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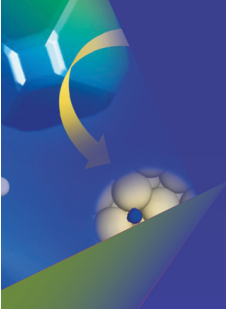


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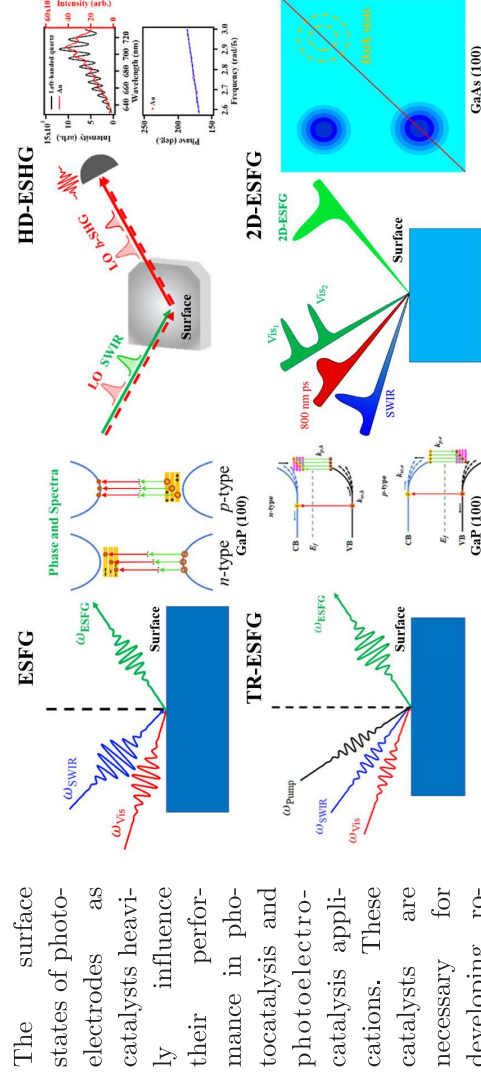
REVIEW

Surface States of Photoelectrodes by Surface-Specific Steady-State and Time-Resolved Sum Frequency Spectroscopies[†]

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The surface states of photoelectrodes as catalysts heavily influence their performance in photocatalysis and photoelectrocatalysis applications. These catalysts are necessary for developing robust solutions to the climate and global energy crises by promoting CO₂ reduction, N₂ reduction, contaminant degradation, and water splitting. The semiconductors that can fill this role are beholden as photoelectrodes to the processes of charge generation, separation, and utilization, which are in turn products of surface states, surface electric fields, and surface carrier dynamics. Methods which are typically used for studying these processes to improve semiconductors are indirect, invasive, not surface specific, not practical under ambient conditions, or a combination thereof. Recently, nonlinear optical processes such as electronic sum-frequency generation (ESFG) and second-harmonic generation (ESHG) have gained popularity in investigations of semiconductor catalysts systems. Such techniques possess many advantages of *in-situ* analysis, interfacial specificity, non-invasiveness, as well as the ability to be used under any conditions. In this review, we detail the importance of surface states and their intimate relationship with catalytic performance, outline methods to investigate semiconductor surface states, electric fields, and carrier dynamics and highlight recent contributions to the field through interface-specific spectroscopy. We will also discuss how the recent development of heterodyne-detected ESHG (HD-ESHG) was used to extract charged surface states through phase information, time-resolved ESFG (TR-ESFG) to obtain *in-situ* dynamic process moni-

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Both Tong Zhang and Yi Rao have graduated from the Beijing National Laboratory of Molecular Sciences, State Key Laboratory of Molecular Reaction Dynamics, Institute of Chemistry, Chinese Academy of Sciences. They greatly benefited from the academic setting and professionalism in the laboratory established by Professors Qihe Zhu and Fanao Kong. Yi Rao also expresses gratitude to Professor Qihe Zhu for the support of his career.

toring, and two-dimensional ESFG (2D-ESFG) to explore surface state couplings, and how further advancements in spectroscopic technology can fill in knowledge gaps to accelerate photoelectrocatalyst utilization. We believe that this work will provide a valuable summary of the importance of semiconductor surface states and interfacial electronic properties, inform a broad audience of the capabilities of nonlinear optical techniques, and inspire future original approaches to improving photocatalytic and photoelectrocatalytic devices.

Key words: Surface state, Photoelectrode, Sum frequency generation, Photocatalysis, Photoelectrocatalysis

I. INTRODUCTION

In recent years, semiconductor materials have seen tremendous use in photocatalysis (PC) and photoelectrocatalysis (PEC) owing to their unique surface and interfacial characteristics [1–10]. For the purposes of this review, a photocatalyst is defined as a material which absorbs incident light energy and is used it to facilitate a chemical reaction, namely photoelectrodes. Accordingly, a photoelectrocatalyst is aided in catalyzing the reaction by an external electric field and doubles as an electrode in an electrochemical cell [11]. In the cases of CO₂ reduction, water splitting, dye degradation, and N₂ reduction, which all have environmental and clean energy relevance, the reaction is thermodynamically unfavorable and therefore needs a catalyst to overcome this barrier [3]. In PC, the two main components are the photocatalyst itself and the surrounding medium which contains other reagents. Generally, the photocatalyst absorbs incident light which generates electrons and holes which migrate to photocatalyst/medium interface where they can participate in reduction and oxidation reactions. Such a simple PC setup often uses photocatalysts in the form of nanoparticles or thin films, as they offer high surface area to volume ratios. In such a system bulk recombinations of electrons and holes are limited, but surface recombinations are enhanced. It also offers many active sites for redox reactions but can make reaction products difficult to separate [3, 12]. The simplest PEC system involves the photoelectrode, a thin film of the absorptive semiconductor deposited on an electrode, a counter electrode, and an electrolyte solution, with the two electrodes being connected in a circuit. Instead of both oxidation and reduction processes occurring at the same material, they are separated depending on the doping of the semiconductor coating. For an n-type coating, photogenerated holes migrate to the semiconductor/electrolyte interface where they facilitate an oxidation reaction. Photogenerated electrons

are removed at the semiconductor/electrode interface and are transported to the counter electrode to take part in the reduction reaction. For a p-type semiconductor, the processes are reversed with electrons reducing on the semiconductor surface and holes oxidizing on the counter electrode surface. There are other configurations and more in-depth descriptions of PEC redox mechanisms in the literatures [3, 12–14]. PEC systems have some advantages over PC systems including spatial carrier separation, easier redox product separation, and the ability to assist the photocatalysis in completing a reaction through added energy. However, the added complexity of PEC systems over PC systems results in extra costs and poor scaling ability. Nevertheless, semiconductor surface properties facilitate both PC and PEC and, therefore, deserve a more thorough discussion.

A. Basic concepts of surface states

The surface characteristics of semiconductors dictate their performance in PC and PEC applications and are a direct consequence of their electronic band structure. For a material to be used in PC or PEC, it must generate electron-hole pairs by absorbing incident photons. When a semiconductor absorbs an incident photon with energy greater than or equal to its bandgap, an electron is excited from the valence band (VB) to the conduction band (CB), leaving a hole behind as depicted in FIG. 1. The image shows the components of the photoelectrode and the role they play in the processes of photoinduced CO₂ reduction, photodegradation, and photoinduced water-splitting that occur at the photoelectrode-electrolyte interface. Moreover, in semiconductor PC, there are three essential steps: carrier generation, separation, and harvesting. Generation is accomplished by absorbing photons, separation keeps carriers from recombining and losing energy, and harvesting makes use of photogenerated carriers in redox reactions.

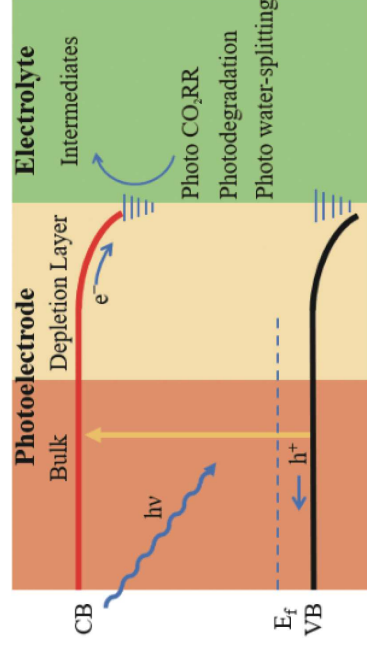


FIG. 1 Schematic of the photoinduced CO_2 reduction reaction (CO_2RR), photodegradation of dyes and contaminants and photoinduced water-splitting at a typical p-type photoelectrode-electrolyte interface.

All three of these steps depend on the electronic structure of the semiconductor and its surface properties which are interrelated. For an intrinsic (not doped) semiconductor, the bulk Fermi level is degenerate with the surface Fermi level, but the electronic band structure of semiconductors can be altered depending on their doping. There are two different types of doping in semiconductors: n and p. In an n-type semiconductor, the Fermi level of the bulk is at a higher energy than that of the surface, which causes electrons to flow from the surface to the bulk of the material. On the other hand, p-type doping causes the Fermi level of the bulk to be at a lower energy than that of the surface, resulting in electron flow from the bulk to the surface [15]. This flow of electrons to or from the surface results in electric fields at the surface of the semiconductor which facilitate charge separation and increase catalytic efficiency. This separation of charge carriers at the surface is why it is referred to as the “space charge region”. When this region is depleted of electrons, it is called the “depletion layer”, and when it is enriched, it is called the “accumulation layer”. These situations result in band bending, where the CB and VB bend upward or downward together with depletion or accumulation, respectively [15]. A visualization of p-type band bending is depicted in FIG. 1 with the CB and VB starting to “bend” downwards at the surface of the photoelectrode. This aids in reactions occurring at the surface like CO_2 reduction, degradation of dyes and contaminants, and water splitting. Semiconductor doping can also impact surface states, which are responsible for some of their interfacial characteristics.

The surfaces of materials are distinct from the bulk medium as the abrupt end of the bulk structure results

in symmetry breakage and unique electronic structure. This symmetry breakage is the result of dangling bonds at the surface of the semiconductor where atoms would be bonded to the next layer of a bulk material. These dangling bonds, as well as other inhomogeneities in the material, result in intermediate energy levels in the band gap called surface states. Since surface states skew the location of the surface Fermi level relative to that of the bulk, they can impact the electronic properties of the semiconductor. In fact, there is a higher concentration of intermediate energy levels caused by surface states than by doping of the bulk material, causing surface states to have a greater effect on the semiconductor band structure than bulk doping [15]. As such, they can significantly impact the efficiency of carrier generation for PC and PEC. Surface states typically lie below the Fermi level in the band gap, which lowers the energy barrier for electrons to move to the conduction band where they can be used in PC and PEC processes. It is important to clarify that surface states are not unique to the open surface of a material, but that they are present at every surface or interface of the semiconductor. Surface states are also referred to as trap states, where an electron or hole can get trapped, interrupting carrier dynamics. Trap states are the result of general defects, including surfaces, interfaces, lattice imperfections, *etc.*, and are not all resultant from surface states [15, 16].

B. History of surface states

Knowledge of the existence of surface states dates back to nearly a century, arising from the change in crystal lattice for pure materials and from surface imperfections [17, 18]. Relevant to PC and PEC, methods for studying semiconductors and the semiconductor/electrode interface are typically performed under high vacuum conditions [19–23]. These techniques include photoelectron emission with and without angular resolution [24, 25], which can have surface-specific characteristics depending on the system [23]. These techniques have been used extensively to investigate semiconductor surface states and trap states for decades and are still in use today [26–29]. For example, foundational work was done by investigating the surface states of silicon [30–33], germanium [34–36], GaAs [37–39], and other semiconductors [40–46]. More recently, photoelectron spectroscopy has been used to study quantum-confined systems [47], oxide film surfaces and interfaces

[48], and topological materials [49]. As noted, these investigations are optimized under non-ambient conditions, resulting in further extrapolation to consider the consequences associated with real-world applications.

The processes of PC and PEC are ideally performed under ambient conditions. In this review we are concerned strictly with experiments conducted under ambient conditions for this reason. An early electrochemical method for studying semiconductor surface states was through measuring surface capacitance from impedance-frequency measurements; where a strong dependence on frequency can indicate that interfacial capacitance is impacted by surface states [19]. An early spectroscopic technique for measuring surface states was photocapacitance spectroscopy, where the sample was irradiated with sub-gap light and the change in interfacial capacitance could be measured as a function of incident frequency [50]. However, techniques which use sub-gap radiation may also probe deeper trap states from the semiconductor bulk, and it can be difficult to differentiate which type of in-band states are being observed [51]. Electroreflectance has also been used to observe semiconductor surface state in which the reflectance of incident light by the semiconductor/electrolyte surface is measured under different applied potentials [52]. Time-resolved photoluminescence was also employed in early studies of surface states because their spectra can elucidate deep and surface states [53, 54]. While these techniques were state-of-the-art for their time and could study surface states in action, none of them were directly surface-specific and thus not directly probing surface states.

II. STUDIES OF SURFACE STATES OF PHOTOELECTRODES

A. Overview of photoelectrodes and purpose

Unlike an overall reaction on a particulate photocatalyst, many PEC studies use half-reactions, like with water oxidation which is performed on the photoelectrode surface [55]. This is because only one type of photogenerated carrier is available for the surface reaction while the other is at the counter electrode [56]. In other words, a photoelectrode can either be a photoanode or a photocathode, which affects the outcome of the reaction. Surface states and electric fields on the photoelectrode surface can affect the PEC process. However, these interactions remain ambiguous, and methods for

investigating surface states and their properties directly are scarce. Many studies which yield surface state information are indirect: conventional spectroscopic and imaging techniques are used for characterizing PEC materials while inferences are made about surface states based on their PEC activity after surface modification. Along this track, much recent work on semiconductors for PEC investigates systems with passivated surface states to try to improve catalytic activity. Through the use of transient absorption, electrochemical impedance spectroscopy, and other techniques, the enhancement of surface state passivation on materials can be quantified, as well as its effect on different inefficient processes such as CO_2 reduction and water splitting.

B. Photocathode and photoanode studies

In an example of surface state passivation, one study used a 3D electrode with a Si base and Pt nanoclusters on GaN nanowires, which showed enhanced water splitting capability with the addition of GaN over bare Pt [57]. In another instance, the introduction of an insulating layer between the GaN and Au promoted charge transfer through GaN surface state passivation and reducing carrier recombination [58]. Transient absorption (TA) spectroscopy showed a longer decay lifetime after the addition of the insulating layer which suggested surface state passivation. It was also shown that ZnO photoelectrodes for water splitting could obtain significant improvements when their surface was passivated [59]. By coating the 3D ZnO nanostructure surface with copper indium gallium sulfide (CIGS) and indium sulfide (In_2S_3) layers, the material's light absorbing properties were enhanced and the passivation of surface states promoted interfacial charge transfer at the electrode/electrolyte interface. Photocurrent spectroscopy of the modified electrode showed a sevenfold increase in charge transfer efficiency. Another complex surface passivation layer was introduced to increase PEC water splitting of CdIn_2S_4 by coating the surface with a InO_x/NiFe -layered double hydroxide (LDH) [60]. Photoelectrochemical impedance spectroscopy (PEIS) and photocurrent spectroscopy showed that photocurrent could be optimized by regulating charge carrier density and surface state distribution proportions. In another case, secondary heat processing of hematite 3D photoelectrodes allowed for virtual surface state passivation and increased water splitting activity [61]. It was shown through an increase in photovoltage for the sample that

the Fermi level pinning by surface states was reduced. Additionally, the surface state treatment reduced resistance at the electrode/electrolyte interface, reducing bulk recombinations and promoting interfacial charge transfer. The deposition of Au nanoparticles on the GaN photoelectrode surface provided enhanced CO_2 reduction ability as well [62]. In fact, the PEC enhancement was multifaceted in that the nanoparticles provided enhancement through light capturing and plasmonic resonance as well as surface state passivation. Another example is the PEC water splitting ability of GaN photoelectrodes being increased by surface state passivation with a layer of FeOOH [63]. The improved carrier transport efficiency after coating contributed to both PEC efficiency and reducing surface corrosion during the process, which was attributed to decreased interfacial resistance as confirmed by electrochemical impedance spectroscopy (EIS). The water splitting ability of graphite carbon nitride (g-CN) photoelectrodes has also been improved by surface coating [64]. In fact, the SiC surface coating enhanced PEC water splitting activity by increasing visible light absorption as well as reducing carrier recombination. Another implementation of SiC in PEC water splitting exhibited catalytic enhancement after anodization [65]. The anodization of the SiC surface created nanoscopic pores which aided in light harvesting. A surface coating of FeOOH completed the nonporous system which had an overall increased PEC water splitting efficiency from light harvesting, carrier separation, and carrier injection. A later study of SiC nanocrystals showed that the outer oxide layer likely promoted carrier recombination [66]. Although much research has been conducted on surface state passivation and indirect techniques have been used to monitor its effect on PEC reactions, an *in-situ* surface state analysis may provide deeper insights into the processes.

C. Indirect studies of structures for surface states

Much work has focused on “fixing” surface states to improve PEC activity, whereas other work has concentrated on utilizing surface states to promote catalytic activity. For example, ultrathin NiO has been recently used to extend the absorptivity of a water splitting electrode into the near-IR, since the amorphous structure increases in-band surface states which allow for lower energy light harvesting [67]. By forming a heterojunction with C_3N_4 , broad absorptivity and efficient interfa-

cial charge transfer were observed. Instead of passivating surface states on SiC nanoparticles, they have been exploited to enhance charge separation for PC CO_2 reduction [68]. The large surface area-to-volume ratio of the nanoparticles produces abundant surface states which reduce surface recombination, and the oxidized surface was found to aid in corrosion resistance. Interestingly, $\text{CuIn}_{0.3}\text{Ga}_{0.7}\text{S}_2$ photoelectrodes used in PEC reduction of CO_2 to CO were shown to have impressive catalytic ability without surface state passivation [69]. Photocurrent spectroscopy and PEIS data showed that the ability of the electrolyte to donate protons greatly impacted the stability and performance of the system. PEC systems such as $\text{CuIn}_{0.3}\text{Ga}_{0.7}\text{S}_2$ could benefit from specific surface state studies to guide further employment of the simplified photoelectrode system.

D. Direct studies of structures for surface states

In recent years many methods have emerged that can directly study surface states under ambient conditions including X-ray photoelectron spectroscopy (XPS) which was used to show that etching of GaN surfaces can result in band bending of up to 0.8 eV [70]. This work further exemplified the impact that electrode surface states can have on their catalytic efficiencies and applicability. It has also been shown that aggregation of passivation ligands can reduce charge transfer efficiency, the opposite of their intended purpose [71]. It was found that charge transfer ligands at high surface concentrations on PbS surfaces caused reduced overlap between the ligand and PbS, decreasing charge transfer. Transient absorption (TA) spectroscopy confirmed the slowed electron transfer, suggesting that monomer ligands and those with more “flexible” bindings to the surface were most efficient. For InP quantum dot semiconductors, it was found that a core-shell morphology with ZnS shell could decrease surface carrier recombinations [72]. Spectroscopic measurements with TA and transient photoluminescence (TPL) showed that the ZnS shell slowed carrier trapping thereby reducing recombinations and enhancing charge transfer. To investigate surface states of semiconductors directly, contactless electroreflectance (CER) was performed on GaN electrodes [73]. Performing CER at elevated temperatures showed that the GaN surface states redistributed at different temperatures. Dye molecules have also been used for surface state passivation at the NiO/perovskite interface [74]. Observa-

tion of surface state properties of the NiO/perovskite interface before and after passivation using TA and TPL spectroscopies showed surface state passivation on both sides of the interface which increased carrier transport for photovoltaic applications. Surface carrier dynamics are also an important factor when considering PEC efficiencies. Recently, an optical pump—terahertz probe spectroscopy has been developed to study carrier dynamics of SiC electrodes [75]. It was found through these studies that increased interfacial carrier density resulted in the slowing of fast transfer processes and the quickening of slow ones, providing fundamental information on the ultrafast carrier dynamics of electrode systems.

E. Studies of dynamics for surface states

While much valuable information was gained by indirectly observing the catalytic ability of different materials, there is much to be gained from observing more direct processes, specifically at their reactive surfaces and interfaces. The final step in PC or PEC is the extraction or utilization of photoelectrons in a chemical or electrical process, which completes the cycle of the complex process known as carrier dynamics. Carrier dynamics is also heavily concerned with the rates of this step as the rate directly affects the efficiency of catalysis [76–89]. Typical methods for studying surface states, electric fields, and carrier dynamics are not ideal as they make indirect observations, are not interface specific, and are not performed under ambient conditions. We believe that to obtain a complete understanding of these properties and to design better catalysis systems, the systems must be studied *in-situ*. For such an investigation, one must turn to methods which are interface specific and can be done under ambient conditions. However, none of these methods previously mentioned have all these properties.

F. Surface-specific techniques

Experimental observations of surface states are difficult because they are optically dark, yet some methods still complete the task. Methods such as angle-resolved photoemission spectroscopy have demonstrated their value in precisely describing the electronic structure of material and have also been extended to quantum sized systems [23, 90–92]. Scanning tunneling microscopy (STM) and spectroscopy (STS) have shown their ability to study surface states with great spatial resolution

[93]. Furthermore, ballistic electron emission microscopy (BEEM), akin to STM and STS, possesses the ability to study subsurface effects of interfacial surface states [94]. However, the common pitfall of these techniques is that they are not conducted under ambient conditions. For applications concerning photocatalysis and electrophotocatalysis, it is crucial to understand semiconductor surface states at standard temperature and pressure, as that is where they are employed [95]. The lack of interface specific techniques coupled with experiments under ambient conditions illustrates a need for a method that fulfills both requirements which can be accomplished through the use of second-order nonlinear optical spectroscopy.

III. SECOND-ORDER NONLINEAR OPTICAL SPECTROSCOPIES FOR SURFACE STATES

Our recent work with sum-frequency generation (SFG) spectroscopy allows for *in situ* analysis of surfaces under ambient conditions and can be deployed to specifically probe vibrational (VSFG) or electronic (ESFG) properties and processes of systems where inversion symmetry is broken, such as surfaces and interfaces [96–161]. Second-order nonlinear optical spectroscopies, like sum-frequency and second-harmonic generation (SHG) find utility in being forbidden from systems with inversion symmetry which results in them being inherently selective for surfaces. In the SFG process, two photons with frequencies ω_1 and ω_2 are incident on a surface and are annihilated, producing one signal photon whose frequency, ω , is the sum of the two incident frequencies: $\omega = \omega_1 + \omega_2$. One of these three photons is often in resonance with a vibrational or electronic transition with the material of interest, and thereby dictates which type of SFG is being employed. In VSFG, one of the incident lasers is in resonance with a vibrational mode of the analyte (IR) and the upconverting pulse (visible or near-IR) produces a signal beam which is in the visible or near-IR range. If the two incident lasers produce a signal which is resonant with an electronic transition of the analyte, this is referred to as ESFG. In ESFG ω_1 is typically in the visible range and ω_2 is in the shortwave-IR (SWIR). However, a special case of $\omega_1 = \omega_2$ (either visible or shortwave IR) results in SHG. SHG was implemented in spectroscopies before SFG due to its simplicity, and both techniques can provide a response spectrum.

In the following text, we will briefly describe the im-

portant theoretical background on SFG and SHG [117, 123, 162–172]. Starting with Eq.(1), we know that the SFG intensity is proportional to the two incident laser intensities, $I(\omega_1)$ and $I(\omega_2)$. In addition, it is also proportional to the square of the absolute value of the effective sum frequency susceptibility, $\chi_{\text{eff}}^{(2)}$, which contains all the measurable information on the response of the molecular system to the incident optical fields at the sum frequency ω [105, 173, 117],

$$I(\omega) = \frac{8\pi^3\omega^2\text{sec}^2\beta}{c_0^3n_1(\omega)n_1(\omega_1)n_1(\omega_2)} \left| \chi_{\text{eff}}^{(2)} \right|^2 I(\omega_1)I(\omega_2) \quad (1)$$

The SF signal intensity is also proportional to the square of the signal frequency, ω , as well as the reflection angle with respect to the surface normal, β . The SF intensity is inversely proportional to the speed of light in vacuum, c , and the refractive index of the three involved frequencies, in the bulk medium, $n_1(\omega_i)$. $\chi_{\text{eff}}^{(2)}$ depends on the experimental polarization and geometry, of which there are an infinite number of combinations. The polarization combinations which are commonly used are SSP, SPS, PSS, and PPP, where S corresponds to light polarized perpendicular to the incident plane and P corresponds to light polarized parallel to the plane. The combinations are listed in order of increasing wavelength: ω_1 (signal), ω_2 (visible), and ω_3 (SWIR).

The macroscopic sum frequency susceptibility tensors, $\chi_{ijk}^{(2)}$, relate to the microscopic hyperpolarizability tensor elements, $\beta_{i'j'k'}^{(2)}$, through an ensemble average over the molecular orientation distribution and the number density of irradiated interfacial molecules, N_s [173]. When this $\beta^{(2)}$ is known the molecular orientation of the surface molecules can then be obtained. In ESFG, $\beta^{(2)}$ can be given by [117, 173, 174]

$$\beta^{(2)} = \beta_{\text{NR}}^{(2)} + \sum_{\text{ss}} \frac{\beta^{\text{ss}}}{\omega - \omega_{\text{ss}} + i\Gamma_{\text{ss}}} \quad (2)$$

The first and second terms in Eq.(2) represent the non-resonant (NR) and surface states (ss) to the molecular response generating $I(\omega)$. The terms β^{ss} , ω_{ss} , and $i\Gamma_{\text{ss}}$ represent the sum frequency strength factor tensor, resonant frequency, and damping constant from the electronic transition of the surface state, respectively.

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IV. EXPERIMENTAL METHODS

Different types of SHG and SFG techniques are used to make specific measurements, and to facilitate this, there are fundamental differences in their experimental setup. In general, they all follow the same basic experimental setup and add additional components to alter the purpose of the experiment to allow for additional data to be collected. Basic experimental setups will be discussed for ESFG and ESHG, heterodyne-detected ESHG (HD-ESHG), time-resolved ESFG (TR-ESFG), and two-dimensional ESFG (2D-ESFG).

A. ESFG and ESHG

ESFG can measure ultrafast electronic properties and collect phase data. Depending on the chosen wavelength, different transitions can be studied for the sample being measured. Historically, ESFG experiments were implemented by tuning the laser wavelength to a single transition [136, 166, 175–178]. However, the tuning ESFG experiments were time-consuming and challenging. In recent years, tremendous efforts have been made in broadband ESFG experiments to eliminate this issue [113, 136, 179]. A broadband visible source was used to implement electronic SFG; however, the chirp with the white light was a serious problem in the ESFG experiments. As a consequence, the temporal chirp and the spectral complexity in the ESFG probe could prevent transient ESFG spectroscopy from revealing ultrafast structural dynamics and chemical reactions at surfaces and interfaces. Thus, a broadband SWIR technique was developed for ESFG experiments to probe ultrafast electronic properties at surfaces and interfaces with less interferences of double resonance (FIG. 2(A)) [180, 181].

B. HD-ESHG

Heterodyne-detected (HD)-ESHG can detect charged surface states through deconvoluting the macroscopic susceptibility into its real and imaginary parts. Usually, the experimental setup of HD-ESFG is similar to ESHG except with the addition of a local oscillator (LO) and a time delay generator. The time delay generator leads to temporal separation of the LO from the SHG signal [121, 182]. This causes the LO to propagate terminally after the signal due to the positive dispersion, but the generated SHG LO and the transmitted fundamental beam remain spatially

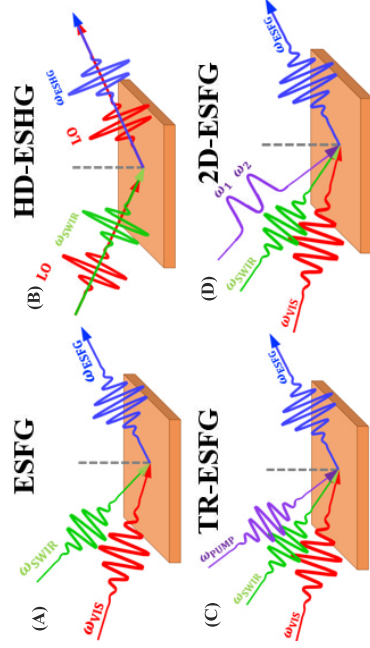


FIG. 2 (A) A schematic of ESFG showing the visible (red) and SWIR (green) beam generating the ESFG signal (blue) when reflected on the sample. (B) A schematic of HD-ESHG showing the SWIR beam (green) generating the ESHG signal (blue) and the addition of the LO (red). (C) A schematic of TR-ESFG showing that it functions the same as ESFG (A) but with the addition of a pump pulse (purple) to measure time-resolved data. (D) A schematic of 2D-ESFG showing that it functions the same as ESFG (A), but with the addition of a visible double pulse (purple) generated by the TWINS to measure 2D data.

collinear when being overlapped at interfaces as shown in FIG. 2(B). The time delay between a LO and measured signals dictates a spectral interference cycle. The larger the time delay, the narrower the spectral interference cycle.

C. TR-ESFG

Time-resolved (TR)-ESFG allows for carrier dynamics of the surface states to be revealed which makes it a vital method for the study of PC and PEC. The basis of TR-ESFG is similar to the previously described methods, but also involves the addition of a pump beam with all three pulses aligned into a single incident plane. One way the spectra can be collected is in a reflection geometry which is then normalized to produce a broadband interfacial electronic spectrum for the sample as shown in FIG. 2(C) [180, 183]. The use of multiple translations stages can be used to control the time delay between each of the three pulses and the pump pulse can be synchronized with the system with the use of a chopper. Because of the introduction of a fs pump pulse, the instrument can be used to collect time-resolved data with an ESFG probe. Additional data can be collected through the use of a motorized rotation stage to measure azimuthal angles allowing for more information to be revealed about the orientation of the sample and other information dependent on the incident angle.

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D. 2D-ESFG

Two-dimensional (2D)-ESFG measurements help to bridge the gap between the visible and IR regions to reveal how structural dynamics for photoexcited electronic states is coupled with vibrations at interfaces and surfaces [156]. Most often, 2D-ESFG is performed by splitting the fundamental light into three beams to generate a narrowband visible pulse, a SWIR source, and a pump beam [156, 184]. 2D-ESFG experiments are usually implemented in a partially collinear geometry, called a pump-probe geometry. The 2D-ESFG spectra in detection wavelength can then be taken as a function of each coherence time and then Fourier transformed into frequency domain in excitation wavelength. Thus, 2D-ESFG spectra can be obtained in both the excitation and detection wavelength. It is important to be able to measure the coherence time and also have precise control over the time delay. One method of accomplishing this is by sending the pump light into a Translating Wedge based Identical pulses eNcoding System (TWINS) to generate a pair of phase-locked pump pulses which was first developed by Cerullo and co-workers [185, 186]. This pump pulse is aligned with the other two beams, SWIR and visible, in a single incident plane as depicted in FIG. 2(D). The coherence time can then be scanned using the TWINS to obtain a 2D-ESFG spectrum.

V. PHYSICAL AND CHEMICAL PROPERTIES OF SURFACE STATES

A. Identification of surface states in photoelectrodes

Due to the nature of surface states, they should be abundant in systems with great surface area-to-volume ratios. Accordingly, nonlinear optical techniques have been used to study surface states in quantum dots (QDs), specifically, ESFG. The ESFG spectra of CdSe QDs revealed two transitions which were previously invisible in linear spectroscopies. It was demonstrated that a lower energy mode was strongly related to surface states by reacting the QD surface and correlating the ESFG intensity with relative surface contributions [175]. Later, ESFG was used to identify surface trap states in CdSe QDs which lie below the bandgap. These two modes below the bandgap were indicative of shallow and deep surface states, which could previously not be resolved in the ESHG experiments. These signals were again confirmed to be from surface states by react-

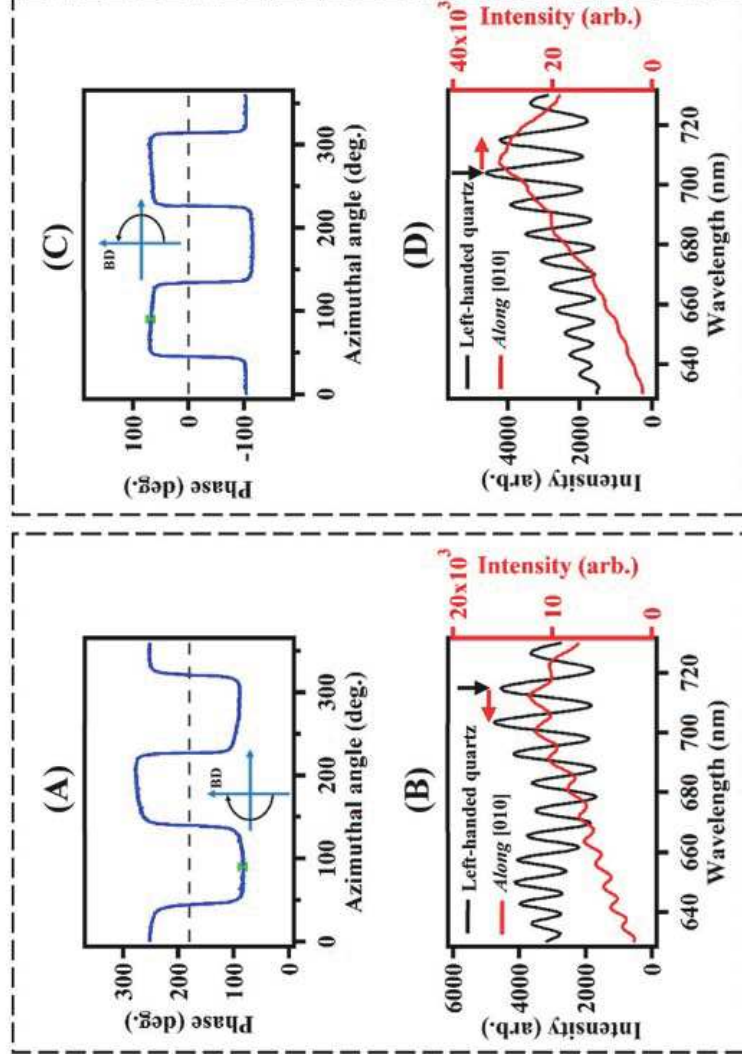


FIG. 3 Absolute phases of n-type (A) and p-type (C) GaP(100) as a function of the azimuthal angle at 700 nm. Interference ESHG spectra for n-type (B) and p-type (D) GaP(100) along the surface-dominant [010] axes. Adapted with permission from Ref.[181], copyright 2022 American Chemical Society.

ing the clean QD surface [187]. These challenging inter-face-specific experiments demonstrated that nonlinear optical techniques are a viable alternative to high-vacuum methods, allowing interfacial electronic structures to be probed under ambient conditions.

1. Identification of GaAs and GaP surface states

GaAs semiconductor surface states have also been investigated by ESFG spectroscopy due to its high density of surface states [180]. For the p-type GaAs, two surface states were identified, one near 660 nm and the other near 745 nm. As such these peaks were attributed to transitions from the surface states above the VB edge to the CB. Time-resolved ESFG experiments were also conducted to observe the population and relaxation of the surface states of p-type GaAs. By comparing their evolution over time, it was found that these surface trapping states exhibited accelerated carrier recombination relative to the material bulk. Interestingly, these TR-ESFG experiments showed that the GaAs surface states were populated at a slower rate than for the bulk process. Not only can ESFG identify surface states in semiconductors, but it can also describe their temporal

evolution under pump-probe conditions, providing pertinent information for the design of efficient PC and PEC electrodes. Surface states have also been identified for GaP using ESFG, as detailed in the next section [181].

In addition, surface states in an organic/silicon photoelectrode were investigated in 2015 by Li *et al.* using ESFG, extracting relevant electronic information for use in solar cell applications. It was shown that the organic's bandgap, when in contact with the silicon support, was narrower and had a different line shape from that of the bulk material whose linear spectra were broad and Gaussian. This demonstrated the necessity of investigating solid/solid interfaces *in situ* when considering their real-world applications [136].

2. Identification of GaP charged surface states

Understanding the charged nature of semiconductor surface states is crucial to developing efficient PC and PEC devices because it impacts interfacial band bending [15]. A method of measuring the charge of surface states under ambient conditions is through interface-specific phase-resolved ESFG spectroscopy. Through

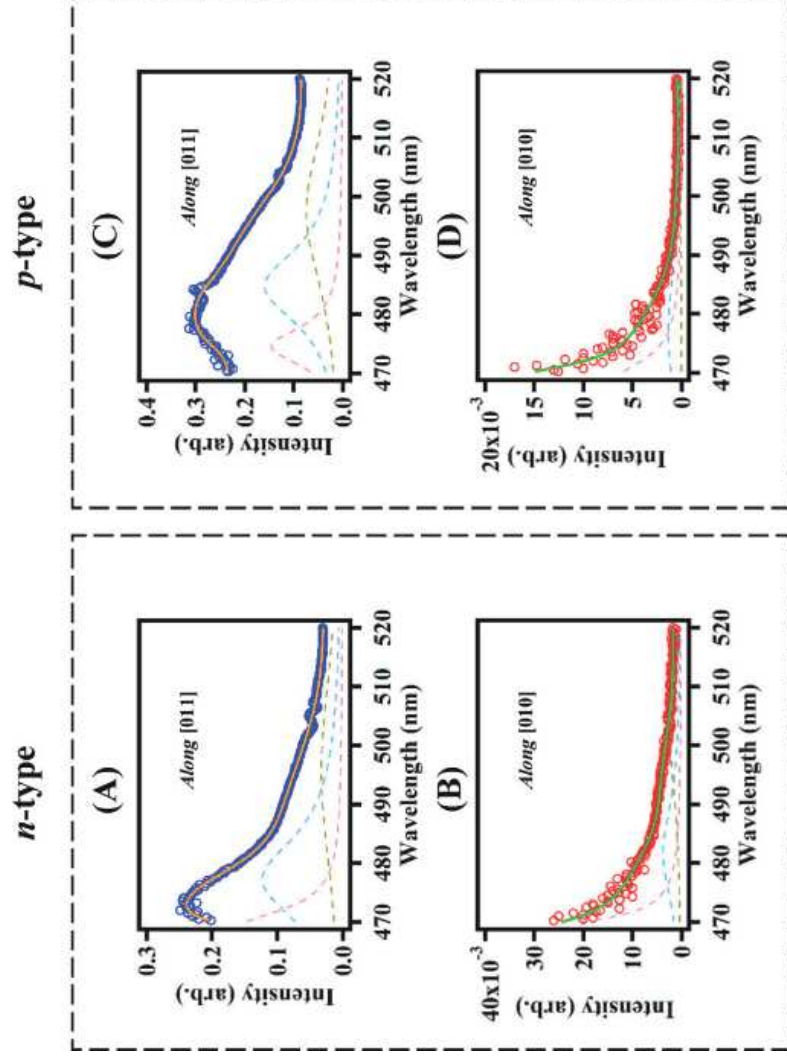


FIG. 4 ESFG spectra of n-type GaP(100) along its bulk- (A) and surface-dominant (B) axes, ESFG spectra of p-type GaP(100) along its bulk- (C) and surface-dominant (D) axes. Adapted with permission from Ref.[181], copyright 2022 American Chemical Society.

phase measurements, the macroscopic susceptibility can then be deconvoluted into its real and imaginary parts, thereby collecting maximum information from experimental data. Zhang *et al.* developed a HD-ESHG method for the direct measurement of spectral phases at interfaces in 2022 [182]. Following this technique, they were later able to measure the interference electronic spectra for n-type and p-type GaP (100) along the surface-dominant [010] directions [181]. FIG. 3 reveals that the interference peaks of both n-type and p-type GaP significantly shift compared to left-handed quartz, n-type with phase lead and p-type with phase lag. The phases along the surface-dominant directions differ by almost 180° between n-type and p-type GaP (100) which indicates that surface charges are separate for n-type (being negative) and p-type (being positive). By collecting ESHG spectra for both n-type and p-type GaP (100), it was found that the ESFG spectra were dependent on doping type. Later, HD-ESHG was combined with ESFG to identify surface states and perform phase measurements [181]. For n-type GaP(100), these three peaks were located at 471, 478, and 495 nm as shown in FIG. 4(A) and (B). For the p-type crystal

however, the three observed peaks were found at 473, 486, and 498 nm (FIG. 4 (C) and (D)). It was shown that the surface states for the n-type photoelectrodes lie at the upper edge of the band gap with a negative charge, and those for p-type GaP exist at the lower edge of the band gap with a positive charge. These surface states represent the transitions from the VB to the acceptor-type states for n-type and from the donor-type states to the CB for p-type GaP. This work showed that ESFG spectroscopy can selectively probe semiconductor surface properties, identify surface states therein, and provide information about their charged sign. Being inherently interface-specific, ESFG can likely be extended to monitor the effects of surface state passivation for improved carrier dynamics. Such information is vital in the design of efficient PC and PEC material interfaces.

Charged surface states can also be measured using surface photovoltage (SPV) spectroscopy which measures the generated voltage at a semiconductor surface under different illumination wavelengths [188, 189]. SPV has been used extensively for decades and has provided much important information including surface

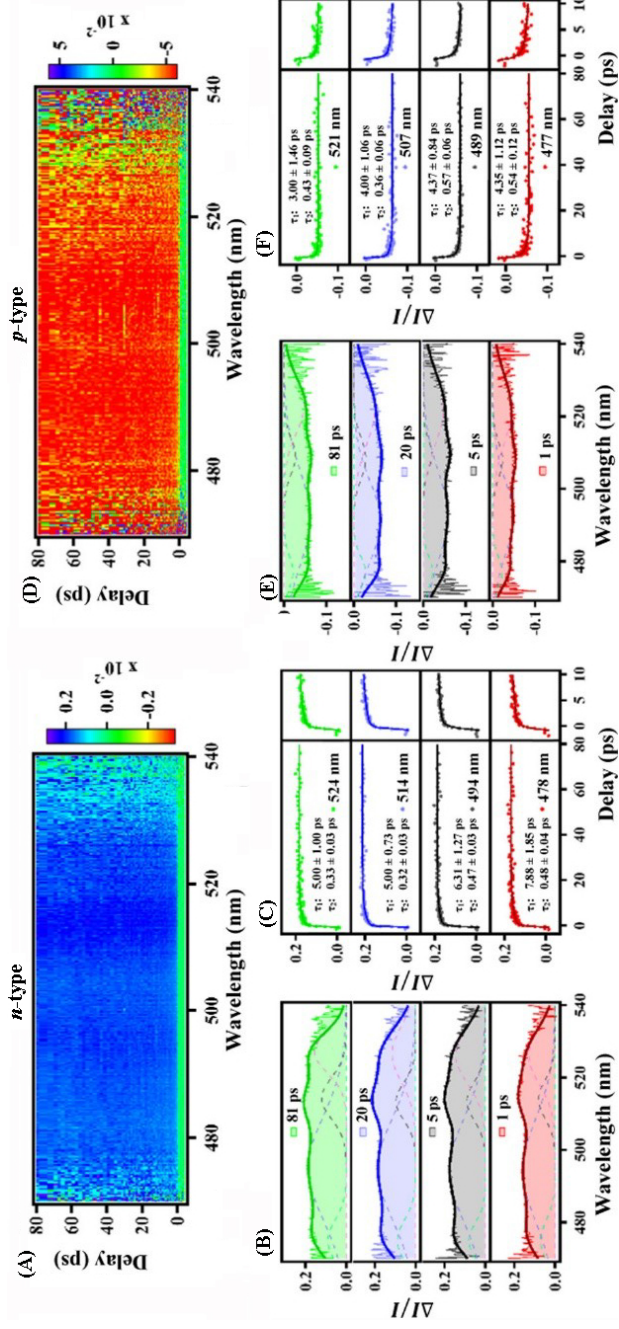


FIG. 5 Time traces from TR-ESFG of n-type at 514 nm (A) and p-type at 507 nm (D) GaP(100) as a function of pump fluence. Fluence-dependent TR-ESFG intensities at 50 ps delay for n-type (B) and p-type (E) GaP(100). Fluence-dependent calculated time constants from double exponential fittings for n-type (C) and p-type (F) GaP(100). Adapted with permission from Ref.[183], copyright 2022 American Chemical Society.

states and doping [190], surface state density [191], and phase information [192], and is still a relevant technique today through implementation in microscopy [193, 194], automated spectroscopy [195], and carrier dynamics with spatial resolution [196]. Notwithstanding the numerous applications of SPV to various systems and the valuable information that it can provide, SPV spectroscopy is not without its flaws. Firstly, SPV is not an inherently surface-selective method. In the case of extreme UV probe, visible pump transient SPV is surface sensitive [197], but must be conducted under vacuum conditions which is not ideal for studying photoelectrodes *in-situ*. Photoelectron spectroscopy which has been used to study SPV effects is also conducted under non-ambient conditions [198–200].

VI. PHOTOINDUCED DYNAMICS OF SURFACE STATES

A. Photoinduced buildup of surface electric fields and surface state population

When a photoelectrode is irradiated with light of the appropriate energy, the transport of generated carriers to the semiconductor surface is facilitated by photoinduced electric fields [15, 201–205]. Surface electric fields can separate electron–hole pairs, which reduces the rate of recombination, therefore, identifying and measuring

these photoinduced surface electric fields is imperative for the improvement of photocatalysts.

1. Photoinduced surface electric fields of GaP

The electric fields at the semiconductor surface which enable carrier transport provide a direct link to the efficiency and dynamics of PC and PEC materials because they influence the presence of carriers to perform chemical reactions. Recently, TR-ESFG spectroscopy was used to track surface state population to understand the roles played by the photoinduced surface electric fields [183]. FIG. 5 shows TR-ESFG spectra and kinetic traces for n-type (left) and p-type (right) GaP (100). From this data it was concluded that transient ESFG signals exhibit positive and negative signs for n-type and p-type GaP (100), respectively. TR-ESFG showed that it could track the movement of photo-generated electrons and holes to the surface of p-type and n-type GaP (100), respectively. Zhang *et al.* found that photoinduced ESFG signals increase for n-type and decrease for p-type GaP (100) upon photoexcitation, suggesting that surface electric fields or surface voltages increase for n-type and decrease for p-type crystals through carrier generation. The ultrafast character of the TR-ESFG provided *in-situ* monitoring of the buildup of the electric fields and observed rates of $2.86 \pm 0.30 \text{ ps}^{-1}$ for n-type and $2.50 \pm 0.25 \text{ ps}^{-1}$ for p-type

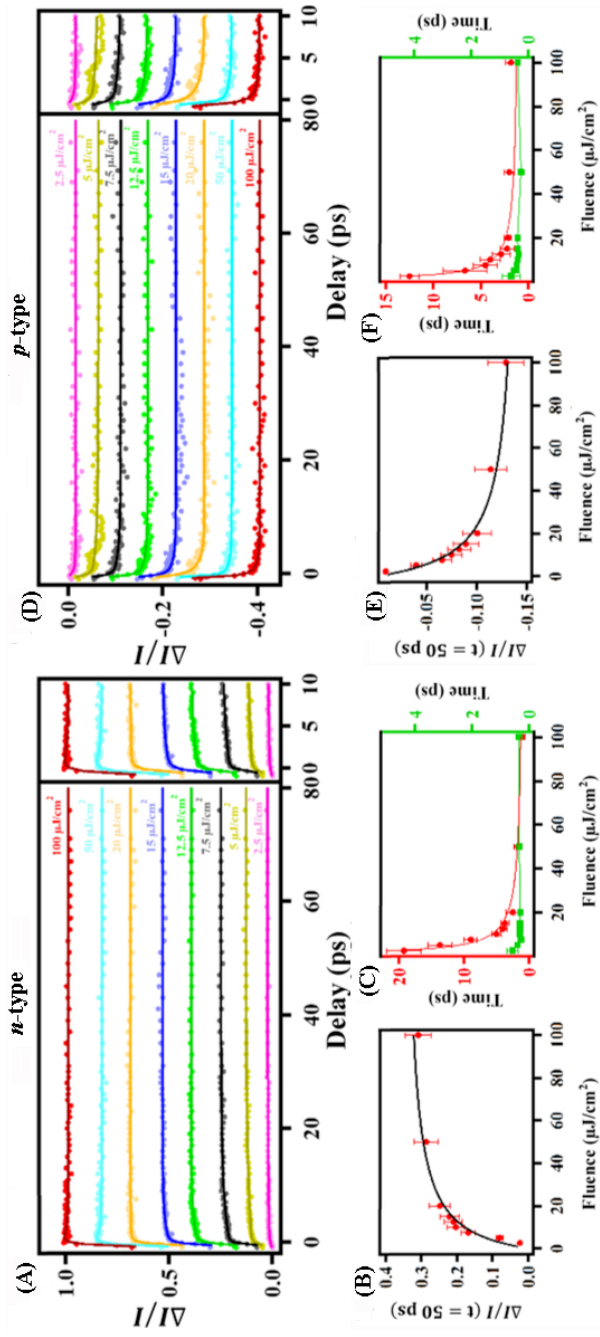


FIG. 6 2D pseudocolor plots of TR-ESFG spectra of n-type (A) and p-type (D) GaP(100). ESFG spectra of n-type (B) and p-type (E) GaP(100) at 1, 5, 20, and 81 ps time delay. Time constants from TR-ESFG of n-type (C) and p-type (F) GaP(100) at fitted maxima. Adapted with permission from Ref.[183], copyright 2022 American Chemical Society.

GaP. Quantifying the buildup rates of surface electric fields in semiconductor materials is important to their performance because they can limit the overall rate at which the PC or PEC processes can proceed.

2. Photoinduced population dynamics of surface states in GaP

The population dynamics in semiconductors are crucial in the efficient use of photogenerated carriers because the catalytic carriers are only used once they have populated excited states. After observing the photoinduced buildup of surface electric fields in GaP (100), population of surface states was studied [183]. First, four photoinduced surface states were identified at 478, 494, 514, and 524 nm, from shallow to deep with respect to the CB for n-type GaP(100) in FIG. 5(A-C). In addition, four surface states at 477, 489, 507, and 521 nm, from shallow to deep with respect to the VB, were also identified for p-type GaP(100) in FIG. 5(D-F). Next, they measured fluence dependent TR-ESFG at 514 nm to further study the dynamics of the identified surface states and electric fields in FIG. 6. It was found that surface population, like electric fields noted above, is different for the two types of doping. Specifically, the population is bimolecular process where n-type GaP showed a rate of $0.020 \pm 0.002 \text{ cm}^2/\text{s}$ while a rate of $0.035 \pm 0.002 \text{ cm}^2/\text{s}$ was observed for p-type. These surface state carriers eventually relax through surface recombination with traps or transport

into the bulk with timescales on the order of nanoseconds. The classical interpretation says that the shallow surface states can provide free carriers, while the deep surface states are generally localized and act as traps to facilitate the separation of electron-hole pairs [206]. However, the results from this study showed that both the delocalized and shallow surface states are involved in the buildup of surface electric fields and surface carrier populations. Furthermore, FIG. 6(B, E) present the differential intensities of the TR-ESFG spectra under different incident fluence, which is relevant to PC and PEC device application as incident fluence may not always be constant. It was found that even under fluence $< 10 \text{ } \mu\text{J}/\text{cm}^2$, $\Delta I/I$ depends on incident fluence for n- and p-type GaP(100). This was also found to be the case for n- and p-type GaAs [180]. Interestingly, recent investigation of carrier dynamics in perovskite materials using TA spectroscopy found that the carrier dynamics were unaffected by incident fluence under very low excitation energy [207]. This highlights the importance of a thorough understanding of the complicated nature of carrier dynamics in different materials for their optimized use in PC and PEC systems. Thus, TR-ESFG is proven to be an effective method for revealing new relaxation and population dynamics of photoinduced electric fields and surface states. Such insights provided with interfacial specificity may lead to more efficient integration of PC and PEC materials into real-

world devices.

B. Relaxation dynamics of surface states

Surface-specific relaxation dynamics in semiconductors are imperative to the performance of PC and PEC materials because they describe the duration of the availability of carriers to be extracted for catalytic uses. Trap states brought about by surface states and other material defects can promote or impede carrier recombination as described in the introduction. For this reason, quantification of relaxation rates is necessary for determining the viability of a material in PC and PEC applications and improving existing materials.

1. Methods to study relaxation dynamics

There have been several methods used to investigate relaxation dynamics. An early technique for studying dynamics in semiconductors was minority-carrier capacitance, which uses capacitance to study the charge states in the depletion region. This method showed promise with its ability to locate recombination centers, describing their concentration and energy depth [208]. Time-resolved microwave conductivity was also able to give perspective on charge carrier recombination rates. Measuring the conductivity of GaP under photoexcitation studied the dynamics of band bending in the depletion layer and showed that recombination occurs on the material surface [209]. Photoemission spectroscopy has been used to measure the relaxation time of carriers at semiconductor surfaces as well. Observing electrons emitted from the surface, it was found that increasing temperature shortened relaxation times [210]. Despite their efforts, these techniques do not provide direct observations of surface carrier dynamics *in situ* under ambient conditions. An earlier implementation of broadband ESFG set out to study relaxation dynamics at organic semiconductor surfaces with interfacial specificity [179]. However, experimental difficulties arising from the broadband generation inhibited the ability to probe ultrafast processes.

2. Relaxation dynamics of GaAs

Understanding ultrafast dynamics in carrier relaxation is imperative in promoting efficient carrier extraction for PC and PEC utilization. Later progress in the development of ESFG and ESHG by Deng *et al.* provided a broadband spectrometer with ultrafast time resolu-

tion [180]. The chosen sample for demonstrating this technique was oxidized p-type GaAs (100) which is commonly used to study surface state properties due to its density of surface states. Initially, the broadband electronic spectrum revealed a broad peak spanning most of the ESHG range attributed to the electronic transition from a surface state near the VB to one at another state located at a higher valley. The authors next introduced the pump pulse to extract dynamic information about this surface transition, as shown in FIG. 7(A and B). The peak at >600 nm is also apparent in the TR image, now negative according to the convention of differential intensity, and corresponds to the increase in the population and subsequent relaxation of surface states. Inspection of the TR spectra at discrete time intervals in FIG. 7(B) showed that the broad peak was composed of two peaks near 660 and 745 nm, which demonstrated the ability of the technique to identify surface states. Moreover, the kinetic traces in FIG. 7(C and D) from the time resolved spectral image showed that both peaks exhibited a comparable relaxation time, following a single exponential fitment. However, the rising traces, those where negative differential intensity increased before relaxation, did not follow a single exponential fitting and had to be modeled with a double exponential curve. The comparisons to the bulk responses showed that the surface processes were significantly slower than those for the bulk, in both rising and relaxation regimes. A benefit to pump-probe techniques is that they offer an added variable of pump fluence which can enrich experimental applications. Collecting fluence-dependent TR interfacial electronic spectra for the GaAs semiconductors allowed further determination of the nature of the surface states. It was shown that while the rate constants for the rising regime of the excitation were unaffected by pump fluence, the relaxation process proceeded faster with increasing fluence. These analyses quantitatively demonstrated that the surface states at 660 and 745 nm have similar energy level barriers for the population of photo-generated electrons. Surface-passivated GaAs systems have also been investigated using electric field-induced second-harmonic (EFISH) techniques. For example, the copper phthalocyanine (CuPc)/GaAs system exhibited variable two-step carrier dynamics: both the n-type GaAs surface and the CuPc/GaAs interfaces hosted carrier separation times of 90 ± 30 fs, and the GaAs/CuPc interface hosted hole injection in fast

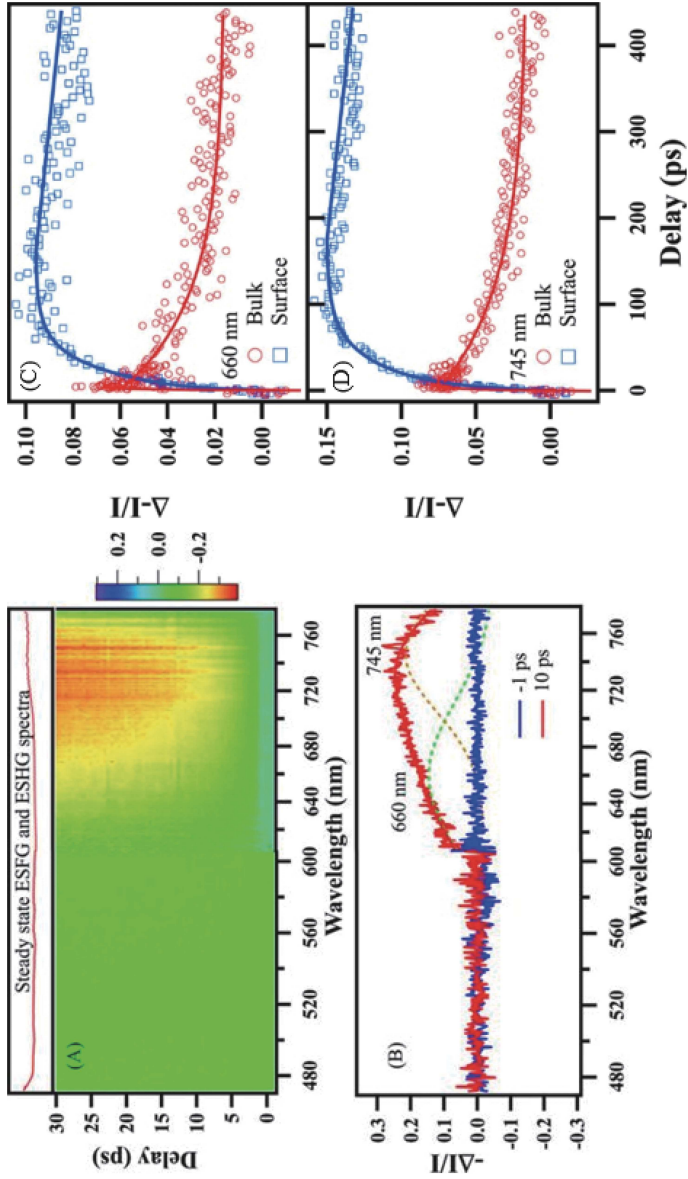


FIG. 7 (A) 2D pseudo-color transient broadband surface spectra from the p-type oxidized GaAs (100) surface, as compared with steady-state surface spectra in the inset (red line). (B) The transient spectra for -1 ps and 10 ps taken from the 2D spectra in (A). (C, D) Comparison of kinetic profiles of the surface and bulk for p-type GaAs (100) at 660 nm (C) and at 745 nm (D). Reproduced from Ref.[180], copyright 2019 AIP Publishing.

(120±30 fs) or slow (1.1±0.2 ps) processes [211]. This work provided important kinetic information about surface state population and band bending for the application of hybrid semiconductor materials. These accounts, TR-ESFG and induced SHG alike, demonstrate the great speed with which carriers undergo separation and relaxation and highlight the necessity for interface-specific tools to better align semiconductor materials with uses in catalytic applications.

VII. COUPLINGS OF SURFACE STATES

The coupling of surface states with one another can influence carrier dynamics in PC and PEC materials by promoting or restricting carrier transport. An effective way to determine different couplings between surface states is through 2D-ESFG or 2D-ESHG because it can reveal couplings that cannot be obtained through one-dimensional TR-ESFG. An example of this is shown by Deng *et al.*, who used 2D-ESFG to reveal surface state couplings of p-type and n-type GaAs [184]. FIG. 8 demonstrates 2D-ESFG spectra for n-type GaAs(100) at a waiting time of 0.8 ps and p-type GaAs(100) at a waiting time of 1.1 ps. The horizontal axis represents a detection wavelength from spectrally resolved ESFG signal with the spectrometer while the vertical axis is

excitation wavelength obtained from Fourier transformation with respect to the stage position and calibrated using the work by Cerullo *et al.* [185, 186]. FIG. 8 reveals several interesting features that reveal surface state couplings. First, only one distinct diagonal peak occurs at (ω_{520} nm, ω_{520} nm) which attributes to the transition from the donor surface state to a higher valley. The second feature is two off-diagonal peaks at (ω_{520} nm, ω_{540} nm) and (ω_{520} nm, ω_{565} nm) that arose from interactions of their corresponding diagonal peaks at (ω_{565} nm, ω_{565} nm) and (ω_{540} nm, ω_{540} nm) with the peak at (ω_{520} nm, ω_{520} nm). However, the two diagonal peaks are not prominent for both the p-type and n-type GaAs(100) surface, suggesting that these two surface states are dark states. In a dipole approximation, surface states are optically dark in steady state at equilibrium. As a result, transitions from the valence band directly to surface states are usually forbidden. Under nonequilibrium, these surface states are populated by electrons from the conduction band for p-type GaAs or by holes from valence band for n-type GaAs [180]. These results suggest that the transition from the donor surface state to a higher valley is strong, while the transitions from the other two surface states are too weak to be observed. The strong off-diagonal peaks (ω_{520} nm,

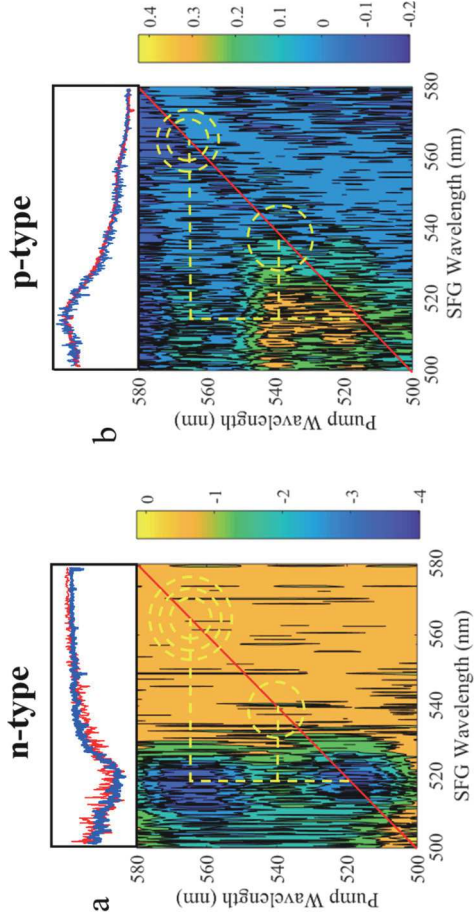


FIG. 8 2D-ESFG spectra of GaAs (100) surface for (a) n-type ($t_w=0.8$ ps) and (b) p-type ($t_w=1.1$ ps). The insets compare projection of the 2D-ESFG spectra (blue) and transient ESFG spectra (red) at corresponding waiting time. The dashed circles in diagonal peaks are labeled in yellow. Adapted with permission from Ref.[184], copyright 2020 American Chemical Society.

ω_{565} nm) in n-type GaAs and (ω_{520} nm, ω_{540} nm) in p-type GaAs are indicative of population transfer among the surface states. Which has been similarly observed before by Borca *et al.* in 2D-ES experiments of semiconductors [212]. They explained that the dominance of one off-diagonal peak, and asymmetry between the two off-diagonal peaks, resulted from the many-body effects in semiconductors [212]. Thus, the off-diagonal peaks in 2D-ESFG provided strong coupling of interactions of surface states in GaAs.

In addition, Deng *et al.* continued to reveal more about the couplings of surface states of GaAs using 2D-ESFG [156]. They chose to use p-type GaAs (100) to minimize scattering as it is a single crystal to demonstrate the interactions of surface states. 2D-ESFG spectra for p-type GaAs (100) at a waiting time of 0.3 ps show that a major diagonal peak is located at (ω_{518} nm, ω_{518} nm) and two off-diagonal peaks at (ω_{518} nm, ω_{540} nm) and (ω_{518} nm, ω_{558} nm) appear in the 2D-ESFG spectra. The author concluded that the two peaks at 518 nm and 558 nm were the result of transitions from the surface states in the bandgap to a higher valley as shown in their previous work [180]. Additionally, the 2D-ESFG spectra revealed other peaks at (ω_{540} nm, ω_{540} nm), which could not be observed with the one-dimensional spectra. The transition from the donor surface state to a higher valley was strong at (ω_{518} nm, ω_{518} nm), with the transitions from the other two surface states at (ω_{558} nm, ω_{558} nm) and (ω_{540} nm, ω_{540} nm) being quite weak. The strong off-diagonal peaks (ω_{518} nm, ω_{558} nm) in p-type GaAs could be explained by

the many-body effects of the surface states in the semiconductors [212]. Therefore, 2D-ESFG provided new information about the coupling of surface states in GaAs. These findings could not have been obtained with the use of one-dimensional ESFG showing the need for further use of 2D-ESFG to understand the couplings of surface states.

VIII. OUTLOOK AND SUMMARY

The effects of surface states, photoinduced electric fields, and carrier dynamics on the efficiency and performance of PC and PEC systems require interface-specific spectroscopic tools. Here, we have provided a unique vantage point on these electronic properties in semiconductor systems: one which is surface-specific and can be conducted under appropriate, ambient conditions. These surface-specific tools of ESFG and its derivative spectroscopies have provided *in-situ* identification of surface states, charged surface states, the buildup of surface electric fields and surface state population, and excited state relaxation. Yet, there are still new avenues to be explored using ESFG methods and like methods, including the application of the dynamic interfacial electronic properties, and the interplay between surface states and polarons.

A. Surface polarons

Polarons are quasiparticles which are formed when a charge carrier is trapped in a defect state [213], which as discussed above may be the result of surface states. The

bond-deficient nature of surface states causes them to act as traps for polarons, and bulk polarons favor migration to the surface [214]. With their surface affinity, polarons likely impact catalytic activity at semiconductor surfaces for PC and PEC processes. Work investigating polaritons has been conducted to establish this hypothesis including impacting catalytic oxygen generation [215], increasing carrier lifetimes [216], affecting QD properties [217], concentrating surface charges [218] and photocurrent density [219], and impact Fermi level pinning [220]. This research has shown that polarons can have a direct effect on the efficiency of photochemical and electro-photochemical reactions, but none of them have offered direct observation in real time. We believe that the specificity of ESFG techniques will provide a necessary *in-situ* analysis of polarons in surface trap states. By understanding the population of polarons though their accumulation rates, we will be able to promote their residence in surface states where their longevity will stimulate catalysis or determine efficient means of reducing polaron content when their presence can restrict reaction propagation.

B. PC and PEC applications of surface states to promote performance

We believe that the future of PC and PEC processes lies in their applications to CO₂ reduction, nitrogen fixation, and water splitting, and that their performance can be drastically enhanced by harnessing surface states and related phenomena. Surface states being in the band gap has promoted catalysis by increasing absorptivity [221], reducing recombination for CO₂ reduction [222], and promoting water splitting [223]. Additionally, reducing surface state influences have improved water splitting efficiency [224, 225] as well as nitrogen reduction [226]. These catalytically demanding processes have also been improved by optimizing surface electric fields in the case of CO₂ reduction [227, 228], water splitting [229, 230], and nitrogen reduction [231]. Intuitively, the motion of charge carriers in catalysts as well as their rates is imperative in their performance. This has been the case for PC CO₂ reduction [76, 232], charge transport in water splitting [233–235], and nitrogen reduction as well as contaminant remediation using novel MXene materials [236]. Nevertheless, these scenarios of increased catalytic efficiency have not been observed in real time. We believe that the *in-situ* analyses afforded by TR- and 2D-ESFG will allow us to form a

better understanding of these enhanced properties. For example, the tracking of charged surface state accumulation and depletion in PEC CO₂ reduction will allow us to understand the barriers with initiating the reaction. Likewise, the direct characterization of surface electric fields and their magnitudes will lead to the more efficient design of semiconductor water splitting photoelectrodes. Lastly, PC and PEC are inherently multi-component systems which involve complex carrier generation and relaxation dynamics and transport across interfaces. The *in-situ* interface specificity of ESFG and complementary techniques will provide deeper insight into nitrogen reduction and contaminant degradation in complex catalytic systems in a non-destructive manner under normal operating conditions.

C. Surface carrier density dynamics

Carrier density at semiconductor surfaces and interfaces as well as their dynamics when in use are imperative to improving catalytic performance. For example, THz nanoprobing was used to show that surface carrier densities in InP and GaAs decay on a ps time scale [237], providing pertinent information on the rates at which PC and PEC processes must proceed for efficient catalysis. Such importance has also been highlighted in recent reviews on the charge dynamics of semiconductors for heterostructures [238] and perovskite materials [239], exemplifying the importance of interfaces and surfaces. Additionally, microarea surface photovoltage has been employed to study the space charge region in MoS₂ and carrier dynamics therein to better inform semiconductor applications in optoelectronics [240]. Paying special attention to the weak-fluence characteristics of perovskite materials, femtosecond TA has also been used to monitor carrier dynamics, revealing long-lived surface trap states which likely contribute to the material's propensity for photovoltaic applications [207]. However, *in-situ* investigation of surface density dynamics during PC and PEC applications has not yet been demonstrated. The work highlighted in this perspective provides *in-situ* surface carrier dynamics, but only at the air/semiconductor interface. We believe that a robust understanding of the roles of surface states in PC and PEC applications can only be obtained by probing the system while they are being utilized in catalytic processes. Through the surface-specific probing of surface carrier dynamics *in-situ* at the semiconductor/electrolyte interface under operational-

ly relevant, low carrier density conditions, we believe that the full potential of catalytic CO₂ reduction, N₂ fixation, and water splitting can be unlocked. To do so, interface-specific spectroscopic methods such as ESFG, TR-ESFG, and 2D-ESFG, must be optimized, and their performance analyzed, to gain accurate PC and PEC performance information.

In summary, nonlinear optical spectroscopies such as ESFG and ESHG can provide an *in-situ* viewpoint of semiconductor surface states and their dynamical processes. ESFG techniques have been used to locate and identify surface states in semiconductor crystals and quantum dots. In p-type GaAs, two in-band surface states were identified which were found to be trap states that can accelerate charge carrier combination. In GaP three charged surface states were identified for both dopings, with n-type doping having negative charge and residing at the upper band gap edge while p-type doping had positive charge and resided at the lower band gap edge. Such identification of surface states allows for insight into recombination pathways in semiconductors which may reduce their efficiency. TR-ESFG experiments also illustrated their abilities to probe photogenerated surface electric fields, where the sign and buildup rates of the fields in n- and p-type GaP were quantified. These electric fields facilitate the transport of charge carriers in PC and PEC materials which makes quantification of their onset rates imperative for device performance. Additionally, four photoinduced surface states have been identified for n- and p-type GaP and their population rates were quantified and determined to occur in a bimolecular process. Like electric field buildup, the population rate of photoinduced surface states is directly related to catalytic performance, as these carriers in these populated states can be utilized to conduct reactions. Albeit the antithesis to buildup and population of surface electric fields and surface states, semiconductor relaxation dynamics can impact catalytic performance as well. For this reason, TR-ESFG techniques have been used to provide *in-situ* monitoring of carrier relaxation in GaAs crystals, as well as in hybrid semiconductors. A thorough understanding of relaxation processes is imperative to PC and PEC performance because if relaxation occurs faster than carrier extraction, they cannot be utilized for their catalytic properties. We believe that the use of ESFG techniques has not only exemplified its utility as a technique for surface-specific electronic property analysis but also has

highlighted crucial processes in semiconductor materials relevant to PC and PEC applications. We believe that though these insights gained and the continued use of such high-performance instrumentation, that efficient PC and PEC for environmental and energetic topics is obtainable.

IX. ACKNOWLEDGEMENTS

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