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STABILIZATION OF N-CADMIUM TELLURIDE  
PHOTOANODES FOR WATER OXIDATION TO O<sub>2</sub>(g) IN  
AQUEOUS ALKALINE ELECTROLYTES USING  
AMORPHOUS TiO<sub>2</sub> FILMS FORMED BY ATOMIC-  
LAYER-DEPOSITION

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**ABSTRACT.** Although II-VI semiconductors such as CdS, CdTe, CdSe, ZnTe, and alloys thereof, can have nearly ideal band gaps and band-edge positions for the production of solar fuels, II-VI photoanodes are well-known to be unstable towards photocorrosion or photopassivation when in contact with aqueous electrolytes. Atomic-layer deposition (ALD) of amorphous, “leaky” TiO<sub>2</sub> films coated with thin films or islands of Ni oxide has been shown to robustly protect Si, GaAs, and other III-V materials from photocorrosion and therefore to facilitate the robust, solar-driven photoelectrochemical oxidation of H<sub>2</sub>O to O<sub>2</sub>(g). We demonstrate herein that ALD-deposited 140-nm thick amorphous TiO<sub>2</sub> films also effectively protect single crystalline n-CdTe photoanodes from corrosion or passivation. An n-CdTe/TiO<sub>2</sub> electrode with a thin overlayer of a Ni-oxide based oxygen-evolution electrocatalyst produced  $435 \pm 15$  mV of photovoltage with a light-limited current density of  $21 \pm 1$  mA cm<sup>-2</sup> under 100 mW cm<sup>-2</sup> of simulated Air Mass 1.5 illumination. The ALD-deposited TiO<sub>2</sub> films are highly optically transparent and electrically conductive. We show that an n-CdTe/TiO<sub>2</sub>/Ni oxide electrode enables the stable solar-driven oxidation of H<sub>2</sub>O to O<sub>2</sub>(g) in strongly alkaline aqueous solutions, where passive, intrinsically safe, efficient systems for solar-driven water-splitting can be operated.

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**BROADER CONTEXT.** High-efficiency photoelectrochemical (PEC) solar-driven water splitting and/or carbon dioxide reduction will require the use of semiconductors capable of delivering a substantial amount of current as well as the photovoltage required to drive the fuel-forming anodic and cathodic half-reactions, respectively. Although metal oxides have received much attention as photoanodes due to their stability against oxidation, such systems generally suffer from low maximum photocurrent densities in sunlight due to the large band gaps of the

materials explored to date. Semiconductors with smaller band gaps, such as CdTe, are better matched to the solar spectrum and have more suitable valence-band positions; however, such materials are generally unstable in aqueous electrolytes under photoanodic conditions. We demonstrate herein that atomic-layer deposition of amorphous TiO<sub>2</sub> films forms a protection layer on n-CdTe photoanodes that, with a Ni-oxide based electrocatalyst layer, allows for photocatalytic water oxidation at the electrolyte interface. Such n-CdTe/TiO<sub>2</sub>/Ni oxide photoanodes yielded quantitative oxidation of water to O<sub>2</sub>(g) with internal quantum yields approaching unity for extended periods of operation under 100 mW cm<sup>-2</sup> of simulated solar illumination.

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CdTe, with a 1.44 eV band gap, has been widely studied since the 1980s<sup>1-6</sup>, and is currently used primarily in thin-film solar cells in which p-CdTe is deposited upon n-CdS to form a buried heterojunction device.<sup>7, 8</sup> CdTe has furthermore been investigated for use in photoelectrochemical (PEC) applications but is known to undergo a number of facile photooxidation or photocorrosion processes in various aqueous, as well as organic, media.<sup>1, 2</sup> Strongly alkaline or strongly acidic media have numerous benefits for the electrolysis of water due to their high conductivity without the need for added electrolyte or buffering species and minimal pH gradients under operating conditions. Further, at high and low pH, viable permselective ionophoric membranes are available to separate the products of electrolysis, and the kinetics of water oxidation with suitable electrocatalysts is rapid, thus making construction of a passive, intrinsically safe and efficient solar-driven water-splitting device possible.<sup>9-11</sup> However, efficient photoanodes typically are unstable and rapidly corrode or passivate when operated in contact with electrolytes in these pH ranges.<sup>12, 13</sup> Recently, a number of reports have been published in which the protection of otherwise unstable materials is carried out using a protecting layer such as TiO<sub>2</sub>, MnO or metal-modified ITO.<sup>14-16</sup> Facile electron conduction is expected through the conduction band of TiO<sub>2</sub>, and hence TiO<sub>2</sub> has been developed as a protection layer for photocathodes. In contrast, stoichiometric TiO<sub>2</sub> should present a tunnel barrier to photogenerated holes at energies near that required for water oxidation. We report herein that 140 nm thick amorphous TiO<sub>2</sub> films deposited by atomic-layer deposition (ALD) and modified by the addition of a Ni oxide catalytic layer effectively protect n-CdTe photoanodes from corrosion or passivation and effect the quantitative oxidation of H<sub>2</sub>O to O<sub>2</sub>(g). Protected n-CdTe photoanodes produced 435 ± 15 mV of photovoltage and light-limited current densities of 21 ± 1 mA cm<sup>-2</sup> under 100 mW cm<sup>-2</sup> of simulated Air Mass (AM) 1.5 illumination.

Atomic-layer deposition (ALD) was employed to deposit films of TiO<sub>2</sub> up to 150 nm in thickness on (111)-oriented n-CdTe samples with a carrier concentration of  $1 \times 10^{17} \text{ cm}^{-3}$ . The electrical characteristics of such films have been described previously.<sup>12</sup> A thin film of Ni was then deposited by sputtering. The Ni layer upon oxidation produces an earth-abundant, highly active, low overpotential Ni oxide electrocatalyst for the oxygen-evolution reaction (OER).<sup>12</sup> Figure 1 shows a cross-sectional scanning-electron micrograph of a resulting photoelectrode.

Figure 2 shows typical current density vs potential ( $J$ - $E$ ) data for (a) an n-CdTe/TiO<sub>2</sub>/Ni photoanode in pH = 14 KOH(aq) plotted against the reversible hydrogen electrode potential, RHE<sup>a</sup>, and (b) an n-CdTe/TiO<sub>2</sub>/Ni photoanode in contact with an aqueous ferro/ferricyanide solution (KCl, Fe(CN)<sub>6</sub><sup>3-</sup>, and Fe(CN)<sub>6</sub><sup>4-</sup>, of 1, 0.05, and 0.35 M concentrations, respectively), both under  $100 \text{ mW cm}^{-2}$  of simulated AM1.5 illumination (Xenon lamp with an AM1.5 filter set). Unetched samples exhibited lower photovoltages and low fill factors (Fig. S1), whereas samples etched for 30 s in Br<sub>2</sub>/CH<sub>3</sub>OH produced superior fill factors, high photocurrents and improved photovoltages. Etching concentrations in the range of 0.1% to 1% Br<sub>2</sub>/CH<sub>3</sub>OH produced the most optimized photoelectrodes from the n-CdTe wafer used in this study. Open-circuit photovoltages of approximately 435 mV and light-limited photocurrent densities of  $21 \text{ mA cm}^{-2}$  were observed for n-CdTe/TiO<sub>2</sub>/Ni photoanodes in pH = 14 KOH (aq) as well as in contact with the aqueous ferri/ferrocyanide solutions (Fig. 2). For comparison, a similarly protected n-Si photoanode has been shown to provide  $28 \text{ mA cm}^{-2}$  of light-limited photocurrent density and 410 mV of photovoltage, a similarly protected n-GaP photoanode has been shown to provide a light-limited photocurrent of  $3.4 \text{ mA cm}^{-2}$  and 590 mV of photovoltage, and a similarly protected gallium arsenide photoanode containing a buried junction, np<sup>+</sup>-GaAs, has been shown

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<sup>a</sup>  $E_{\text{RHE}} = E_{\text{NHE}} + 0.059 \times \text{pH} = E_{\text{Ag/AgCl}} + 0.197 + 0.059 \times \text{pH}$ . Water oxidation at any pH and STP occurs at 1.23V vs RHE.

to provide photocurrent densities of  $14.3 \text{ mA cm}^{-2}$  and photovoltages of 810 mV.<sup>12</sup> To provide perspective on the performance produced provided by the protection scheme, load-line analysis indicated that obtaining the observed  $J$ - $E$  performance of the n-CdTe/TiO<sub>2</sub>/Ni photoanode using a Si photovoltaic (PV) cell electrically in series with an electrocatalytic anode that exhibited identical  $J$ - $E$  behavior to that of a 2 nm Ni film on a titanium electrode<sup>17</sup> would require the use of a 7.5% efficient Si PV cell with a  $V_{oc}$  of 0.48 V, a  $J_{sc}$  of  $22 \text{ mA cm}^{-2}$ , and a  $ff$  of 0.71.

Scanning-electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were used to further analyze the n-CdTe/TiO<sub>2</sub>/Ni interface. As shown in the cross-sectional view (Fig. 1), the thickness of the TiO<sub>2</sub> layer was 140 nm, which implies a growth rate of  $0.056 \text{ nm cycle}^{-1}$  for the 2500 cycle TiO<sub>2</sub> sample. Figures S2 and Table S1 show the EDS data obtained at various locations in the n-CdTe/TiO<sub>2</sub>/Ni structure. Notably, the EDS data indicated that a slightly Cd-poor region was present at the interface, as would be expected for an oxidizing etch that produced a Cd-poor, acceptor-rich interface. This behavior suggests that the interfacial layer is key to producing the photovoltage exhibited by these samples, and agrees well with prior suggestions that such etches form an acceptor-rich, Cd-poor surface at the CdTe interface<sup>18</sup> which pins the photovoltage to  $\sim 0.5 \text{ V}$  under similar illumination conditions.<sup>19</sup>

XPS experiments were performed to characterize the surface properties of the etched n-CdTe wafers prior to the ALD of the TiO<sub>2</sub> overlayer. An unetched wafer showed nearly equal amounts of tellurium and cadmium at the surface, in addition to a substantial amount of tellurium oxide (Fig. S3 and Table S2), whereas the Br<sub>2</sub>/CH<sub>3</sub>OH-etched samples had a 0.75:1 ratio of cadmium to tellurium at the surface and exhibited a much smaller tellurium oxide peak. This ratio suggests the formation of a p-type layer at the surface of the n-CdTe wafer, which influences the magnitude of the observed photovoltages. Brief (15 s) argon-ion sputter-etching

between XPS scans quickly returned the Te: Cd ratio to unity before leading to a Cd-rich surface, due to the different sputter-etching rates of tellurium and cadmium. While the different sputter-etching rates made rigorous depth profiling difficult using this experimental technique, these results show that the Br<sub>2</sub>/CH<sub>3</sub>OH etch only created this p-type layer within a very narrow layer at the surface, with a depth on the order of nanometers.

The spectral response data for n-CdTe/TiO<sub>2</sub>/Ni electrodes indicated a high quantum yield for water oxidation (Fig. 3), with minimal absorption of light by the TiO<sub>2</sub>/Ni overlayers. Spectral response measurements were undertaken at 2.07 V vs RHE; this potential was chosen as it allows for data to be collected in high photocurrent regions (at the light-limited current density). Based on integration of the spectral response data with the wavelength-dependent irradiance of the AM 1.5G solar spectrum, the sample etched with 1% Br<sub>2</sub> in CH<sub>3</sub>OH resulted in photoelectrodes that exhibited excellent quantum yields in lower-wavelength regions, as well as high quantum yields at long wavelengths. Integration of the wavelength-dependent quantum yield of such electrodes with respect to the spectral irradiance distribution of the AM 1.5G solar spectrum produced a light-limited photocurrent density of 20.5 mA cm<sup>-2</sup>, which compared well with the observed value of 21.5 mA cm<sup>-2</sup> (Fig. 2) at 2.07 V vs RHE.

Similar to the behavior of n-Si/TiO<sub>2</sub>/Ni photoelectrodes<sup>8</sup>, n-CdTe/TiO<sub>2</sub>/Ni photoelectrodes were stable for > 100 hours of continuous operation during photoanodic current flow (Fig. 4a). An n-CdTe sample etched in the same manner but with only Ni deposited by sputtering, in the absence of ALD TiO<sub>2</sub>, exhibited a decay in performance of ~40% over this same period of operation (Fig. S4). Figure S5 shows a comparison of the *J-E* behavior before and after 4 h of potentiostatic electrolysis at 2.07 V vs RHE. The n-CdTe/TiO<sub>2</sub>/Ni electrode remained effectively unchanged whereas both the photocurrent density and fill factor of an n-



CdTe/Ni electrode decayed substantially over the same time period. Approximately 20 times more holes were passed through the circuit over 100 hours than atoms present in the entire CdTe electrode, which strongly suggests that the photocurrent shown in Figure 4a was predominantly associated with the faradaic oxidation of water to O<sub>2</sub>. Direct verification of this hypothesis was obtained using an oxygen detector,<sup>20</sup> which revealed that n-CdTe/TiO<sub>2</sub>/Ni samples operated in pH = 14 KOH(aq) (see ESI for details) produced an amount of O<sub>2</sub> detected by the probe that was within experimental error of the amount of oxygen calculated based on the coulometry assuming 100% faradaic efficiency for O<sub>2</sub> production (Fig. 4b). The flat regions in the data before, in between, and after the measurement of photocurrent, and the time evolution of the detected O<sub>2</sub>, correlated completely with the photoanodic current flow for two thirty minute periods, strongly indicating that the detected O<sub>2</sub> was the result of water oxidation by the photoanode.

The amorphous TiO<sub>2</sub> coatings prepared by ALD yield buried junctions in which the semiconductor surface is protected from corrosion or passivation by the contacting electrolyte. The photovoltage of systems that do not contain a n-p<sup>+</sup> type base-emitter buried junction, such as n-CdTe/TiO<sub>2</sub>/Ni electrodes, could be improved further through chemical control over the interfacial energetics at the semiconductor/oxide interface, including the introduction of surface dipoles, band-edge engineering, and other approaches to reduce the majority-carrier currents in the device. Nevertheless, this work shows that CdTe, generally believed to be unstable and not suited for investigation as a photoanode for the oxidation of water to O<sub>2</sub>(g), can be beneficially used at least on the laboratory time scale for such purposes. Experiments are currently underway to quantify the methods by which the photovoltage and electrode stability can be further optimized in such systems.

**SUPPLEMENTARY INFORMATION AVAILABLE.** Detailed experimental methods, SEM/EDS data, XPS data, and other photoelectrochemical information are available in the Supporting Information.

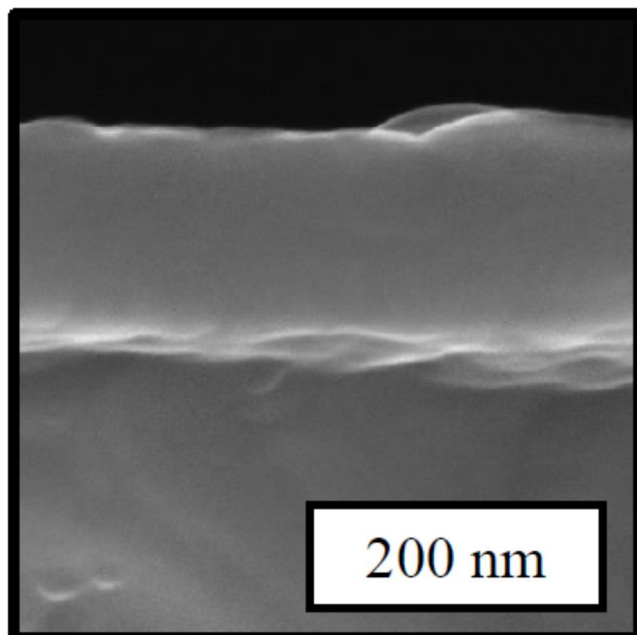
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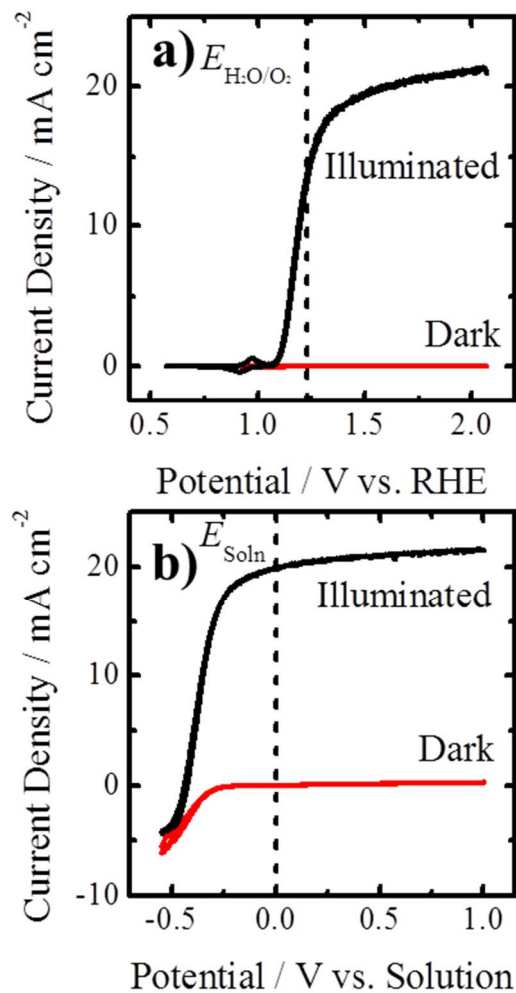
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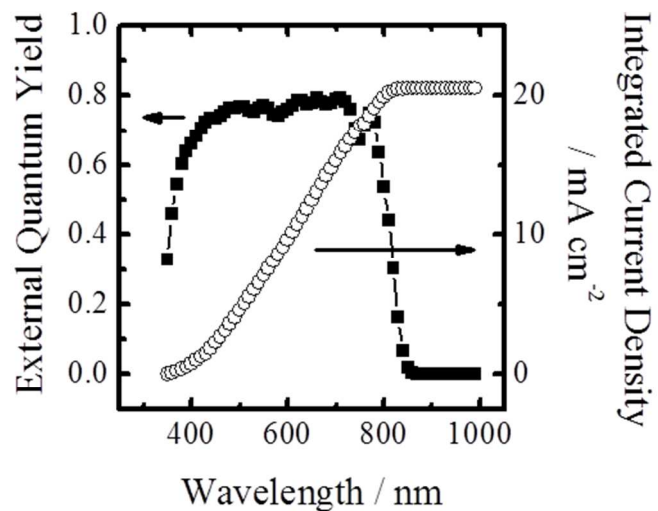
## FIGURES.



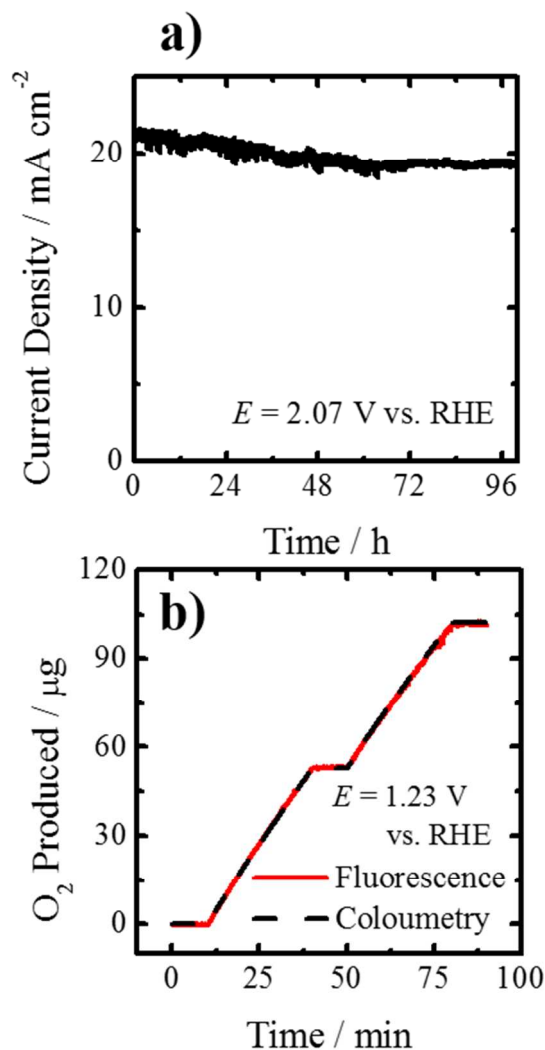
**Figure 1.** Representative cross-sectional scanning electron micrograph of a n-CdTe/TiO<sub>2</sub>/Ni electrode depicting the ALD-grown TiO<sub>2</sub> film above the n-CdTe wafer section. The Ni deposited onto the TiO<sub>2</sub> is not visible in this micrograph but was detected by EDS (see ESI Figure S3).



**Figure 2.**  $J$ - $E$  data obtained with a n-CdTe/TiO<sub>2</sub>/Ni electrode in the dark and under illumination in (a) pH = 14 KOH(aq) and (b) a Fe(CN)<sub>6</sub><sup>3-/4-</sup> solution. Illumination was provided by a Xenon arc lamp with an AM 1.5 filter set and the light intensity was calibrated to 100 mW cm<sup>-2</sup> of AM 1.5G illumination using a secondary standard calibrated Si solar cell.

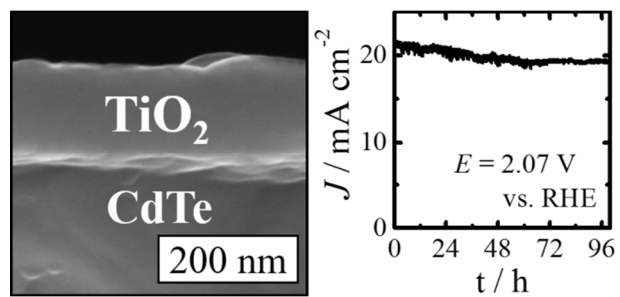


**Figure 3.** External quantum yield for a n-CdTe/TiO<sub>2</sub>/Ni electrode biased at 2.07 V vs. RHE in pH = 14 KOH(aq) solution and derived current density from integration against the AM 1.5G spectrum.



**Figure 4.** (a) Current density as a function of time during potentiostatic electrolysis at 2.07 V vs. RHE in pH = 14 KOH(aq). (b) Oxygen production detected by a fluorescent probe and derived from coulometry during constant potential electrolysis at 1.23 V vs. RHE in pH = 14 KOH(aq). In (a), the n-CdTe/TiO<sub>2</sub>/Ni electrode was illuminated by a Xenon arc lamp that had been calibrated to provide 100 mW cm<sup>-2</sup> of simulated AM 1.5G illumination; in (b), 20mW cm<sup>-2</sup> was used to prevent bubble formation.

Table of Contents Graphic:



Text:

Protection of n-CdTe by ALD-grown  $\text{TiO}_2$  film for water oxidation to  $\text{O}_2(\text{g})$  in alkaline media