Photocatalytic water splitting represents an emerging technology well positioned to satisfy the growing need for low-energy, low CO₂, economically viable hydrogen gas production. As such, stable, high-surface-area electrodes are increasingly being investigated as electrodes for the photochemical conversion of solar energy into hydrogen fuel. We present a titanium dioxide (TiO₂)/zinc oxide (ZnO) nanowire array using a hybrid hydrothermal/atomic layer deposition (ALD) for use as a solar-powered photoelectrochemical device. The nanowire array consists of single crystalline, wurtzite ZnO nanowires with a 40 nm ALD TiO₂ coating. By using a TiO₂ nanocoating on the high surface area-ZnO array, three advancements have been accomplished in this work: (1) high aspect ratio nanowires with TiO₂ for water splitting (over 8 μm), (2) improved stability over bare ZnO nanowires during photocatalysis, and (3) excellent onset voltage. As such, this process opens up new class of the micro/nanofabrication process for making efficient photocatalytic gas harvesting systems.

1. Introduction

It has been estimated that 37.7 Mt/yr of hydrogen gas (H₂) would be enough to replace all coal currently used in the United States [1]. However, steam reformation—the dominant method for producing H₂ today—involves burning methane with high-temperature steam to create H₂, producing carbon dioxide as a by-product (CH₄ + H₂O (+ heat) → CO + 3H₂). Other methods include electrolysis by solar cells, renewable liquid reformation, and fermentation; these are plagued by low solar-energy-to-water efficiency, low yields, and poor selectivity [2].

By contrast, photoelectrochemical (PEC) water splitting has the potential to passively convert solar energy into H₂ more effectively than electrolysis through the use of photovoltaics (PV). PEC water splitting is capable of higher yield and selectivity while producing zero carbon emissions. Utilizing photogenerated electron/hole pairs, the PEC process involves oxidizing water (2H₂O + 4h⁺ → 4H⁺ + O₂) and reducing the resulting H⁺ ions (4e⁻ + 4H⁺ → 2H₂) at the semiconductor/electrolyte interface while being submerged in an aqueous medium, as shown in Figure 1(a). In contrast to PV electrolysis, this process is theoretically more efficient since the PEC process experiences fewer losses to attain the required bias voltage [3]. Furthermore, water splitting scales easily with the area of the semiconducting material, making it ideal for large-scale, high-yield hydrogen harvesting. The selectivity of the PEC process is tunable with the band structure. That is, the bandgap, E₉, must be positioned correctly to allow for the reduction/oxidation reactions necessary to split water; conduction band should be above the reduction potential, and valence band should be below the oxidation potential. A Schottky barrier is formed at the photoelectrode-electrolyte interface. The system is designed such that minority carriers move into the electrolyte and begin reduction/oxidation of water. Majority carriers oxidize/reduce water at the counter electrode-electrolyte interface [4]. Figure 1(b) shows the energy band diagram for the photocatalytic system using an n-type, TiO₂ photoanode.
ZnO nanowire array through an ALD TiO$_2$ nanocoating respectively. These reactions result in oxygen and hydrogen gas production. (b) Proposed band gap structure of TiO$_2@$ZnO: high-aspect ratio TiO$_2$ experiences charge separation at the electrolyte-TiO$_2$ interface, moving holes into the electrolyte and electrons into the single-crystalline texturizing TiO$_2$ has not been able to produce high-aspect ratio due to poor light absorption. Moreover, previous work on usage as a PEC photoanode is plagued by lower photocurrent and performance. This hybrid hydrothermal/ALD texturization allows for conversion efficiency and improved onset voltage compared to untexturized, planar electrodes.

In the past, nanowires have shown three distinct improvements over untextured substrates: (1) enhanced light trapping due to light-concentrating properties of standing nanowires [11], (2) increased surface area, leading to increased active surface sites upon which water splitting can occur, and (3) reduced minority carrier distances, decreasing the rate of recombination and increasing charge separation [12].

TiO$_2$ is an intrinsically n-type semiconductor material with an energy band gap of 3.2 eV [13, 14]. Its band edge positions straddle water redox potentials, as shown in Figure 1(b). Moreover, TiO$_2$ is relatively inexpensive [15] and is used extensively in environmental photocatalysis [16], because of its high stability, even in a highly oxidizing aqueous environment [17]. However, the state-of-art TiO$_2$ usage as a PEC photoanode is plagued by lower photocurrent due to poor light absorption. Moreover, previous work on texturizing TiO$_2$ has not been able to produce high-aspect ratio TiO$_2$ nanowires due to undesirable compact layers at the bottom of the wire arrays [18]. In this work, we fabricate high-aspect ratio ZnO/TiO$_2$ nanowire arrays using a hybrid hydrothermal/ALD process. After growing the high-aspect ratio ZnO nanowires using the hydrothermal methods, we apply a uniform coating of TiO$_2$ by ALD. The resulting ratio TiO$_2$ nanowires experience charge separation at the electrolyte-TiO$_2$ interface, moving holes into the electrolyte and electrons into the single-crystalline ZnO nanowire.

Numerous studies have been aimed at achieving stable and efficient PEC systems using metal oxides responsive to solar spectrum, but they have suffered from three major drawbacks [5–7]: (1) low conversion efficiency due to recombination and quality of materials (for example, non-ideal crystallinity, where recombination can occur at grain boundaries), (2) high-onset voltages, and (3) poor material stability in the photocatalytic process [8]. Thus, much subsequent research has focused on either stabilization layers or texturization of the surface to increase conversion efficiencies in a highly oxidizing environment [9, 10]. By utilizing a hybrid hydrothermal/atomic layer deposition (ALD) ZnO/TiO$_2$ nanowire array, we are able to both stabilize the ZnO nanowire array through an ALD TiO$_2$ nanocoating while leveraging the architecture of the cell to improve performance. This hybrid hydrothermal/ALD texturization allows for conversion efficiency and improved onset voltage compared to untexturized, planar electrodes.

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The process was repeated 3 times to ensure adequate quantum dot formation. The wafer was annealed at 350°C for 30 min to ensure seed layer adhesion onto the wafer before being submerged in a growth solution containing zinc nitrate hexahydrate (Sigma), hexamethylenetetramine (Sigma), and ammonium hydroxide (Alfa Aesar) at 90°C for 8 hrs. The wafer was removed from the solution and cleaned with deionized water.

After the samples were dried, uniform deposition of TiO$_2$ over ZnO nanowires was performed using ALD, as

![Figure 1: (a) Water splitting cell: incident light creates photogenerated electron-hole pairs. Given an appropriate band structure (straddling water reduction/oxidation potentials), holes and electrons will oxidize water at the photoanode and reduce resulting H$^+$ ions at the cathode, respectively. These reactions result in oxygen and hydrogen gas production. (b) Proposed band gap structure of TiO$_2@$ZnO: high-aspect ratio TiO$_2$ experiences charge separation at the electrolyte-TiO$_2$ interface, moving holes into the electrolyte and electrons into the single-crystalline texturizing TiO$_2$ has not been able to produce high-aspect ratio due to poor light absorption. Moreover, previous work on usage as a PEC photoanode is plagued by lower photocurrent and performance. This hybrid hydrothermal/ALD texturization allows for conversion efficiency and improved onset voltage compared to untexturized, planar electrodes.](image-url)
shown in Figure 3. ALD, a highly precise chemical vapor deposition method, creates uniform, conformal coverage of polycrystalline TiO$_2$ using a self-limiting reaction. To deposit TiO$_2$, tetrakis(dimethylamido)titanium (TDMAT) was introduced into the deposition chamber through an argon carrier gas and allowed to adsorb onto the substrate surface for 0.6 s. Excess (unadsorbed) TDMAT was removed from the chamber with argon gas for 5 s. Next, H$_2$O was introduced for 0.25 s, beginning a self-limiting reaction with adsorbed TDMAT. The excess H$_2$O and reaction by-products were removed with argon gas for 5 s, leaving a single layer of TiO$_2$. In this way, gaseous precursors were introduced in a systematic and cyclic manner to create a self-limiting reaction—one layer of TiO$_2$ was deposited per cycle. This makes ALD an ideal deposition method for high-quality, Ångström-level precision over very high-aspect ratio substrates. The ZnO nanowire array was coated by 1000 cycles of thermally grown ALD TiO$_2$ (~0.4 Å/cycle) at a process temperature of 250°C, as reported in a previous work [19].

Electrical contact is established using copper tape and insulated tin wire. To isolate the active material, electrodes were passivated onto a glass substrate using epoxy (Figure 4(a)). Photoelectrochemical water splitting was tested using a 3-electrode set-up in 0.5 M H$_2$SO$_4$ solution vs. Ag/AgCl with a platinum wire as the counter electrode. An Asahi MAX-303 Xenon lamp was used as the solar simulator and the system was enclosed in TB4 Thorlabs black-out hardboard (5 mm thick with foam core). Electrochemical measurements were conducted using a Gamry Ref. 600 potentiostat (Figure 4(b)). Linear sweep voltammetry was conducted from 0 V vs. Ag/AgCl to 1 V vs. Ag/AgCl, since the aqueous solution had an electrochemical voltage limit of 1.2 V (standard electrode potential of 1.23 V for the O$_2$ + 4H$^+$ + 4e$^-$ $\rightarrow$ 2H$_2$O reaction). The scans were conducted in dark conditions (covered in a black-out cardboard housing) and light conditions, as well as chopped light—dark alternating with light.

2.1. Cell Efficiency. The ultimate efficiency of a cell (adapted from Hisatomi et al.) [20] can be described by the following equations. First, the solar-to-hydrogen efficiency is

$$\text{STH} = \frac{\text{Representative H}_2\text{output energy}}{\text{Energy of incident solar light}} = \frac{r_{\text{H}_2} \times \Delta G}{P_{\text{sun}} \times S},$$

where $r_{\text{H}_2}$ is the rate of hydrogen production, $\Delta G$ is the change in Gibbs energy, $P_{\text{sun}}$ is the energy flux of irradiation, and $S$ is the area of the electrode. However, electrodes that require bias voltage in order to produce measurable photocurrent require voltage compensation in order to calculate cell efficiency. Therefore, the applied-bias-compensated solar-to-hydrogen efficiency and half-cell (to be used with a two-electrode cell) is employed:

$$\text{AB − STH} = \frac{|I| \times \eta_F \times (V_{\text{th}} - V_{\text{bias}})}{P_{\text{sun}}},$$

where $I$ is the photocurrent density, $\eta_F$ is the faradaic efficiency, $V_{\text{th}}$ is the theoretical voltage for water splitting.
(1.23 V), and $V_{\text{bias}}$ is the applied bias potential. The half-cell STH for a photoanode is therefore

$$\text{HC} - \text{STH} = \frac{|I| \times (E_{\text{O}_2/\text{H}_2\text{O}} - E_{\text{RHE}})}{P_{\text{sun}}},$$

(3)

where $E_{\text{O}_2/\text{H}_2\text{O}}$ is the theoretical standard electrode potential for the $\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}$ reaction vs. RHE, and $E_{\text{RHE}}$ is the pH-dependent potential of the photoanode in the electrolyte:

$$E_{\text{RHE}} = E_{\text{measured}} - E_{\text{Ag-AgCl}}^0 + \frac{RT \ln 10}{F} \cdot \text{pH},$$

(4)

where $E_{\text{measured}}$ and $E_{\text{Ag-AgCl}}^0$ are the potential measured relative to an Ag/AgCl reference electrode and the standard potential of the Ag/AgCl reaction, respectively. $R$, $T$, and $F$ are the gas constant, temperature, and Faraday constant, respectively. Therefore, the cell efficiency is dependent not only on the measured photocurrent density but also on the applied bias potential. Furthermore, texturization, catalysts, and coelectrodes to promote charge separation have been readily shown as methods to increase photocurrent, while fewer work exists on methods to decrease onset voltage, aside from material choices.

### 3. Results and Discussion

**3.1. Characterization.** The phase structure of hydrothermally grown ZnO nanowires was characterized using powder X-ray diffraction (XRD). Figure 5 displays the X-ray diffraction peaks, which confirm excellent crystallinity and hexagonal wurtzite ZnO phase (JCPDS card No. 36-1451). The surface morphology of the nanowire array was analyzed using a field emission scanning electron microscopy (FESEM). SEM images before ALD processing show highly ordered, 10 μm-tall nanowires with diameters of less than 50 nm. Furthermore, the nanowires show polygonal cross sections, implying single-crystalline nature (Figures 6(a), 6(d), and 6(g)). SEM images of the nanowire array post-ALD show complete coverage of TiO₂. As shown in Figures 6(a) and 6(b), a single ZnO nanowire is uniformly coated by TiO₂ when coated at 1000 ALD cycles (Figures 6(c), 6(f), and
6(j)), as opposed to 20-cycle coatings of TiO₂, which shows incomplete coverage (Figures 6(b), 6(e), and 6(h)). Transmission electron microscopy (TEM) was employed for the characterization of the single nanowire. Figure 7(a) exhibits a single ZnO nanowire with a hexagonal shape (single-crystalline), and (e) single nanowire view of 20-cycle TiO₂ on ZnO, showing incomplete coverage, (f) conformally and fully coated 1000-cycle TiO₂@ZnO, (g) side view of ZnO nanowires, (h) side view of 20 cycles TiO₂@ZnO, and (j) side view of 1000 cycles TiO₂@ZnO.

Figure 6: SEM images of ZnO, 20 cycles TiO₂@ZnO (incomplete coverage), and 1000 cycles TiO₂@ZnO (complete and conformal coverage). (a) Top-down view of ZnO nanowire forest, (b) top-down view of 20-cycle TiO₂-coated ZnO nanowire forest, (c) top-down view of 1000-cycle TiO₂-coated ZnO nanowire forest, (d) single nanowire view of ZnO, showing hexagonal shape (single-crystalline), (e) single nanowire view of 20-cycle TiO₂ on ZnO, showing incomplete coverage, (f) conformally and fully coated 1000-cycle TiO₂@ZnO, (g) side view of ZnO nanowires, (h) side view of 20 cycles TiO₂@ZnO, and (j) side view of 1000 cycles TiO₂@ZnO.

Figure 7: (a) TEM image of a lone ZnO nanowire, with hexagonal shape. (b) TEM image of a 1000-cycle TiO₂@ZnO nanowire, showing conformal coverage along the body of the nanowire.

3.2. Electrochemical Performance. As shown in Figure 8, the ALD TiO₂ shows significant differences in current outputs between light and dark conditions, implying photocurrent under lit conditions, with photocurrent increasing with increasing voltage. While the signal-to-noise is poor due to the low photocurrent, Figure 8 also shows that photocurrent is generated even at very low voltages (low onset voltage). The planar structure made of 1000-cycle TiO₂ coatings shows only marginal improvement in photocurrent over that of 20-cycle TiO₂ (Figures 8(a) and 8(b)) structure; in comparison, texturized TiO₂ as shown in Figure 8(c) shows significantly increased photocurrent. For example, at 0 V vs. Ag/AgCl, 1000-cycle TiO₂ shows an order of magnitude more photocurrent than 20-cycle TiO₂. Furthermore, it is noted that the electrode performances in these tests are in the absence of surface catalysts, which have been shown to greatly increase detectable photocurrent.

As seen in Figure 9(a), the PEC response of the bare ZnO nanoarray is mostly obscured by side reactions, despite cleaning the ZnO with ethanol and DI water. The side reactions cause peaking and sharp increases in current. However, when coated with ALD TiO₂, the electrode is significantly more stable, showing a marked lack of reactions that obscure photocurrent response of the bare ZnO (Figure 9(b)). The results suggest that the hydrothermal growth method for...
ZnO results in impurities and instabilities that make the ZnO nanowire array unsuitable for photocatalytic water splitting. However, these instabilities are not observed in the ALD TiO$_2$-coated samples, implying that TiO$_2$ is capable of stabilization of a ZnO nanowire system as demonstrated in a previous work [21].

Since the grain boundaries of ALD TiO$_2$ are potential recombination sites, ALD TiO$_2$ is susceptible to low performance as a PEC electrode. In contrast, the ZnO nanowires are single-crystalline and less vulnerable to recombination sites. By limiting the TiO$_2$ to a 40 nm coating on the ZnO nanowire, the travel distance of minority carriers to a single-crystalline substrate is greatly reduced, promoting conductivity and reducing recombination. Since the band gap of ZnO relative to TiO$_2$ is smaller, the generated photoelectrons in TiO$_2$ should not experience build-up and subsequent recombination at the semiconductor junction.

4. Conclusion

High-aspect ratio and vertically ordered ZnO/TiO$_2$ nanowires as long as 10 $\mu$m and less than 50 nm in diameter were successfully synthesized for applications in solar-powered hydrogen ($H_2$) gas harvesters. Hybrid hydrothermal/ALD processing was used to achieve high-aspect ratio and high-quality nanowire arrays. Surface morphology and phase
structure were analyzed to confirm TiO$_2$-coated ZnO nanowires. Photoelectrochemical responses of synthesized nanowires were measured to investigate their performance as hydrogen gas harvesters. Nanowires with TiO$_2$ demonstrated improved stability over bare ZnO nanowires during photocatalysis with low bias voltage. Results show that favorable geometry and high-quality nanowires not only enhanced chemical stability but also improved required bias voltage to yield photocurrent.

Data Availability
The data used to support the findings of this study are available from the corresponding author upon request.

Disclosure
This manuscript is based on the IEEE MEMS 2017 conference paper with the addition of (1) investigation into number of cycles on coverage of the ZnO core with corresponding characterization; (2) LSV under dark and lit conditions, indicating low-onset voltage; (3) performance comparison of planar and texturized, low- and high-cycle number ALD; and (4) band analysis of ZnO-TiO$_2$ core shell, indicating favorable band structure for water splitting.

Conflicts of Interest
The authors declare that they have no conflicts of interest.

Authors’ Contributions
Emmeline Kao and Hyun Sung Park are co-first authors, and contributed equally to this work.

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