

Dense layers of vertically oriented WO₃ crystals as anodes for photoelectrochemical water oxidation

Supporting Information

Dong-Dong Qin,^a Chun-Lan Tao,^b Stuart A. Friesen,^c Tsing-Hai Wang,^c Oomman K. Varghese,^c Ning-Zhong Bao^d, Zheng-Yin Yang,^{a*} Thomas E. Mallouk,^{c*} and Craig A. Grimes^{d*}

Experimental section

Tungsten foil (99.99% pure, 0.25 mm thick), nitric acid and hydrochloric acid were purchased from Sigma Aldrich. Tungsten foil was immersed in a 10 mL solution containing nitric acid and hydrochloric acid in a volume ratio of 1:3 in a 23 mL Teflon-lined autoclave at 80 °C for 2-17 hr. After cooling to room temperature, the as-formed oxide film on the tungsten substrate was rinsed with DI water and dried with N₂. Sample annealing was conducted at 500 or 700 °C for 2 hr in air at a ramp rate of 2 °C /min. The morphology of the samples was imaged using a field-emission scanning electron microscope (FE-SEM; JSM6700F, JEOL). Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were performed using a Phillips EM 420 instrument. X-ray diffraction (XRD) patterns were measured using a Scintag X2 diffractometer (Cu K α radiation, $\lambda = 1.5418 \text{ \AA}$). Diffuse reflectance UV-vis spectra were recorded with a Perkin-Elmer Lambda 950 spectrophotometer. Linear sweep voltammetry was obtained at a scan rate of 50 mV/s using a BAS 100B electrochemical workstation. Photoelectrochemical properties were investigated in a three-electrode configuration with a WO₃ film as the working photoelectrode, Ag/AgCl (3 M NaCl) as the reference and platinum foil as the counter electrode in 0.1 M Na₂SO₄. Sunlight was simulated with a 300 W xenon lamp (Spectra Physics) and AM 1.5 filter (Oriel). The light intensity was set using an

NREL-calibrated crystalline silicon solar cell. Electrochemical impedance spectroscopy (EIS) was performed using a Solartron 1260 Impedance/Gain-Phase Analyzer and capacitance data were fit using ZView software. The superimposed ac signal was maintained at 10 mV while the frequency was scanned between 100 KHz to 0.1 Hz at potentials between -0.3 and 0.1 V vs $V_{Ag/AgCl}$ in the dark and under illumination in a 0.1 M Na_2SO_4 electrolyte. The incident photon conversion efficiency (IPCE) was measured using a 300 W xenon lamp (Spectra Physics) integrated with parabolic reflector, passing the light through a monochromator, at 0.5 V DC bias; an Oriel-calibrated silicon photodiode was used to measure the incident light power density. Samples were measured using a WO_3 film as the working photoelectrode and platinum foil as the counter electrode in 0.1 M Na_2SO_4 .

Fig. S1

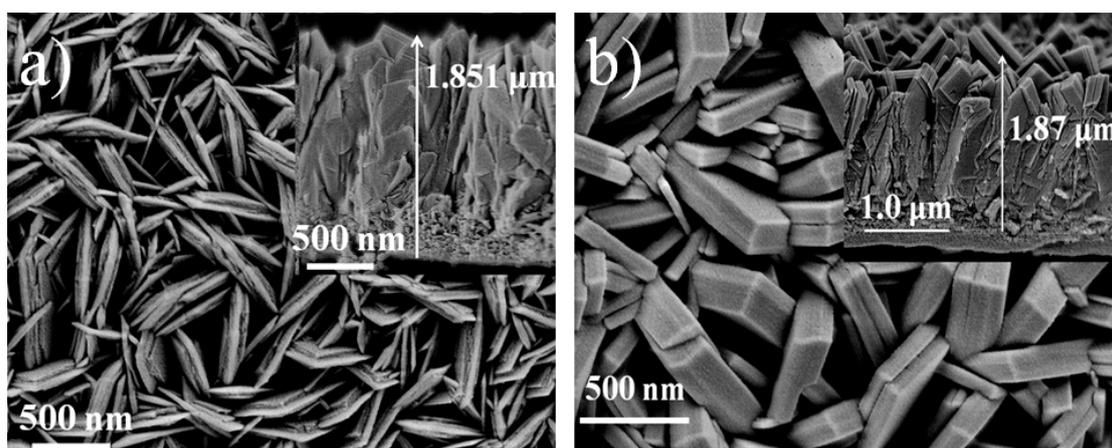


Fig. S1 FE-SEM images of samples fabricated for durations of 2 hr (a) and 8hr (b).

Fig. S2

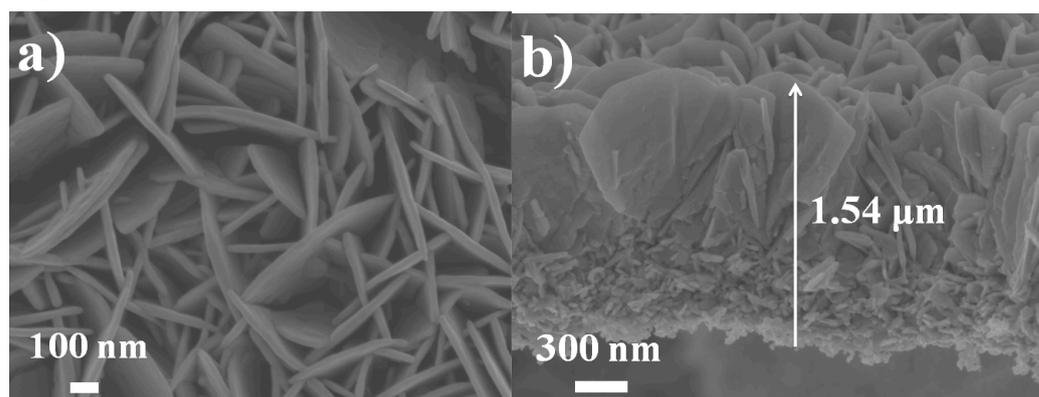


Fig. S2 FE-SEM images of 2h samples annealed at 500 °C. (a) top view and (b) cross-sectional view.

Fig. S3

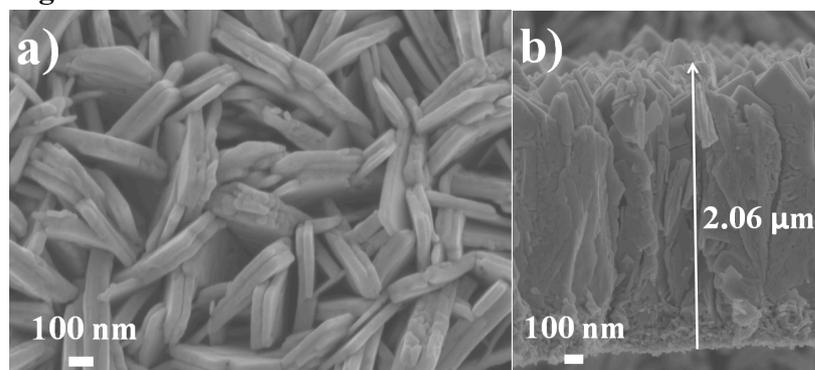
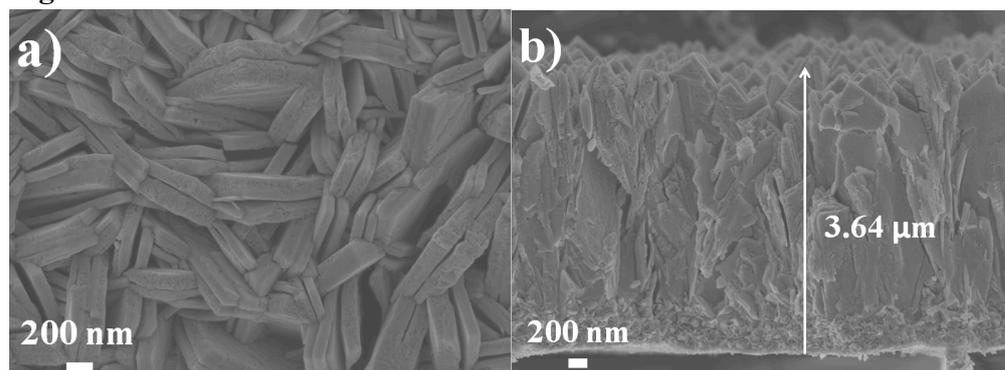


Fig. S3 FE-SEM images of 8h samples annealed at 500 °C. (a) top view and (b) cross-sectional view.

Fig. S4



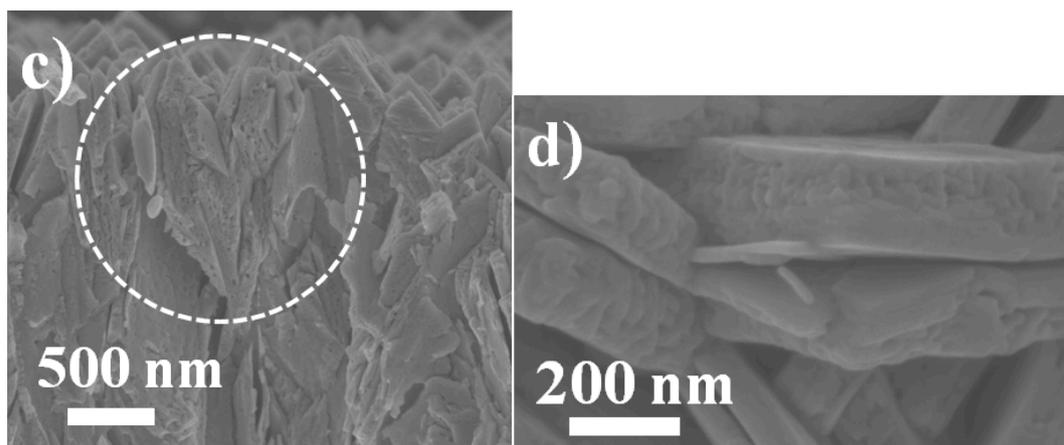


Fig. S4 FE-SEM images of 17h samples annealed at 500 °C. (a) top view; (b) cross-sectional view; (c) is a magnification of (b), white dashed line marks the mesoporous features; (d) is magnification of (a), showing the nanoparticulate morphology of the flakes.

Fig. S5

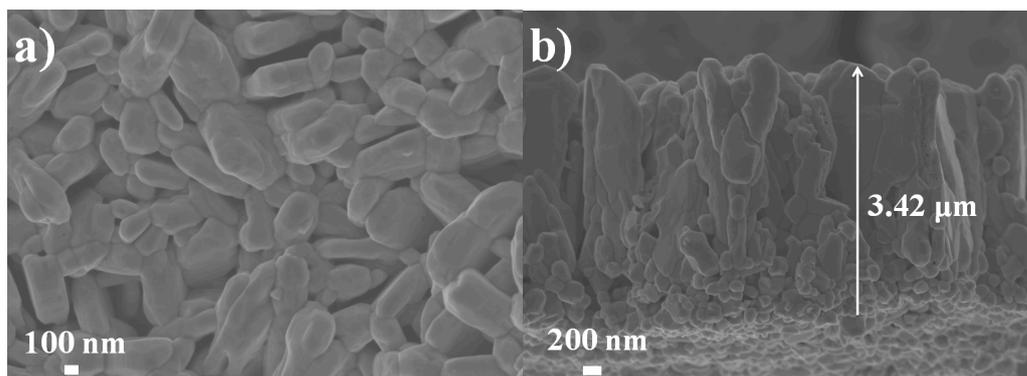


Fig. S5 FE-SEM images of 17h samples annealed at 700 °C. (a) top view and (b) cross-sectional view.

Fig. S6

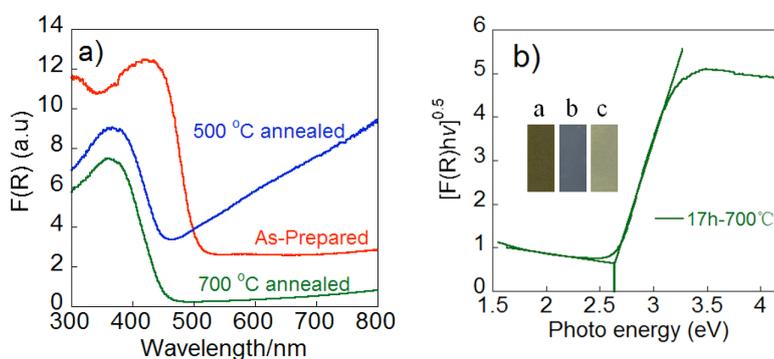


Fig.S6 (a) Reflectance spectra of 17 h samples. (b) Plot of the square root of the Kubelka-Munk function $F(R)$ vs. photon energy for a 17 h sample annealed at 700 °C. Inset shows photographs of 17 h samples, a: as-prepared; b: annealed at 500 °C and c: annealed at 700 °C.