A 1.23 V electrochemical difference is required as a minimum to drive PEC water-splitting, which can only be provided by a single semiconductor with an excessively large band-gap. An alternative strategy is to use two small band-gap semiconductors placed electrically in series. One semiconductor operates as the photocathode to drive H2-evolution while the other operates as the photoanode to drive O2-evolution, as shown in Figure 1. In this case, the electrochemical potential difference required to split water is partially provided by each semiconductor. However, small band-gap semiconductors typically dissolve or develop insulating oxide coatings during PEC operation. Current research is focused on developing various techniques for stabilizing small band-gap semiconductors for use in a technologically
viable, efficient, and stable solar-driven water-splitting system.

Surface modification is commonly used in PEC cells [31,32] as well as a variety of additional applications such as electronic devices [16–21], data storage [22], chemical sensing [23–25], molecular nanopatterning [26], and bioengineering [27–30]. In PEC applications, chemical attachment of organic molecules is a versatile technique used to enhance the stability of low-gap semiconductors while controlling the physiochemical properties of the surface [33]. For example, Lewis et al. have shown that forming covalent Si-C bonds on the surface of Si(111) photoelectrodes prevents oxidation of the surface [34]. Alternatively, depositing a thin layer of metal oxide such as SiO₂ [35], Al₂O₃ [36,37], TiO₂ [38–42], or ZnO [43] has been shown to passivate a variety of semiconductor surfaces. Although functionalizing a semiconductor with organic molecules or passivation layers stabilizes the surface, the modification often results in a less preferable onset potential of the semiconductor photoelectrode as shown for a p-type photocathode (more negative) and n-type photoanode (more positive) in Figure 2(a) and Figure 2(b), respectively.

An understanding of how surface modification influences charge transport and reduces the onset potential of a functionalized semiconductor photoelectrode is still lacking. This creates a roadblock for further improvements in device performance and a lack of design rules for identifying candidate materials for functionalization. In this review, we discuss how computational modeling can be used to provide insight into charge transfer across heterojunction structures. Specifically, we show examples of applying first-principles density functional theory and finite-element device simulations to investigate the effects of organic functionalization and passivating layers on charge transport across an underlying semiconductor surface.

Figure 1. Schematic of a two-electrode photoelectrochemical water-splitting cell where a p-type semiconductor operates as the photocathode to evolve hydrogen while an n-type semiconductor operates as a photoanode to evolve oxygen.

Figure 2. Commonly observed impact of surface functionalization on the photocurrent versus voltage response of a (a) p-type semiconductor photocathode and (b) n-type semiconductor photoanode.

2. Experimental methods

2.1. Photocurrent versus voltage response

Photocathode performance can be quantified experimentally by measuring the photocurrent density versus voltage (J-V) response for a specified potential range under solar illumination in contact with a redox couple. Two benchmarks directly related to the performance are obtained from the J-V curve: (1) short-circuit current density (Jsc), which is the maximum observed current at 0 V applied potential and (2) onset potential for the redox reaction (Von,A), which is the voltage at which the net current across the device is zero.

The onset potential is a key metric of performance for photoelectrochemical devices because it is related to the open-circuit photovoltage, Voc, which is the maximum energy that can be obtained from the collection of photons to drive electrical current and/or a chemical reaction. The Voc can be calculated from Von,A using [44]

\[ V_{oc} = E(A/A^-) - V_{on,A} \]  

where E(A/A⁻) is the formal redox potential of the redox couple in contact with the photocathode. The maximum Voc that can be achieved for a device is limited by recombination processes in the bulk of the material and can be calculated for a p-type semiconductor as [45]
where \( J_{ph} \) is the photocurrent density, \( L_n \) is the minority carrier diffusion length, \( D_n \) the minority carrier diffusion coefficient, \( N_c \) the effective density of states in the conduction band, and \( V_p \) the difference in energy between the Fermi and valence band energies in the bulk. A similar equation can be written for an n-type semiconductor. A \( V_{oc} \) less than the value calculated by Equation (2) is a consequence of deleterious surface or bulk effects in the semiconductor such as poor diffusion lengths, thermionic emission or tunneling across heterojunctions or surface barriers, transport through chemical imperfections, surface/bulk state recombination, or Fermi level pinning [45, 46].

2.2. Dipole measurements

Functionalization of a photoelectrode with organic molecules has been observed to dramatically affect the \( V_{oc} \) due to a change in the magnitude and direction of the surface dipole induced by the organic molecule. For a p-type semiconductor, a molecule that induces a large positive dipole (negative charge on the molecule, positive charge on the substrate) increases the \( V_{oc} \) by increasing the barrier height and depletion width at the surface as shown in Figure 3(a), while a negative dipole (positive charge on the molecule, negative charge on the substrate) decreases the barrier height and depletion width as shown in Figure 3(b). For an n-type semiconductor the behavior is reversed and a molecule with a negative dipole increases the \( V_{oc} \) by increasing the barrier height and depletion width at the surface.

The surface dipole (\( \delta \)) is defined as the difference between the electron affinity at the surface (\( \chi_s \)) and the electron affinity in the bulk (\( \chi_B \)) of the semiconductor

\[
\delta = \chi_s - \chi_B. \tag{3}
\]

\( \chi_s \) can be expressed in terms of the work function at the surface (\( \Phi_s \)), band gap of the semiconductor (\( E_g \)), and the absolute energy difference between the valence band edge and the Fermi level (\( |E_v-E_F| \)) at the surface resulting in an expression for the surface dipole as

\[
\delta = \Phi_s - E_g + |E_v-E_F|_s - \chi_B. \tag{4}
\]

Equation (4) allows for a direct determination of the surface dipole because the values of \( E_g \) and \( \chi_B \) can be found in literature while the magnitude of \( \Phi_s \) and \( |E_v-E_F|_s \) can be measured from ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy data (XPS), respectively [47–49].

The work function of a semiconductor can be determined using UPS via the following expression

\[
\Phi_s = h\nu - E_{cutoff}. \tag{5}
\]

where \( h\nu \) is the excitation energy (typically He I emission at 21.2 eV) and \( E_{cutoff} \) is the secondary electron cutoff energy in the photoelectron spectra [50]. The secondary emission is due to secondary electrons, which are defined as those that have lost energy due to inelastic collisions when traveling to the sample surface. The secondary emission is characterized by a broad, continuous peak. \( E_{cutoff} \) is determined graphically by extrapolating the secondary electron cutoff energy to the background intensity as shown in Figure 4(a). \( |E_v-E_F|_s \) can be determined using XPS with He II emission at 40.82 eV. The value of \( |E_v-E_F|_s \) is determined graphically by extrapolating the steep emission onset in the spectra to zero signal as shown in Figure 4(b). Once \( \Phi_s \) and \( |E_v-E_F|_s \) are determined the sign and magnitude of the surface dipole can be calculated using Equation (4).

3. Theoretical methods

We demonstrate simulation-based improvement of charge transport across modified semiconductor surfaces by utilizing two independent computational methods: first-principles density functional theory [51,52] and a finite element-based device simulator known as wxAMPS [53]. Density functional theory is utilized to investigate the electronic properties of the semiconductor surface at the atomic level while wxAMPS provides insight into the performance of the semiconductor.
system is approximated as a collection of non-interacting electrons moving in an effective potential, $V_{\text{eff}}$. Equation (6) then becomes a one-electron Schrödinger equation for a 3-coordinate system described by Equation (7) where $\varepsilon_i$ is the energy eigenvalue corresponding to the Kohn-Sham one-electron wavefunction, $\psi_i(\vec{r})$. The charge density, $\rho(\vec{r})$ for the N-electron system is obtained as a sum over occupied states by Equation (8)

$$H(V_{\text{eff}}(\vec{r}))\psi_i(\vec{r}) = \varepsilon_i\psi_i(\vec{r})$$

$$\rho(\vec{r}) = \sum_{i} |\psi_i(\vec{r})|^2 .$$

The use of Kohn-Sham DFT requires an approximate exchange-correlation functional chosen to represent the spatial dependence of the effective potential. The accuracy of DFT in modeling various systems is limited by the chosen functional for the system. However, because DFT is often used to calculate the energy difference between various systems, errors due to the exchange-correlation functional often cancel leading to reliable results.

The most commonly chosen functionals are LDA [54] and PBE [55] due to their computational reliability and low computational cost. Nowadays, more sophisticated options are available such as hybrid functionals, however, these are often still computationally limiting. Many codes are available to compute DFT calculations including VASP [56–60], Quantum Espresso [61], and SIESTA [62].

### 3.1. Density functional theory

Density functional theory (DFT) is a quantum mechanical modeling method applicable to atomic scale systems and widely employed in the field of computational chemistry and physics. DFT is used to investigate the electronic structure of many-body systems by solving the Schrödinger equation to yield the total energy (E) of a system

$$H\psi(\vec{r}, \vec{R}) = E\psi(\vec{r}, \vec{R})$$

where $H$ is the Hamiltonian operator and $\psi$ is the wavefunction depending on the spatial coordinates of electrons, $\vec{r}$, and nuclei, $\vec{R}$, in the system.

Equation (6) represents a many-body system with N electrons and 3N total spatial coordinates, which is computationally intractable. Therefore, an approximation known as Kohn-Sham DFT is often used in which the photoelectrode at the device level. Utilizing both computational methods provides a theoretical tool for analyzing the system from the atomic to the device level as shown in Figure 5.

#### 3.1.1. Modeling surfaces

First-principles calculations based on DFT have become a powerful tool for calculating surface properties of semiconductors [63–72]. Surface calculations using DFT are often computed using a planewave basis [73] and a slab configuration (see Figure 6). The slab is placed within a 3D periodic super-cell and a vacuum layer is added on either side of the slab to mimic the 2D periodicity of an actual surface. The number of slab layers should be thick enough to minimize surface-surface interactions and recover a bulk-like interior. Similarly, the vacuum

![Figure 4](image1.png)

**Figure 4.** (a) Schematic of ultraviolet photoelectron emission data with the value of the cutoff energy indicated on the plot. (b) Schematic of X-ray photoelectron spectroscopy data with the value of the absolute energy difference between the valence band-edge and the Fermi level ($|E_v - E_F|$) at the surface indicated on the plot.

![Figure 5](image2.png)

**Figure 5.** Schematic of the two computational methods described in this review. First-principles modeling is on the scale of electrons/atoms while device simulations are on the micron/device scale.
3.1.2. Quantifying a surface dipole

The interfacial dipole of a semiconductor functionalized with an arbitrary functional group can be calculated using DFT by a procedure known as nanosmoothing developed by Rabe et al. [75]. Nanosmoothing is used to eliminate bulk effects and extract well-defined, unique values of the interfacial charge and dipole densities for a system. The procedure involves calculating a smoothed charge density, $\bar{\rho}(z)$, in which periodic bulk oscillations in the microscopic charge density are removed by convoluting the planar-averaged charge density calculated in Equation (9) with a smoothing function $f(z)$ as shown in Equation (10) [74, 76]

$$\rho(z) = \frac{1}{A} \int_{0}^{A} \rho(x, y, z)dx\,dy$$ \hspace{1cm} (9)

$$\bar{\rho}(z) = \int \rho(z') f(z - z') dz'$$ \hspace{1cm} (10)

where $A$ is the surface area of the slab in the $z$-direction. The planar-average charge density and the nanosmoothed charge density are shown in Figure 7(a) and 7(b), respectively, for the symmetric terminated Si(111) slab configuration shown in Figure 6(b).

The smoothed charge density is a continuous function that approaches zero at regions far from the interface. The interface is defined as the region where the smoothed charge density deviates away from zero. The nanosmoothed dipole density, $\bar{p}$, is unique and well defined if $z_1$ and $z_2$ are in regions where the smoothed charge density is zero and is calculated using

$$\bar{p} = \int_{z_1}^{z_2} \bar{\rho}(z)dz$$ \hspace{1cm} (11)

3.2. Finite-element device simulations

wxAMPS is a drift-diffusion solid-state device simulation application based on AMPS, a solar cell simulation program developed by Fonash et al. at Pennsylvania State University [77]. wxAMPS has the same user inputs and physical principles as AMPS but incorporates a more advanced algorithm combining the Newton and Gummel methods [78] to facilitate convergence and improved models of recombination and tunneling [79,80]. wxAMPS is available free of charge on the web and has an easy-to-use graphical user interface [81]. wxAMPS has been demonstrated to model a variety of complex devices including dye-sensitized solar cells [82] and functionalized photoelectrodes [83,84].

wxAMPS simulates charge generation, recombination, and transport across single or multijunction devices by solving Poisson’s equation, the continuity equation for free holes, and the continuity equation for
4. Application of computational methods

4.1. Organic functionalization

Chemical attachment of organic molecules to a semiconductor surface may alter the direction and magnitude of the dipole at the surface [32]. We describe here how density functional theory and wxAMPS can be combined to quantify the dipole of an arbitrary functionalization and the methods are then compared with experimental measurements.

4.1.1. Band-edge control of silicon

Galli et al. conducted a combined theoretical and experimental study on the band-edge control of functionalized silicon [71]. Theoretical methods included electronic structure calculations using DFT and many-body perturbation theory (MBPT), while experimental methods included photoelectron spectroscopy and electrical device measurements. In their work, the ionization potential (IP), defined as the energy of the maximum valence band-edge relative to vacuum, of -H, -CH₃, -C₂H₅, -Cl, and -Br terminated Si(111) surfaces were compared.

The IPs were determined experimentally by measuring the work function using ultraviolet photoelectron spectroscopy and calculating the IPs from

\[
IP = \frac{WF - \left( E_{F} - E_{vb} \right) - \left( E_{vs} - E_{vb} \right)}{q}
\]

where \( E_{F} \) and \( E_{vb} \) are the bulk and surface valence-band levels, respectively, \( E_{vs} \) is calculated from the dopant density and \( E_{vb} \) is derived via a methodology described in Ref [48]. The IPs were calculated using DFT with local density approximation (LDA) exchange potentials and MBPT with the perturbative G₀W₀ approach.

At the LDA level, the calculated IPs were underestimated by 0.5–0.7 eV compared to the experimental results, while the values improved significantly using G₀W₀. However, the relative shifts in the IP between a given functionalization and Si(111)-H, \( \Delta IP \), were the same for both LDA and GW and also in satisfactory agreement with experiments. Therefore, they suggested that LDA is adequate for predicting the absolute value for IP, \( IP^{prod} \), without resorting to expensive GW calculations. This is done by calculating the shift between a given functionalization and a well-defined reference state, \( \Delta IP^{DFT}_{Ref} \), and using

\[
IP^{prod} \approx \Delta IP^{DFT}_{Ref} + IP^{exp}(Ref)
\]

where \( IP^{exp}(Ref) \) is the experimental known value of the IP for the reference state used to calculate \( \Delta IP^{DFT}_{Ref} \).
Shifts in the IP are a consequence of a shift in the surface potential, $\Delta V_{surf}$, which is related to the formation of a surface dipole normal to the surface plane of the unit cell, $\mu_{surf,z}$, by

$$\Delta V_{surf} = \frac{-4\pi \mu_{surf,z}}{A} \quad (17)$$

$\mu_{surf,z}$ can be quantified as the sum of the dipole moment formed in the adsorbate radical, $\mu_{rad}$, and the induced dipole moment due to charge transfer between the substrate and the adsorbed molecule, $\mu_{ind}$. To gain an understanding of how the magnitude of $\mu_{surf,z}$ depends on the composition and coverage of the adsorbate, Galli et al. computed $\mu_{surf,z}$ and $\mu_{ind}$ for a variety of terminal groups at both one-quarter and full coverage [71]. $\mu_{ind}$ was calculated using $\mu_{ind,z} = \mu_{surf,z} - \mu_{rad}$. They found that for non-polar terminal groups, $\mu_{ind} = 0$, trends in electronegativity dictated the charge exchange at the adsorbate/substrate interface and hence could be used to predict the magnitude of $\mu_{surf,z}$. They found that for polar terminal groups the magnitude of $\mu_{surf,z}$ depends on the orientation and surface coverage of the adsorbate, strength of intermolecular screening, and molecular polarizability.

In another study, the composition and coverage of mixed monolayers on Si(111) was found to have a significant effect on the interfacial dipole. The dipole as a function of coverage of 3,4,5-trifluorophenylacetylene (TFPA) moieties on Si(111) for both mixed methyl/TFPA and mixed chlorine/TFPA terminated surfaces was calculated using the nanosmoothing method discussed in section 3.1.2 [85]. The method was validated and the calculated trends were consistent with previously published experimental data. Significant interactions were found between neighboring species on the functionalized surface that significantly altered the magnitude of the interfacial dipole as shown in Figure 8. These results imply that the chemical species passivating non-bonded sites (i.e. -H, -Cl, -CH$_3$, etc.) must match the experimental surface when predicting surface dipoles using DFT. These findings also suggest that the effective band-edge energies of a surface can be engineered to have a specific value by tuning the interfacial dipole with the chemical make-up of a mixed monolayer.

wxAMPS can also be used to predict the magnitude of an interfacial dipole on a functionalized semiconductor by fitting experimental data [83]. For example, Lewis et al. previously measured the $V_{oc}$ for n- and p-type Si(111)-H and Si(111)-CH$_3$ photoelectrodes in contact with a series of redox couples in CH$_3$CN-1.0 M LiClO$_4$ [33]. Two different behaviors were observed for Si(111)-H and Si(111)-CH$_3$. The magnitude of the surface dipole was predicted using wxAMPS by fitting the experimental trends. Because an interfacial dipole modifies the effective electron affinity of the surface of the semiconductor, the magnitude of the electron affinity was adjusted until the calculated trend in $V_{oc}$ versus redox formal potential matched the experimental data. The results predicted a dipole shift of $-0.35$ eV between Si(111)-H and Si(111)-CH$_3$ [83].

The dipole shift between Si(111)-H and Si(111)-CH$_3$ was calculated in Galli’s work with DFT and many-body perturbation theory (MBPT) and found to be $-0.8$ eV in contact with vacuum [71]. The dipole shift determined using impedance spectroscopy in contact with octamethylferrocene-CH$_3$CN-1.0 M LiClO$_4$ is measured as $-0.4$ V and $-0.25$ V for n- and p-Si(111), respectively [33]. The dipole shift determined using photoelectron spectroscopy in contact with vacuum is measured as $-0.49$ eV [48,49], [86,87]. These results are summarized in Table 1 below.

As can be seen in Table 1 the dipole shift determined from wxAMPS is in better agreement with the experimental values than DFT and MBPT. In experiment, partial screening of a surface dipole occurs in the presence of an electrolyte. This effect is captured by wxAMPS because the value is determined by fitting experimental data directly. The resulting value includes both the raw dipole and the screening effects to yield the true final dipole of the complete system. The presence of the electrolyte is ignored when predicting the dipole using DFT and MBPT since the surface is simulated in contact with vacuum. Therefore, the difference between the values of the dipole determined by wxAMPS and DFT/MBPT provides insight into the degree of electrolyte screening occurring in a system ($-0.45$ eV in the example above). We note that the screening effect reduces the dipole by a factor of two or more. However, we have found that DFT is reliable for computing relative values of interfacial dipole.

| Impedance [33] | Photoelectron Spectroscopy [48,49], [86,87] | wxAMPS [83] | DFT & MBPT [71] |
|---------------|---------------------------------|-------------|-----------------|
| $-0.40$ V (n-Si) | $-0.49$ eV | $-0.35$ eV | $-0.80$ eV |
| $-0.25$ V (p-Si) | $-0.49$ eV | $-0.80$ eV | |
4.1.2. Organic-metal interfaces
Pennino et al. conducted a combined theoretical and experimental study on the work-function changes of metals functionalized by organic adsorbates [88]. Comparison between experiment and theory provided a clear picture of the role of molecular dipole moment, charge transfer, and Pauli repulsion on the work-function changes induced by functionalization. Theoretical methods included electronic structure calculations using DFT while experimental methods included photoelectron spectroscopy. The work-function changes of dimethyl disulfide, (CH$_3$)$_2$S (DMDS), and methylthiolate, CH$_3$S (MT) terminated Au(111) were compared. The work function changes were determined experimentally using UPS and theoretically by calculating the difference between the electrostatic potential in vacuum, $V_{\text{vacuum}}$, and the Fermi level of the Au(111), $E_{\text{Fermi}}$:
\[
\Phi = V_{\text{vacuum}} - E_{\text{Fermi}} \quad (18)
\]
The experimentally observed work-function changes for DMDS and MT terminated Au(111) were found to be $-1.2$ and $-1.5$ to $-1.7$ eV, respectively, relative to the clean Au(111) surface, which is in good agreement with the calculated values of $-1.2$ and $-1.6$ eV, respectively.

To determine the main mechanism for the observed work-function shift the electrostatic potential for the total system, $V_{\text{total}}$, was compared with the sum of the electrostatic potential of the two subsystems, $V_{\text{subsystems}}$, which consisted of the Au surface slab and molecular layer. For MT terminated Au(111), $V_{\text{total}} - V_{\text{subsystems}}$ remains constant across the interface implying no charge transfer and that the dominant mechanism responsible for the work-function shift is the molecular dipole moment intrinsic to MT. This was confirmed by the good agreement between the calculated molecular dipole of DMDS and MT. For DMDS-terminated Au(111), $V_{\text{total}} - V_{\text{subsystems}}$ decreases across the interface implying a transfer of electrons from the adsorbate layer to the Au substrate. Because the electron affinity of DMDS is the same as Au, the charge displacement must arise from compression of the Au surface charge density into the Au bulk due to Pauli repulsion with electrons in the DMDS layer. This comparison is illustrated in Figure 9.

4.2. Passivation layers
Coating a photoelectrode with a thin film metal oxide passivation layer is commonly employed to protect semiconductor surfaces against oxidation. However, metal oxide passivation layers may increase or decrease the onset potential of the electrode depending on the deposition conditions of the metal oxide and thus how charge is transferred across the heterostructure [42]. Javey et al. have observed that the photovoltage of $p$-InP photoelectrodes, which were passivated with TiO$_2$ grown by atomic layer deposition (ALD), strongly depends on the type of titanium precursor used to grow the film. They found that in one case the TiO$_2$ was ‘leaky’ and allowed significant hole conduction across the film resulting in a lower photovoltage. In an alternative case, the TiO$_2$ was ‘non-leaky’ and hole conduction was blocked, resulting in a higher photovoltage [42].

We describe here how the link between the charge transport behavior and the magnitude and direction of the induced shift in open-circuit potential can be understood by using wxAMPS to model the generation, recombination, and charge transport across semiconductor/metal-oxide heterostructures.

4.2.1. Leaky amorphous titanium dioxide
In semiconductor/metal-oxide heterostructures, a large valence band offset is usually observed between the wide-gap metal oxide and a relatively low-gap underlying semiconductor, which results in a barrier to hole transport across the photoelectrode. However, recent studies of amorphous TiO$_2$ (‘a-TiO$_2$’) grown by ALD using a nitrogen-based precursor resulted in a new ‘leaky dielectric’ passivation layer in which sufficient hole transport is observed through films hundreds of nanometers thick [89, 90]. The hole charge transport mechanism responsible for this leakage current is poorly understood experimentally due to the lack of methods available for probing such transport.

wxAMPS has been used to investigate the ‘leaky’ dielectric transport mechanism. Rose et al. measured the anodic photocurrent of $n$-Si(111)-CH$_3$|a-TiO$_2$ electrodes as a function of a-TiO$_2$ thickness [39]. They found that a maximum hole current was observed for sufficiently thin a-TiO$_2$, decreasing beyond a critical thickness and resulting in negligible current as shown in Figure 10(a).

Two different hole conduction mechanism have been suggested for this observed behavior: tunneling and defect mediated transport. Both transport mechanisms were simulated in wxAMPS for $n$-Si(111)|CH$_3$|a-TiO$_2$ photoelectrodes. The tunneling simulation results in an immediate, exponentially decreasing current versus TiO$_2$ thickness which did not match the experimental observation. The defect mediated transport mechanism...
simulations predicted that the reduction in the onset potential could be avoided by utilizing a UV light filter and only exciting the CFO/TiO₂ photocathode with visible light. Excluding the UV light, the TiO₂ acts as a protective electron-selective contact between the CFO and the electrolyte and the trap states in the TiO₂ do not influence the onset potential. The simulation results predicted an onset potential of ~1.9 V versus a reversible hydrogen electrode (RHE). This indicated that the V_{oc} of TiO₂-coated CFO under longer wavelength irradiation should provide enough electrochemical potential to evolve H₂ in a PEC water-splitting cell without an external applied voltage.

The simulation predictions were validated experimentally. First, the onset potential of the CFO/TiO₂ photocathode under visible light irradiation was measured and found to be at minimum 1.6 V versus RHE. The actual onset potential could not be observed due to the onset of water electrolysis allowing current flow. The optimized TiO₂-coated CFO under visible light irradiation had the most positive onset potential among the oxide photocathodes ever reported for PEC water-splitting, which was achieved by understanding the charge transport using wxAMPS. The TiO₂-coated CFO photocathode was connected in series with a RuO₂-loaded Pt system and under 470 nm excitation (visible light), shown in Figure 10(b), where holes move through a defect band in the band gap of the TiO₂, was shown by wxAMPS to match the experimentally observed photocurrent versus thickness response.

4.2.2. Non-leaky amorphous titanium dioxide

CaFe₂O₄ (CFO) is a promising p-type semiconductor to serve as a photocathode for H₂-evolution in a PEC water-splitting system [91,92]. TiO₂ has been introduced as a passivation layer on CFO and shown to improve the chemical stability of the material [84]. Despite improved stability, the onset potential of the photocathode upon TiO₂ deposition is reduced. wxAMPS was used to determine the charge transport limitation behind the reduced onset potential and predict ways to improve the TiO₂-coated CFO photocathode [84].

Modeling both the coated and uncoated CFO photocathode behaviors showed that the reduction in onset potential upon coating CFO with TiO₂ was a consequence of photo-generated charge trapping in the TiO₂. When the CFO/TiO₂ photocathode is under irradiation from a full spectrum solar simulator, the wavelengths of light that exceed the band-gap of TiO₂ result in photoexcitation of carriers within the TiO₂ layer. These accumulate in surface trap states, resulting in an electric field in the TiO₂ that reduces the V_{oc}. The simulations predicted that the reduction in the onset potential could be avoided by utilizing a UV light filter and only exciting the CFO/TiO₂ photocathode with visible light. Excluding the UV light, the TiO₂ acts as a protective electron-selective contact between the CFO and the electrolyte and the trap states in the TiO₂ do not influence the onset potential. The simulation results predicted an onset potential of ~1.9 V versus a reversible hydrogen electrode (RHE). This indicated that the V_{oc} of TiO₂-coated CFO under longer wavelength irradiation should provide enough electrochemical potential to evolve H₂ in a PEC water-splitting cell without an external applied voltage.

The simulation predictions were validated experimentally. First, the onset potential of the CFO/TiO₂ photocathode under visible light irradiation was measured and found to be at minimum 1.6 V versus RHE. The actual onset potential could not be observed due to the onset of water electrolysis allowing current flow. The optimized TiO₂-coated CFO under visible light irradiation had the most positive onset potential among the oxide photocathodes ever reported for PEC water-splitting, which was achieved by understanding the charge transport using wxAMPS. The TiO₂-coated CFO photocathode was connected in series with a RuO₂-loaded Pt system and under 470 nm excitation (visible light),
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