Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

SUPPORTING INFORMATION

WO_3-α-Fe_2O_3 composite photoelectrodes with low onset potential for solar water oxidation

Peng Zhao,[1] Coleman X. Kronawitter,[2] Xiaofang Yang,[2] Jie Fu,[1] Bruce E. Koel[2,*]

[1]Department of Chemistry, [2]Department of Chemical and Biological Engineering, Princeton University, Princeton, New Jersey 08544, United States

Experimental Section

Film preparation

Films were deposited onto transparent conducting fluorine-doped tin oxide (FTO) coated glass substrates (Pilkington, TEC15) by simultaneous sputter-deposition of α-Fe_2O_3 and WO_3 targets (2" diameter × 0.125" thick disk, 99.9%, AJA International) using a AJA Dielectric Sputterer. The substrate was held at room temperature and under high vacuum conditions (~10^{-6} Torr) with a 3:1 O_2 and Ar mixture as the sputtering gas. The substrate holder could be rotated, and the source to substrate distance was 20 cm. After deposition the samples were annealed in 1-atm O_2 at temperatures ranging from 300 to 800 °C for 4 h in a box furnace. The temperature was brought from room temperature to the desired annealing temperature at a rate of 20 °C/min, and the samples were allowed to cool naturally after the desired hold time was reached.

Film characterization

The morphology and composition of the samples were characterized by a high-resolution SEM (FEI Quanta 200 FEG Environmental-SEM) along with an EVEX EDX system, using a 10 kV focus voltage. The FEI Quanta 200 FEG SEM was also used to perform EDS. XRD patterns were acquired with a Rigaku MiniFlex X-Ray Diffractometer using Cu Kα radiation. The visible absorption spectra of the materials were recorded with a Hitachi U-3010 Spectrometer using a blank FTO-coated glass substrate as a baseline standard. Raman spectroscopy was undertaken using a HORIBA Jobin Yvon LabRAM HR (with 632.8 nm He-Ne laser) Raman spectrophotometer. XPS data were collected using a PHI 10-360 spherical capacitor analyzer (SCA) and an Al Kα X-ray source.

Electrochemical testing

The electrochemical and photoelectrochemical properties of each sample were tested using a three-electrode electrochemical cell with a Ag/AgCl reference electrode and Pt wire counter electrode. The working electrode (photoanode with a WO_3-α-Fe_2O_3 film), with an illuminated area of 0.5 cm^2, was immersed in 0.5 M Na_2SO_4 under simulated AM 1.5 illumination on the front-side using a 100 W Xe lamp (Osram). The photoresponse was measured by a potentiostat (Princeton Applied Research). The scan rate for cyclic voltammetry was 50 mV/s. A monochromator (Oriel) was also employed to study the spectral response and was used in conjunction with a power meter and photodiode (Newport) to calculate IPCE.

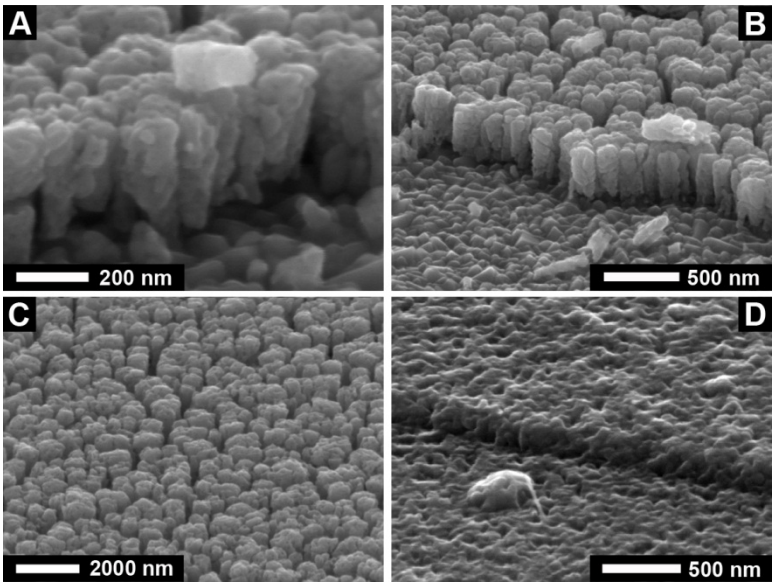

Figure S1. SEM images of WO_3-α-Fe_2O_3 samples (A, B, C) and α-Fe_2O_3 samples (D) annealed at 700 ^oC. All images are side views obtained at 65^o tilt.

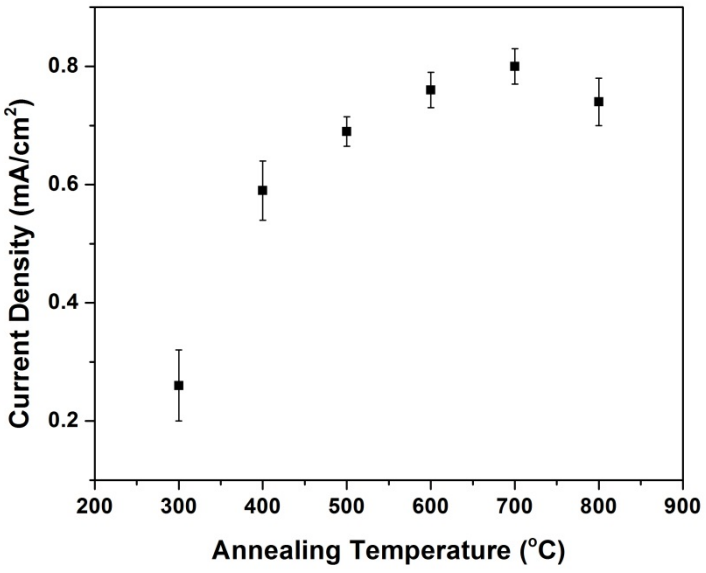

Figure S2. Change in the photocurrent at 0.40 $V_{Ag/AgCl}$ (1.01 V_{RHE}) of WO_3-α-Fe_2O_3 films prepared at increasing annealing temperatures. The photocurrent measurements were performed in 0.5 M Na_2SO_4 in the dark and under AM 1.5 illumination.

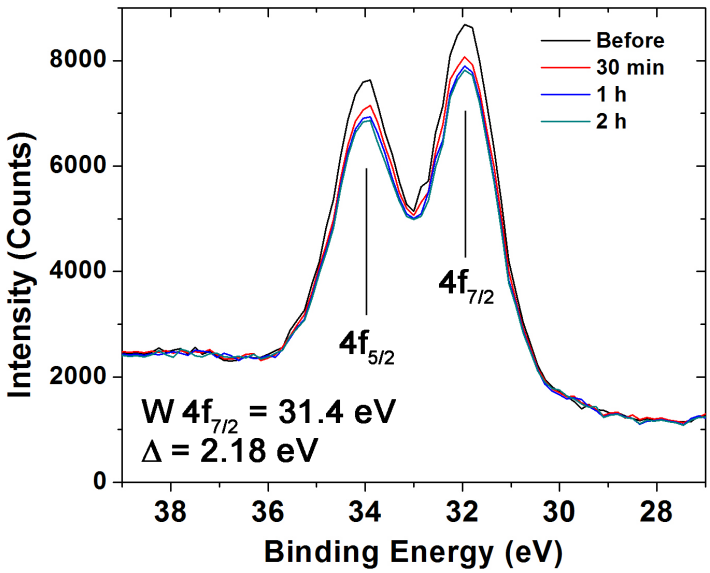

Figure S3. W 4f region in XPS scans of WO_3-α-Fe_2O_3 films before and after 30 min, 1 h, and 2h of photoelectrochemical reaction in Na_2SO_4 solution.