

Supplementary Information for:

STABILIZATION OF N-CADMIUM TELLURIDE
PHOTOANODES FOR WATER OXIDATION TO O₂(g) IN
AQUEOUS ALKALINE ELECTROLYTES USING
AMORPHOUS TiO₂ FILMS FORMED BY ATOMIC-
LAYER-DEPOSITION

MICHAEL F. LICHTERMAN^{1,2}, AZHAR I. CARIM¹, MATTHEW T. MCDOWELL^{1,2}, SHU HU^{1,2},

HARRY B. GRAY^{2,3}, BRUCE S. BRUNSCHWIG^{1,3}, AND NATHAN S. LEWIS¹⁻⁴

¹Division of Chemistry and Chemical Engineering

²The Joint Center for Artificial Photosynthesis

³Beckman Institute

⁴Kavli Nanoscience Institute

California Institute of Technology

Pasadena, CA 91125

S1. Contents

This document contains detailed descriptions of the experimental procedures used in this work (Section S2), photoelectrochemical data detailing the effect of Br₂/CH₃OH etching on photoelectrode performance (Section S3), energy dispersive X-ray spectroscopy of the interface of an n-CdTe/TiO₂/Ni electrode (Section S4), X-ray photoelectron spectroscopic analysis of the Br₂/CH₃OH etched n-CdTe surface (S5), and photoelectrochemical data describing the stability of n-CdTe/Ni electrodes in comparison to n-CdTe/TiO₂/Ni electrodes (Section S6)

S2. Experimental Methods

Preparation of Electrodes

CdTe pieces were cut from an n-CdTe(111) (carrier concentration $5.5 \times 10^{17} \text{ cm}^{-3}$) wafer that had previously been polished and contacted at the back with evaporated In. Pieces were etched for 30 s in a freshly prepared solution of Br_2 (Sigma Aldrich, 99.999%)/ CH_3OH (EMD Millipore, >99.9%) dissolved in CH_3OH , rinsed vigorously with CH_3OH , and immersed in CH_3OH until being dried with a stream of $\text{N}_2(\text{g})$ before being placed in the atomic-layer deposition (ALD) chamber (Cambridge Nanotechnology). TiO_2 was deposited by ALD using H_2O and tetrakis(dimethylamido)titanium(IV) (TDMAT) (Sigma, 99.999%). A 0.1 s pulse of TDMAT was followed by a 15 s purge with $\text{N}_2(\text{g})$ at 20 sccm, followed by a 0.015 s pulse of H_2O and another 15 s purge. The coating cycle was repeated 2500 times, and the deposition was performed out at 150°C . Substantial experimentation was performed to optimize this system, and varying the ALD temperatures generally resulted in poorer or completely nonconductive films. The results presented herein are currently the most optimized results from these experiments thus far. Ni deposition was performed in a sputterer (AJA International) under an Ar atmosphere at 8.5 mtorr. RF power was used with the Ni target (Kurt Lesker, 99.995%) to deposit $\sim 2 \text{ nm}$ of material.

Final assembly of the electrodes began with application of Ga-In eutectic (Sigma Aldrich, 99.99%) onto the back of the n-CdTe, followed by use of Ag paint (SPI Supplies) to contact the sample to a Cu wire. The area around the wire and n-CdTe was then coated with non-conductive epoxy (Hysol 9460). Electrode areas were derived from computer captured optical images analyzed with ImageJ software.

Electrode Characterization

Spectral response data were collected using a 300 W Xe lamp in conjunction with a monochromator (Newport Oriel Instruments) and lock-in amplifiers (Stanford Research Instruments). The voltammetry, chronoamperometry, and electrochemical impedance experiments were performed using a Bio-Logic SP-200 potentiostat.

Voltammetric measurements in pH 14 KOH (aq) were performed using a 3- or 4-necked 50-mL round-bottom flask that had been modified with a planar quartz window. The power of the Xenon lamp (Newport) used for illumination was adjusted to produce the desired incident illumination power. A ground glass diffuser ensured a uniform illumination intensity. The light intensity was adjusted to produce the same short-circuit current density as produced by 100 mW cm⁻² of Air Mass (AM) 1.5G sunlight on a secondary standard Si photodiode. A three-electrode configuration was used with a saturated calomel electrode (SCE) or a Ag/AgCl(sat) reference electrode (BAS Inc.) and a Pt gauze counter electrode located in a fritted compartment that contained the same pH 14 or Fe(CN)₆^{3-/4-} electrolyte as in the main cell compartment.

For experiments with Fe(CN)₆^{3-/4-}, a solution containing 0.050 M K₃Fe(CN)₆, 0.350 M K₄Fe(CN)₆, and 0.500 M K₂SO₄(aq) was prepared prior to use. This solution was contained in an electrochemical cell that had a small separation between the cell edge and the working electrode surface, to minimize the absorbing effects of the Fe(CN)₆^{3-/4-} solution. A Pt wire and Pt gauze were the reference and counter electrodes, respectively, for these measurements.

For O₂(g) evolution experiments, a Neofix fluorescence probe was used in an airtight cell, along with a Ag/AgCl(sat) reference electrode. The Pt gauze counter electrode was positioned in a separate, fritted compartment. The cell volume was 51 mL, and the cell was purged with a stream of Ar(g) for ~1 h prior to data collection. The experiment was run for 30 min after a 10 min waiting period at open circuit, then held at open circuit for ten minutes, then

run for another 30 minutes to show that oxygen had been produced electrochemically and did not simply leak into the cell. The electrode area was 0.25 cm².

Scanning-electron micrographs (SEM) were obtained using a FEI Nova NanoSEM 450 at an accelerating voltage of 15 kV with a working distance of 5 mm and an in-lens secondary electron detector. Energy-dispersive X-ray spectroscopy was performed in the SEM at a working distance of 12 mm, using an accelerating voltage of 15 kV and an Oxford Instruments Si drift detector.

X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Axis Nova system with a base pressure of $< 2 \times 10^{-9}$ torr. A monochromatic Al K α source was used to irradiate the sample with X-rays with an energy of 1486.7 eV at a power of 450 W. A hemispherical analyzer oriented for detection along the sample surface normal was used for maximum depth sensitivity. High-resolution spectra were acquired at a resolution of 50 meV with a pass energy of 10 eV. An octopole ion gun was used to sputter-etch the sample surface with 500 eV Ar⁺ ions in increments of 15 s.

S1. Photoelectrochemical Behavior of n-CdTe/TiO₂/Ni Electrodes with or without Etching

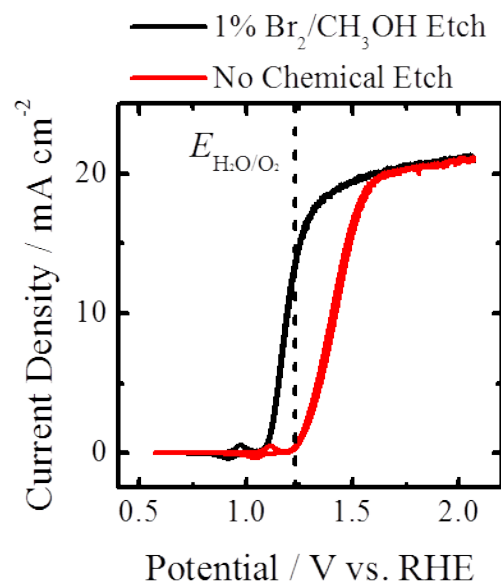


Figure S1. *J-E* data of n-CdTe/TiO₂/Ni photoelectrodes in pH = 14 KOH(aq) under illumination with a Xe arc lamp calibrated to 100 mW cm⁻² of AM 1.5G illumination. The n-CdTe was either etched with 1% Br₂/CH₃OH, or not chemically etched at all (beyond cleaning with CH₃OH) prior to deposition of the TiO₂.

S2. Energy Dispersive X-Ray Spectroscopy of an n-CdTe/TiO₂/Ni Interface

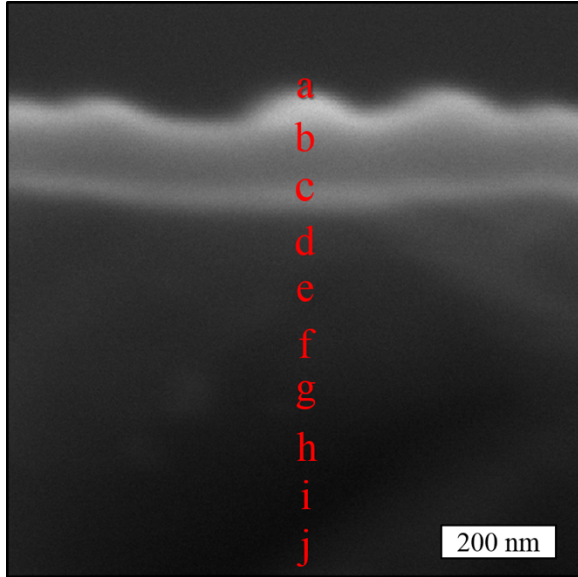


Figure S2. Cross-sectional scanning-electron micrograph of an n-CdTe/TiO₂/Ni electrode showing the ALD-grown TiO₂ film above the n-CdTe wafer section. The labels denote the positions where the EDS data in Table S1 were acquired.

Position	Cd	Te	Ti	Ni
a	1.16	1.00	3.70	2.04
b	1.06	1.00	4.83	0.39
c	1.09	1.00	2.64	
d	0.93	1.00	0.69	
e	0.93	1.00	0.30	
f	0.92	1.00	0.17	
g	0.99	1.00	0.12	
h	0.97	1.00	0.05	
i	0.94	1.00		
j	1.00	1.00		

Table S1. Atomic ratios derived from EDS acquired from an n-CdTe/TiO₂/Ni electrode at the positions indicated in Figure S1. All of the values were normalized to those of Te.

S3. X-Ray Photoelectron Spectroscopic Analysis of the Br₂/CH₃OH Etched n-CdTe Surface

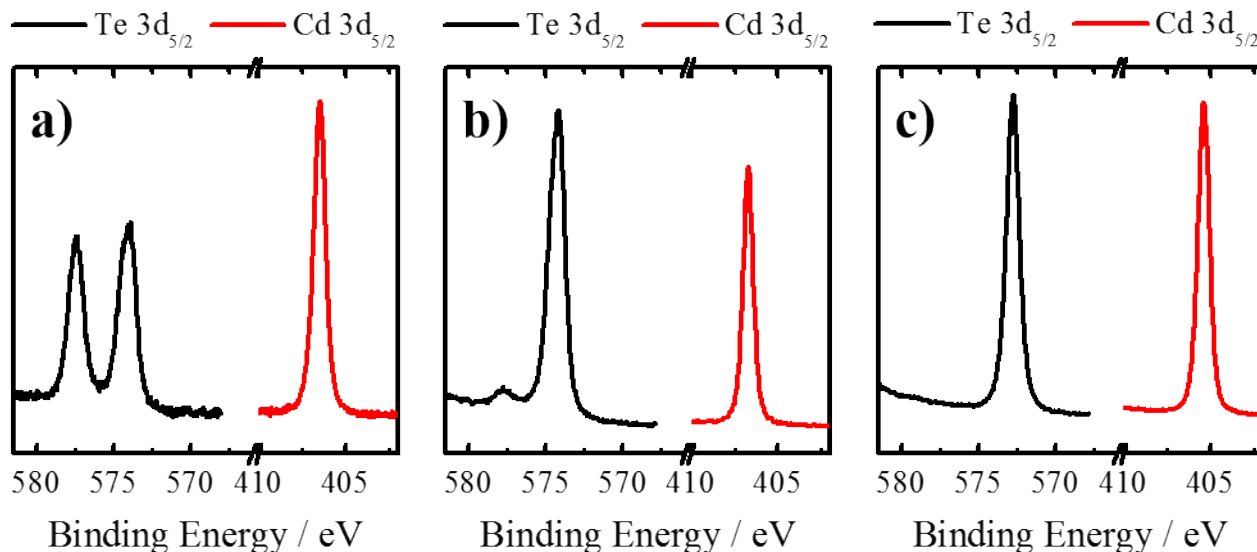


Figure S3. High-resolution X-ray photoelectron spectra in the regions of the Te 3d_{5/2} and Cd 3d_{5/2} core levels of (a) as-delivered n-CdTe. (b) 1% Br₂/CH₃OH etched n-CdTe and (c) the same as (b) after 15 s of Ar⁺ sputter-etching.

Preparation	Ratio Cd:Te
As-Delivered	.93
Etched	.75
Etched / 15 s Ar ⁺ Sputtered	1.07
Etched / 30 s Ar ⁺ Sputtered	1.16
Etched / 45 s Ar ⁺ Sputtered	1.16

Table S2. Te:Cd atomic ratio as determined by X-Ray photoelectron spectroscopy for an as-delivered n-CdTe, n-CdTe etched with 1 % Br₂/CH₃OH and n-CdTe etched with 1 % Br₂/CH₃OH and then sputter-etched with Ar⁺ ions for 15s, 30 s or 45 s.

S4. Photoelectrochemical Stability of n-CdTe/Ni and n-CdTe/TiO₂/Ni Electrodes

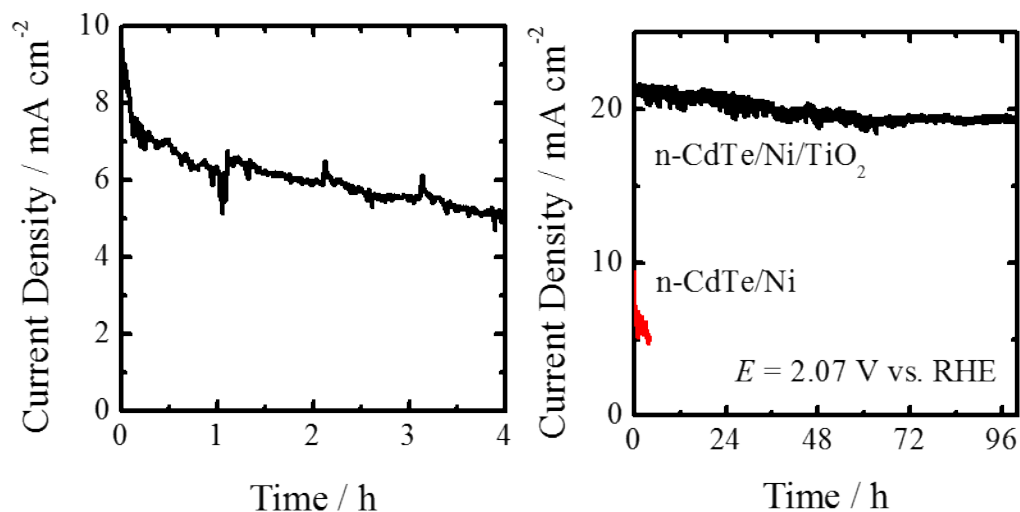


Figure S4. Current density as a function of time during potentiostatic electrolysis with an n-CdTe/Ni electrode (left) and plotted against data from an n-CdTe/TiO₂/Ni electrode under the same conditions at 2.07 V vs. RHE in pH = 14 KOH(aq) under illumination with a Xe arc lamp calibrated to 100 mW cm⁻² of AM 1.5G illumination.

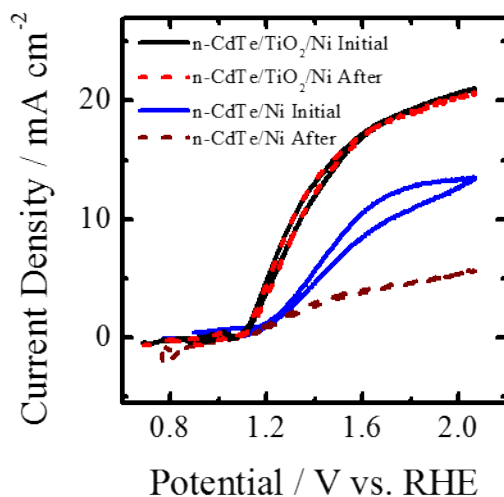


Figure S5. *J-E* data obtained with n-CdTe/Ni and n-CdTe/TiO₂/Ni electrodes, respectively, in pH = 14 KOH(aq) under illumination by a Xe arc lamp calibrated to 100 mW cm⁻² of AM 1.5G illumination. *J-E* data were obtained before and after 4 h of potentiostatic electrolysis under illumination at 2.07 V vs. RHE.