thick TiO_2 nanowire thin film under simulated AM 1.5 G illumination in different electrolytes: 1 M NaOH, 10 mM NaOH, and 10 mM NaOH + 0.5 M Na_2SO_4. In the latter case Na_2SO_4 was added to compensate the ionic concentration of the electrolyte solution. All curves have a similar shape, although the curves for solutions with lower pH show a higher photocurrent onset potential in accordance with the Nernst relation. There is a significant drop of photocurrent by switching the electrolyte from 1 M NaOH to 10 mM NaOH, which is mainly due to the greater degree of photoanode polarization in the 10 mM NaOH. The lower conductivity of the 10 mM NaOH also makes a small contribution: adding 0.5 M Na_2SO_4 to compensate the lower ionic concentration increases the photocurrent up by 20%, which is significantly lower than the photocurrent in 1 M NaOH. We also studied the power dependence of the photocurrent in the 10 mM NaOH + 0.5 M Na_2SO_4 solution (Figure S2(b)) at the thermodynamic potential threshold for oxygen evolution, which shows the same saturation behavior as the 10 mM NaOH with a photocurrent that is about 20% higher at each incident light intensity. These data indicate that the significant saturation behavior seen in the 10 mM NaOH (Figure 2(d)) is not due to its lower total ion concentration but is controlled by the OH^- diffusion near the photoanode.

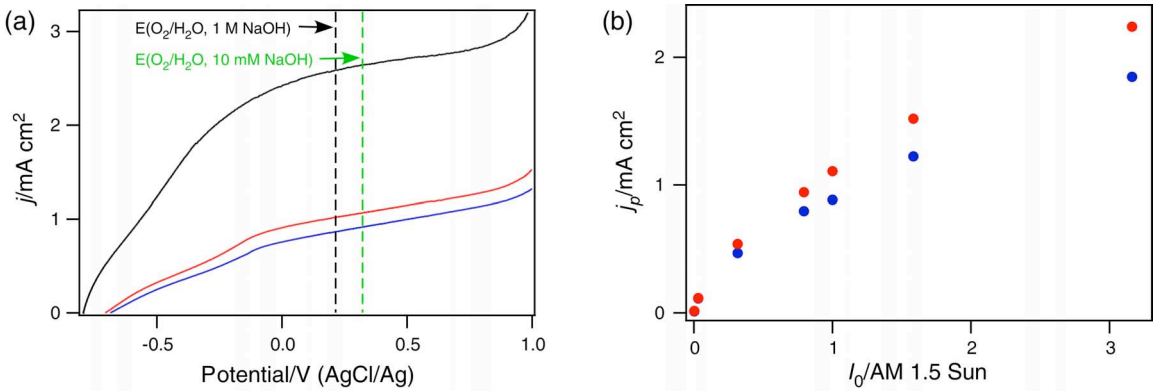

Figure S2. (a) Current density (j) - potential curves in simulated AM 1.5 illumination for a 22-μm TiO_2 nanowire thin film in 1 M NaOH (black line), 10 mM NaOH (blue line), and 10 mM NaOH + 0.5 M Na_2SO_4 (red line) electrolytes. The thermodynamic potential thresholds for oxygen evolution are labeled by the vertical black (green) line for the 1M (10 mM) NaOH solution. (b) Power dependence of the photocurrent density (j_p) at the thermodynamic potential threshold for oxygen evolution in 10 mM NaOH (blue dots) and in 10 mM NaOH + 0.5 M Na_2SO_4 (red dots) electrolytes.

3. Diffuse reflectance spectrum.

The diffuse reflectance spectrum was measured with a 3100K halogen lamp with a spectral range of 340nm – 2000nm. The collimated beam from the lamp illuminated the sample at a 45^{o} incident angle. The diffusely reflected light was collected by a 10x microscope objective and focused on the entrance slit of a grating spectrometer. The spectrum was recorded on a high-sensitivity charge coupled device (CCD) camera. A reference spectrum was taken by directly measuring the output beam of the light source at normal incidence. The reflectivity is then calculated as the ratio of the sample spectrum to the reference spectrum. The data is normalized so that the reflectivity of the TiO_2 nanowires before the thermal annealing reaches unity at long wavelengths (Figue 3(b)). This normalization procedure is reasonable as the TiO_2 nanowires appear white before the thermal annealing.