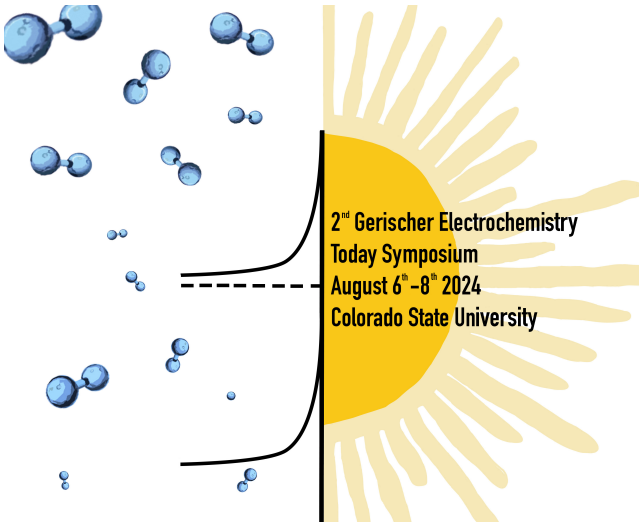
# Gerischer Electrochemistry Today

ABSTRACT

Semiconductor photoelectrochemistry is a dynamic and interdisciplinary field at the forefront of research in solar fuels, energy conversion, and catalysis. This Perspective captures the collective insights from the 2nd *Gerischer Electrochemistry Today Symposium*, held at Colorado State University in Fort Collins, CO, in August 2024, which convened leading researchers, early-career scientists, and industry partners to define the critical next steps for the field. Through interactive sessions, technical talks, panel discussions, and training initiatives—including a Semiconductor Electrochemistry Bootcamp—the symposium emphasized three pillars of advancement: (*i*) facilitating the exchange of new ideas in semiconductor electrochemistry and charge separation; (*ii*) fostering the development of future researchers, research topics and participation in the semiconductor workforce; and (*iii*) building community. This *Energy Focus* article distills key themes from the meeting and identifies major knowledge gaps in the following areas: mechanisms of charge separation and recombination, role of defects and disorder, dynamic and operando characterization methods, interfacial chemistry and surface passivation, theoretical and modeling limitations, and standardization and benchmarking. The inclusive and collaborative structure of the symposium enabled the generation of this comprehensive report that will serve as a roadmap for fundamental and applied research in the rapidly evolving field of semiconductor electrochemistry over the next decade.

**TOC GRAPHICS**




Semiconductor photoelectrochemistry is a vibrant and rapidly evolving field, providing vast opportunities for both fundamental research and technological innovations aimed at meeting the global energy demands of 2050. With implications spanning fine chemical production to large-scale solar fuel generation, this field holds potential for addressing global energy and sustainability challenges. Building on the momentum of the 2nd Gerischer Electrochemistry Today Symposium, this perspective article captures attendee's collective insights, defining key knowledge gaps and charting the critical next steps that will drive the field forward in the coming decade.

The 2nd Gerischer Electrochemistry Today Symposium was held on August 6-8, 2024, in Fort Collins, CO and organized by Justin Sambur (Colorado State University), Michael Rose (The University of Texas at Austin), Katharina Brinkert (University of Bremen and University of Warwick), and Shu Hu (Yale University). This symposium honored the scientific legacies of Heinz Gerischer[1,2] and Hans-Joachim (Achim) Lewerenz,[3] both of whom contributed to the fundamental understanding of semiconductor electrochemistry, photoelectrochemical cells, fuel-generating systems, and semiconductor surface science. The symposium featured 10 technical sessions spanning diverse aspects of semiconductor electrochemistry, two panel discussions, an industry networking event, a symposium banquet, and a 'report out' outlook session to summarize the highlights of the symposium. By the numbers, the 2nd Gerischer Electrochemistry Today Symposium brought together 138 attendees, awarded 70 Student/Postdoc Travel Awards, featured 51 talks over 3 days, including 20 early career researcher presentations, and engaged 125 participants in the technical program as poster presenters, oral presenters, lightning talk presenters, session chairs, session recorders, and session report leaders.

The symposium organizers aimed to energize the field of semiconductor photoelectrochemistry by focusing on three key priority areas: (1) building community, (2) fostering training and workforce development, and (3) facilitating the exchange of research and ideas. To build community, the symposium incorporated two unique panel discussion sessions, networking events with academicians, national laboratory members, industry representatives, and journal editors, fostering an inclusive and collaborative atmosphere. One notable feature was the "tag team" talks, pairing principal investigators with early career researchers who conducted the work. Randomized seating arrangements at events encouraged attendees from diverse backgrounds to interact, promoting cross-disciplinary collaboration. The symposium was designed to be fun, interactive, informative, and transformative, and aimed to provide a jargon-free learning environment, fostering collaboration and innovation in semiconductor electrochemistry.

To foster training and workforce development, the symposium opened with a "Semiconductor Electrochemistry Bootcamp" session, designed to demystify the jargon of the field. Session leaders taught fundamental concepts of semiconductor electrochemistry at the level of advanced undergraduate and first year graduate students. The symposium organizers disseminated literature[4–6] to symposium attendees before the session. The learning goals for attendees were to be able to (1) recognize major differences between the properties of metal and semiconductor electrodes; (2) identify and explain terminology in the semiconductor electrochemistry community (e.g., band edges, band bending, flat band potential, surface states, majority/minority carriers, charge generation/recombination, depletion versus accumulation layers, capacitance, space–charge/depletion regions, drift and diffusion); and (3) explain "the Gerischer view" of electron transfer at solid/liquid interfaces, and be able to explain what electronic and physical properties of electrode materials and molecules dictate the electron-transfer rate. This innovative format prepared participants to engage with more advanced topics and to teach these concepts to their peers.

The symposium was designed with a clear objective to produce a comprehensive symposium report that serves as a roadmap for the next decade of semiconductor electrochemistry. This report aims to (1) highlight the societal importance of acquiring fundamental scientific knowledge in this field, (2) identify major knowledge gaps, and (3) define critical avenues of inquiry for the next decade. This is accomplished through a descriptive narrative of the presentations and subsequent discussions with historical context. Indeed, the organizers developed an inclusive and collaborative approach. Early career researchers were invited to participate as "reporters," documenting key discussion points from panelists, speakers, and other symposium attendees during Q&A sessions. These reporters worked closely with appointed session chairs, who synthesized the discussions and ensured diverse viewpoints were represented in the report. At the symposium's business meeting, a draft outline of the report was presented, allowing attendees to provide immediate feedback and discuss strategies for disseminating the final document to the broader scientific community. This structured approach ensured that the symposium report captured the collective insights

and aspirations of the semiconductor electrochemistry community, fostering progress and innovation in the field. The following sections provide a session-by-session review of the 2nd Gerischer Electrochemistry Today Symposium. Roel van de Krol and Francesca Toma will organize the 3rd Gerischer Electrochemistry Symposium, which will be held in Germany in 2027.

**Summary of Panel Discussion 1: Who were Heinz Gerischer and Achim Lewerenz, and what was their Legacy on Semiconductor Electrochemistry?** *Session Chair: Mike Rose (The University of Texas at Austin); Session Recorders: Devan Solanki (Yale University) & Oshnik Maurya (Institute of Chemical Technology, Mumbai); Session Report Leaders: Gerald Meyer (University of North Carolina, Chapel Hill), Krishnan Rajeshwar (The University of Texas at Arlington), Mark Spitler (University of North Carolina, Chapel Hill).*

The panel discussion on Heinz Gerischer and Achim Lewerenz shed light on their significant contributions to semiconductor electrochemistry and photoelectrochemical research. Krishnan Rajeshwar highlighted the twists and turns in photoelectrochemical research, beginning with the discovery of $TiO_2$ photoactivity by Fujishima and Honda in 1972,[7] marking the early years of photoelectrochemical cell development. Rajeshwar emphasized two major developments that shaped the trajectory of the field: photoelectrode stabilization and the later emergence of dye-sensitized solar cells (DSSCs). Despite 50 years of research, no commercial solar water-splitting process has emerged, leading to questions about whether the field was hindered by the focus on regenerative photoelectrode stabilization. However, Rajeshwar emphasized that alternative photoelectrochemical technologies, such as $CO_2$ reduction and nitrogen fixation, also hold promise for future innovation. His discussion also touched on the competition posed by lithium-ion batteries, which have garnered more attention and funding despite early optimism surrounding photoelectrochemistry.

Art Nozik provided a historical overview of key milestones in photoelectrochemical cell development and major symposiums from the 1970s to the 1980s that brought photoelectrochemistry research into the spotlight. He credited Gerischer for three significant contributions to photoelectrochemistry: (1) the kinetics and energetics of charge transfer from illuminated semiconductors into Gaussian distributions of electronic redox states in electrolytes, (2) the concept of the quasi-Fermi level under illumination, and (3) the balance between photo-corrosion of semiconductors and beneficial photo-redox reactions.

Bruce Parkinson and Mark Spitler offered personal reflections on Heinz Gerischer and Achim Lewerenz, providing deeper insights into their legacies and the influence they had on the photoelectrochemistry research community. Parkinson recounted Gerischer's integrity and reserved nature, which contrasted with the outsized positive impact that Gerischer made on the scientific community, despite not mingling with early-career researchers. He also emphasized the historical trajectory of

photoelectrochemistry, acknowledging the foundational role Gerischer and Lewerenz played in advancing our understanding of solar energy conversion processes. Spitler reflected on Gerischer's collaborations with his wife, Renate Gerischer, who was also a prominent physical chemist. He emphasized several of Gerischer's notable students, including Gerhard Ertl, who received the Nobel Prize in Chemistry for his contributions to surface science, and Dieter Kolb and Frank Willig, who advanced Gerischer's theories in the areas of electrochemical double layers and electron transport. Spitler emphasized Gerischer's unique approach to electron transfer theory, which deviated from Marcus theory by utilizing partition functions. Importantly, Gerischer's model of multi-step electron transfer at semiconductor interfaces, particularly the challenge of managing exchange current densities across conduction band (CB) and valence band (VB) edges, remains a cornerstone of photoelectrochemistry theory and, remarkably, also remains at the cutting edge of experimental science at semiconductor interfaces. Spitler also noted Gerischer's focus on understanding how to design catalysts that facilitate efficient multi-electron-transfer reactions—a challenge still being addressed today.

Nathan Lewis said he first met Heinz Gerischer in 1983, when Gerischer visited Caltech as a Fairchild Scholar and was supportive and encouraging of his work as a young faculty member. He recalled that although Gerischer's students challenged his findings, Gerischer himself defended the work and was always willing to help whenever asked. Lewis noted that in the 1990s Gerischer created diagrams to explain the density of states at semiconductor–electrolyte interfaces, which his group later tested and extended. He emphasized that Achim Lewerenz made important contributions that deserve greater recognition, and remembered his passion for electrochemistry as well as their lighter moments together, such as air-guitar sessions and trips to Howl at the Moon in University City, Hollywood and to watch the movie Rock of Ages. Lewis concluded that both Gerischer and Lewerenz underscored the enduring challenge of creating systems that are truly stable.

The session closed with reflections on how the solar energy conversion community has evolved over the past five decades, with an acknowledgment of the continued challenges in achieving commercial viability for solar water splitting. Together, the contributions of Gerischer and Lewerenz laid the groundwork for the modern understanding of photoelectrochemical systems and their potential for solar energy conversion.

**Summary of Scientific Session 1: Semiconductor Photoelectrochemistry Bootcamp.** *Session Chair: Katharina Brinkert (University of Bremen); Session Recorders: Avishek Banik (Colorado State University) & Patrick Aghadiuno (Columbia University); Session Report Leaders: Stephen Maldonado (University of Michigan), Wolfram Jaegermann (Technical University of Darmstadt), Frances Houle (Lawrence Berkeley National Laboratory), Gerald Meyer (University of North Carolina, Chapel Hill)*

This session focused on communicating fundamental concepts of semiconductor electrochemistry at the level of advanced undergraduate and first-year graduate students for early career researchers. The expected learning outcomes from this session were to (1) recognize major differences between the properties of metal and semiconductor electrodes; (2) identify and explain terminology in the semiconductor electrochemistry community (e.g., band edges, band bending, flatband potential, surface states, majority/minority carriers, charge generation/recombination, depletion versus accumulation layers, capacitance, space charge/depletion regions, drift and diffusion); and (3) explain "the Gerischer view" of electron transfer at solid/liquid interfaces, and be able to explain what electronic and physical properties of electrode materials and molecules dictate the electron-transfer rate.

Stephen Maldonado opened the session and emphasized that while semiconductor electrochemistry has historically been perceived as too complex to analyze rigorously, this does not have to be the case. He outlined a systematic methodology for interpreting voltammetry with semiconductor electrodes by considering how the applied potential is distributed, the experimental timescale, and their collective impact on heterogeneous charge transfer.[8–10] This framework provides a clearer path for researchers to extract meaningful insights from electrochemical measurements in semiconductor systems.

Wolfram Jaegermann discussed semiconductor electrochemistry from a surface science perspective. He explained that in-depth analyses of semiconductor/electrolyte interfaces are needed to interpret bulk and interfacial electron-transfer processes, which in most cases are coupled to chemical reactions. To glean mechanistic information the involved elementary reaction steps must be addressed on an atomistic level ranging from quasi-equilibrium condition to non-equilibrium conditions involving time scales from picoseconds to hours.

Figure 1 shows the semiconductor/redox electrolyte interface in the dark.[5,4] The energy level diagram depicts the semiconductor band edges and occupied/unoccupied electronic states relative to the electrolyte density of states (described by a Gaussian distribution of electronic states expected for a reversible one-electron transfer couple). Reaction rates under non-equilibrium conditions are deduced by assuming electron transfer reactions rates occur from the occupied valence band and non-occupied conduction band states to the occupied and non-occupied electronic states in the electrolyte, which are thermally broadened. Deviations due to surface states derived from truncated semiconductor dangling bonds or surface-adsorbed molecules are sometimes included to account for Fermi level pinning,[11] or from idealized (photo-)current voltage behavior often without a detailed characterization and investigation of their chemical or electronic interfacial properties. Junctions of materials are modified by bulk electronic states, surface/interface states, electrolyte-induced states due to surface interactions caused by chemical reactions and defect state modifications. Surface reactivity can be analyzed using model systems that isolate adsorption of electrolyte species. *In situ* X-ray photoelectron spectroscopy measurement capabilities under operational conditions

are in development. These modifications are dynamic, and the community does not currently understand how to integrate these practical aspects into the "Gerischer view", leading to the open questions in Figure 1.

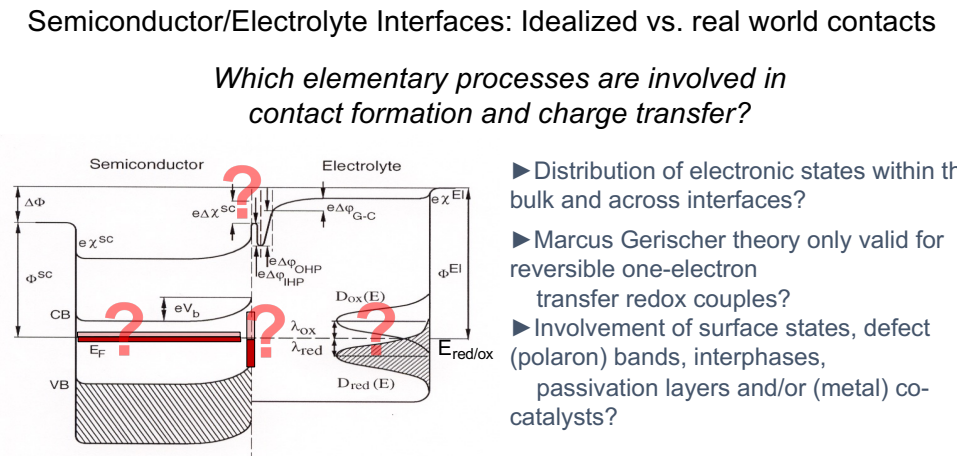



**Figure 1.** PowerPoint slide from Wolfram Jaegermann's talk that introduced the "Gerischer view" of the semiconductor/electrolyte interface. The slide depicts a schematic representation of a semiconductor/electrolyte (SC/El) contact for idealized conditions. The red question marks highlight unknown quantities or descriptions, especially for complex SC/EI contacts with adsorbed electrolyte or redox-active species, coatings, or co-catalysts. Abbreviations: SC valence band (VB) maximum, conduction band (CB) minimum, Fermi level ($E_F$), $E_{red/ox}$ is the formal redox potential of a one electron reversible redox couple, $\Phi^{SC}$ and $\Phi^{El}$ represent SC and electrolyte work functions, $e\chi^{SC}$ and $e\chi^{El}$ represent surface double layer potentials or surface dipoles, $D_{ox}(E)$ and $D_{red}(E)$ represent time and space averaged occupied and empty density of states (DOS) of a one electron reversible redox couple, $\lambda_{ox}$ and $\lambda_{red}$ represent the reorganization energies of the oxidized/reduced state of the redox couple, $\Delta\Phi$ SC/El is the contact potential difference at the SC/electrolyte interface, $eV_b$ is the magnitude of band bending in the semiconductor, $e\Delta\chi^{SC}$ ,$e\Delta\varphi_{OHP}$, $e\Delta\varphi_{IHP}$ $e\Delta\varphi_{G-C}$ represent surface double layer changes of the SC, inner Helmholtz layer, outer Helmholtz layer, and Gouy-Chapman layer, $E_D$(bulk) and $E_{SS}$ represent bulk defect DOS and surface states, which are expected to be complex for many SCs.

Gerald (Jerry) Meyer presented a detailed analysis of interfacial electron transfer within the electric double layer (EDL) through the lens of Marcus-Gerischer theory. He emphasized the importance of careful naming conventions for theoretical models and equations, highlighting the foundational contributions of Marcus (harmonic oscillator model and free energy considerations) and Hush (metal-to-particle and metal-to-ligand charge transfer). Meyer explained that kinetic data can be analyzed using Marcus-Gerischer theory to extract parameters for predicting electron-transfer rates, especially within the EDL, where kinetic barriers are decreased. Meyer also discussed how increasing driving force can extend photoexcited charge carrier lifetimes. The talk further addressed the complexities of the EDL structure and how ionic bridges and sensitizers can be used to probe the reduced dielectric constant at interfaces. Finally, Meyer noted the critical dependence of electron transfer on potential and proton transfer on pH, connecting historical theoretical interpretations to modern electrochemical understanding.

Frances Houle discussed the basic principles on how energetics control charge transfer in complex photoelectrochemical systems. It is not always clear how to analyze the influence of energy levels when many steps are involved in a mechanism. A more useful picture is to consider that a hole at the surface is a weakened or broken bond, that an electron at the surface adds charge to an assembly of atoms, and that key steps may be thermal, and follow the chemical pathways that emerge (Figure 2). Two examples were presented: etching of Si by F (experimental study)[12,13] and water oxidation on $TiO_2$ (computational study).[14,15] The Si etching reaction is highly exothermic, with a series of spontaneous fluorination seps, converting Si into $SiF_3$ and $SiF_4$ as volatile products. Thermal processes lead to branching ratios between formation of each reaction product that are dopant dependent. Holes (weakened Si-Si bonds) favor $SiF_4$ formation while electrons favor reactions that form SiF bonds and displace $SiF_3$. Absorption of light generates additional electrons and holes, which leads to desorption of $SiF_3$ mediated by electron-hole recombination. This example shows that photogenerated electrons and holes can affect an already efficient thermal reaction by accelerating the rate of SiF bond formation at a particular location. As a second example, water oxidation on $TiO_2$ is not spontaneous, but does involve a mixture of thermal and hole-driven reaction steps once the reaction is initiated by photo-induced deprotonation of water. This catalytic cycle has been well-studied, but there remain opportunities to better understand the interplay between thermal and light-driven steps. A critical question was whether the mobility of photogenerated holes at the surface was important to the water oxidation mechanism. Two scenarios were examined: fully mobile holes, and deeply trapped holes. It was found that for both scenarios the reaction rate saturates as light intensity increases because the thermal reactions become limiting due to a buildup of the least thermally reactive species. Simulations provide insight into coverages of surface intermediates that are influenced by the degree of hole mobility, which inform that experimental observations are most consistent with immobile holes. Whether thermal or redox reactions are rate limiting depends on light intensity and on charge-carrier mobility. Identifying materials that provide control over reaction pathways is a frontier in photoelectrochemical research.

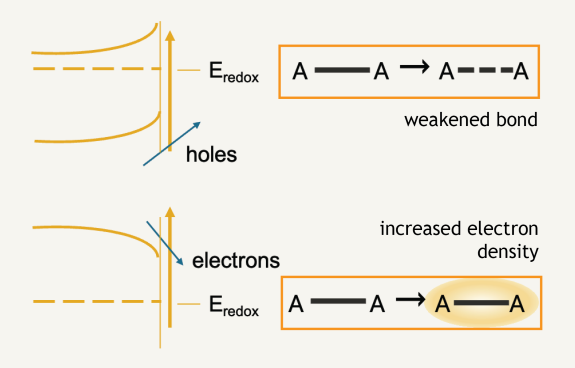



**Figure 2.** Excess charge carriers at a semiconductor surface affect bond strengths and charge density, and therefore reactivity, via doping or photogeneration. They can participate in every step in a mechanism or only a few steps, and they can indirectly influence thermal reactions by affecting chemical populations. Charge carrier influences can be observed even for exothermic processes. *Image Credit*: Frances Houle.

**Summary of Scientific Session 2: Photoelectrochemical Cells in Action 1.** *Session Chair: Shu Hu (Yale University); Session Recorders: Sam Magpantay (Yale University) & Colby Evans (National Institutes of Standards and Technology); Session Report Leaders: Thomas Hannappel (Technical University of Ilmenau), Zetian Mi (University of Michigan)*

The efficiency of solar-driven chemical processes, particularly $CO_2$ reduction and water splitting, is influenced by semiconductor design. This session highlighted innovative approaches to PEC cell design. James Cahoon discussed molecule-oxide-semiconductor tunnel junctions to enhance solar-driven $CO_2$ reduction using molecular catalysts. He proposed creating "metal-like" behavior in semiconductors by leveraging inversion layers to enable efficient electron tunneling through metal oxide layers. The utility of this approach is supported by experiments performed with thermal oxide-terminated silicon that demonstrate higher photovoltages and stable photocurrents, despite the challenges of tunneling through the metal oxide.[16] His findings highlight the potential for chemically treating semiconductor surfaces to enhance minority carrier transport, making them more metal-like and improving catalytic performance for solar-driven reactions.

Zetian Mi and Zhengwei Ye reported on GaN as an industry-ready platform for scalable artificial photosynthesis. As the second most produced semiconductor, GaN's tunable bandgap energy (via doping) across the solar spectrum makes it a promising photoelectrode material.[17] The researchers emphasized the stability and catalytic efficiency of GaN, particularly on gallium oxynitride surfaces that resist corrosion and form spontaneously on the GaN surface. They showcased advancements in photoelectrochemical water splitting and $CO_2$ reduction using Cu derivatized surfaces on GaN, achieving high selectivity and stability. The work demonstrated the scalability and robustness of GaN for sustainable solar-driven chemical processes,[18] with continuous operation exceeding 3000 hours without performance degradation.

Jacob Schneidewind discussed multi-step pathways for photocatalytic solar energy conversion, focusing on systems that offer scalability and environmental benefits. Techno-economic analyses that included Monte Carlo simulations predicted how various parameters, including energy conversion efficiency and catalyst concentration, are predicted to influence future costs.[19] Schneidewind stressed that conventional approaches, which separate light harvesting and catalysis, introduce losses — while multi-step pathways can reduce these losses by integrating light absorption and redox reactions at the same site. His work revealed that using multiple wavelengths in catalytic cycles can enhance yields but also presents challenges due to the lifetime of intermediates. Schneidewind's research included testing advanced materials like carbon nitrides and conjugated polymers, supported by automated photocatalyst testing systems, to achieve optimized multi-step pathways.

Thomas Hannappel discussed the design of efficient tandem cells for photoelectrochemical solar fuel production (Figure 3), with a particular focus on the role of electronic charge carrier-selective transport. He underscored the importance of using tandem cells to achieve both the required chemical potential (and resulting photovoltage) *and* efficient sunlight absorption for high-efficiency operation.[20] Figure 3 illustrates an idealized band diagram of a tandem PEC cell designed for solar water splitting. Efficient conversion of solar energy into chemical fuels, such as hydrogen, requires tandem cell architectures that can both generate sufficient photovoltage and utilize the solar spectrum effectively.[21] In Figure 3, the Fermi level splitting (represented by the red dashed lines) in the two subcells (top and bottom, labeled 1 and 2) indicates the total photovoltage generated by the system. This voltage must be equal to or greater than the free energy required to split water (1.23 eV), plus the additional overpotentials needed to drive the oxygen and hydrogen evolution reactions at the anode and cathode. To ensure efficient charge generation and collection, the diffusion lengths of minority carriers in the light-absorbing semiconductors must exceed the optical penetration depth $1/\alpha$), minimizing bulk recombination losses. Charge carriers must then be efficiently separated and transported through selective contacts and across the tunnel junction between the two cells. In addition to these electronic considerations, the system must also employ stable and active catalysts at both electrodes to ensure long-term operation and high reaction rates. Hannappel outlined critical factors such as driving forces on charge carriers, chemical reactions, electronic charge carrier separation and transport, and photochemical stability that are necessary in order to optimize device performance. He also stressed the importance of multiple correlated measurements to understand surface properties and their impact on device efficiency. This includes the need for appropriate *in situ* and *operando* measurements that directly address the interfacial structure and optoelectronic properties, in the spirit of Herbert Kroemer's famous phrase 'the interface is the device'.[22] Hannappel showed that the growth of high-performance epitaxial layer structures can be controlled down to the atomic scale using optical *in situ* spectroscopy, such as reflection anisotropy spectroscopy,[23,24] while the absorber properties and interfacial quality can be

assessed by (time-resolved) photoluminescence spectroscopy or by quantifying photoluminescence quantum yields, which directly reflect the potential of an absorber to efficiently convert light.[25,26] Additionally, he highlighted the need for sustainable practices, including maximizing device lifetimes and improving recycling methods, to ensure the long-term viability of these advanced materials.

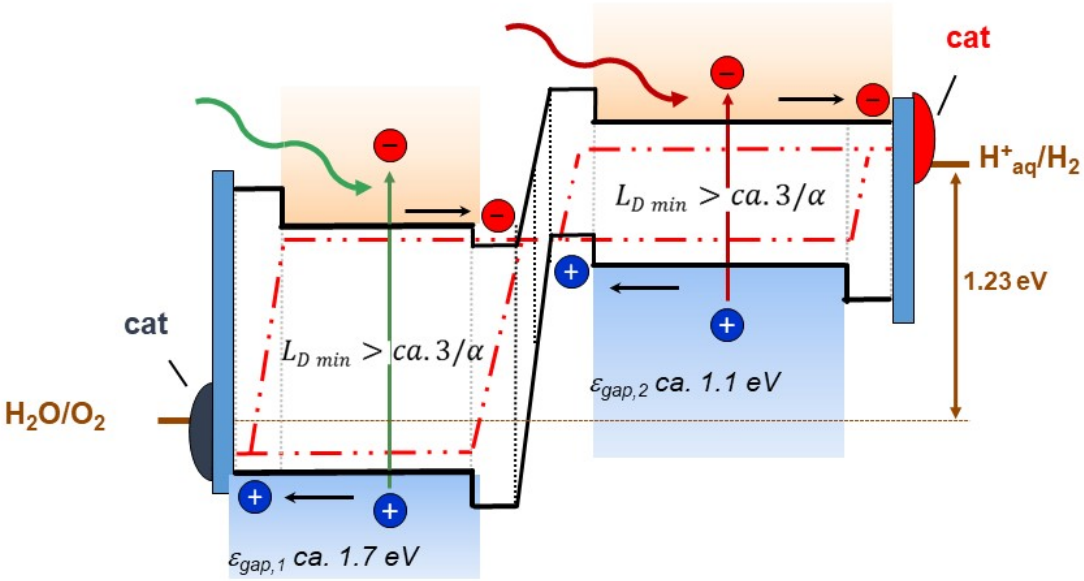



**Figure 3.** Tandem cells can create favorable conditions for photoinduced charge separation to drive reactions. cat represents catalyst, $L_{D\ min}$ is the diffusion lengths of minority charge carriers, $\alpha$ is the absorption coefficient, $e_{gap,1}$ and $e_{gap,2}$ are the band gap energies of absorber 1 (top cell) and absorber 2 (bottom cell), respectively. Image credit: Thomas Hannappel.

**Summary of Panel Discussion 2: Photoelectrochemistry 2035 Roadmap.** *Session Chair: Dan Esposito (Columbia University); Session Recorders: Aaron Kaufman (University of Oregon) & William Stinson (Columbia University); Session Report Leaders: Todd Deutsch (National Renewable Energy Laboratory), Jillian Dempsey (University of North Carolina, Chapel Hill).*

This session explored the challenges and potential of photoelectrochemical solar energy conversion technologies, with experts reflecting on the progress made since Fujishima and Honda's landmark discovery >50 years ago.[7] The short talks from the four speakers provided context, challenges, and opportunities for the symposium attendees to discuss. Brian DeBruine (Colorado Hydrogen Network) framed $H_2$ as a critical aspect of this discussion, stressing the need to create a viable market for hydrogen technologies. He highlighted the importance of achieving cost parity with petroleum, including exploration of innovative extraction methods, such as leveraging petroleum extraction technology to find and harvest geologic $H_2$ to economically incentivize a clean energy transition. DeBruine's talk underscored the broader societal

impacts, discussing how local initiatives like Colorado's Hydrogen Day serve as vital steps toward scaling $H_2$ technologies and engaging the public.

Todd Deutsch addressed technological hurdles and discussed potential ways to generate greater value from solar-driven $H_2$ production, providing insight into the most promising pathways. He re-emphasized that achieving ambitious targets, such as \$1/kg for green $H_2$, requires overcoming high materials costs and low efficiencies in production-scale systems. Deutsch discussed the need for research into innovative alternative reactions to traditional water splitting, that could yield products with greater economic value than $H_2$ and $O_2$ (e.g., $CO_2$ reduction, plastic reformation) or systems that generate $H_2$ at elevated pressure to reduce downstream processing costs.

Jillian Dempsey continued the discussion of the value of reaction products, focusing on the challenge of product selectivity in the context of $CO_2$ reduction, imploring the field to identify target fuels and chemicals. Dempsey provoked discussion about whether our field should diverge or focus on the most promising product beyond $H_2$ and highlighted opportunities for selective catalysts or reactor designs (e.g., cascade) to achieve this goal.[27] Dempsey and Deutsch encouraged the community to explore these less-common approaches, stressing the importance of identifying reaction products derived from semiconductor electrochemistry that can provide unique benefits.

Shannon Boettcher tackled the complexities of the semiconductor/electrolyte interface, emphasizing its central role in the future of solar energy conversion. Boettcher focused on the need for improved theoretical models to better understand interfacial phenomena at the semiconductor/electrolyte interphase, emphasizing that bridging the gap between simplified models and real-world systems is the key to discovering new paths in PEC technology. All speakers highlighted the importance of moving beyond narrow technical demonstrations to address the larger question of societal relevance.

An open discussion among conference attendees followed the speaker panel, which primarily focused on the question of "*What product should we make*?" There was some skepticism about whether the field could advance beyond water-splitting reactions, which have seen limited commercial success over the past ~50 years. The informal, conversational pace of the open discussion section encouraged conference attendees to ask thought-provoking questions such as "*What advantages do photoelectrochemical systems offer over photovoltaic-electrolysis*?" While no consensus was reached, ideas were brought forth about the diurnal nature of sunlight as an opportunity for photoelectrode repair. Some conference attendees noted that considerations beyond economics are sometimes of equal, or greater, importance depending on end-use requirements. Finally, an overarching theme emerged from the discussion about the need for an initial entry point into the market, from which real progress can be made. The questions of "*How*?" and "*How to get there faster*?" remained unresolved during this period.

**Summary of SOLARIZE Industry Event and Poster Session.** *Session Chair: Justin Sambur (Colorado State University); Session Recorders: Devan Solanki (Yale University) & Patrick Aghadiuno (Columbia University); Session Report Leaders: Aaron Kaufman (University of Oregon) & Nathaniel Gomez (University of California, Irvine).*

The SOLARIZE event, a mixer bringing together experts from academia, national laboratories, and industry, challenged early career researchers to each present a concise and impactful idea through a three-minute "elevator pitch" lightning talk. A key goal was to help these researchers communicate complex scientific ideas in a way that resonates with an industrial audience. Many presenters found the experience valuable, as it encouraged them to focus on the core message of their work and convey it clearly. The feedback from panelists consistently emphasized the need to relate scientific findings to practical applications and familiar concepts to engage the audience effectively.

The lightning talks covered a variety of cutting-edge topics, from wireless photovoltage measurements in photoelectrochemical systems to solar fuel production systems. Feedback from industry representatives Timothy Arthur (Toyota Research Institute of North America), Benjamin Martindale (Nature Catalysis), David Ingram (Fortescue), and Brian DeBruine (Colorado Hydrogen Network) stressed the importance of making ideas accessible by grounding technical findings in real-world applications and highlighting the benefits of the research, not just the features. Presenters were encouraged to emphasize time-saving innovations, practical solutions to efficiency problems, and the broader impact of their research. Overall, the session reinforced the importance of communication skills in bridging the gap between academic research and industry applications. Conference attendees voted Asmita Jana (Lawrence Berkeley National Lab) and Marco Salvi (University of Bologna) as the most engaging speakers.

**Summary of Session 3: Charge Separation Strategies Beyond Built-in Space Charge Fields.** *Session Chair: Robert Coridan (University of Arkansas); Session Recorders: Avishek Banik (Colorado State University) & Patrick Aghadiuno (Columbia University) Session Report Leader: Shane Ardo (University of California, Irvine)*

In the realm of semiconductor electrochemistry, the conventional band bending picture has long been the cornerstone for understanding photoinduced charge separation in materials. However, as we delve into the complexities of smaller particles and novel materials, it has become clear that we need to move beyond this traditional framework. This point was also recently emphasized in the literature,[28] which reinforces its relevance to the broader community. This session aimed to explore innovative mechanisms and advanced strategies for photoinduced charge separation that extend past built-in electric fields. It delved into cutting-edge research and methodologies that address the challenges posed by nanoscale materials, where

conventional space–charge fields are insufficient or inapplicable. While unified in discussing aspects of charge separation, talks mostly focused on properties that are specific to each of crystalline inorganic semiconductors, semiconductor nanocrystals, and ion-permeable soft polymers.

Shane Ardo and graduate student Honghao Liu presented a typical band diagram, and expounded on it to show all contributions to the electrochemical potential of electrons and holes whose slopes quantify relative forces that dictate the direction of species transport. Band bending at semiconductor/electrolyte interfaces induces electronic charge separation because electric fields propel electrons and holes in opposite directions. However, other forces can propel electrons and holes in the same direction, e.g. due to straddling band offsets in a Type I heterojunction. Knowledge of species conductivity, which is the product of the concentration and mobility, is needed to determine if there is selective species flux. In this case, when it is assumed that charge carriers are thermalized, a so-called selective contact forms when species conductivities differ. There was a lively discussion as to whether there are multiple forces that are each responsible for microscopic reversibility or a single net force, but everyone agreed that each force alone does not drive a current that generates heat via Joule heating. These points have now been further clarified in a recent article.[29] Liu discussed results from a model that he developed based purely on continuity of mass, with mass transfer driven by differences in chemical potential, and thus no electric fields, and mass action dictating reaction selectivity. Figure 4 illustrates that selective reactions at semiconductor/electrolyte junctions alone enable photoinduced charge separation and that a photodiode-like relationship results from varying the availability of solution-phase redox-active chemical species, e.g., due to flow. The speakers recognized that ratios of various properties could serve as useful figures-of-merit to most easily predict charge separation ability.

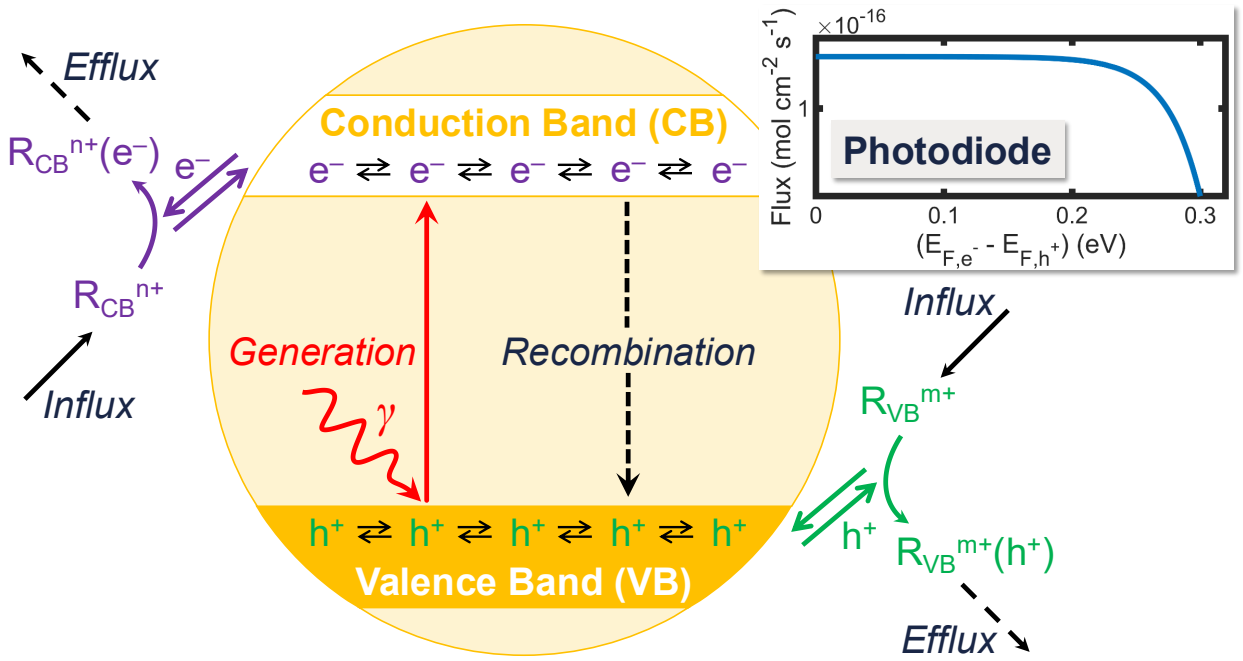



**Figure 4.** Processes simulated to occur for an illuminated single particulate photocatalyst semiconductor using a one-dimensional modeling domain. Microscopically reversible processes (each shown by a set of two arrows) include (i) generation and recombination of electronic species (gamma stands for photons), (ii) diffusive transport of electronic species ($e^-$ and $h^+$ stand for conduction-band (CB) electrons and valence-band (VB) holes, respectively), and (iii) perfectly selective interfacial redox reactions ($R^{n+}{}_{CB}$ and $R^{m+}{}_{VB}$ stand for solution-phase chemical species desired to react with CB states and VB states, respectively, to form $R^{n+}{}_{CB}(e^-)$ and $R^{m+}{}_{VB}(h^+)$). Solution-phase species influx and efflux were assumed to be irreversible. Photoinduced charge separation was a result of perfect selectivity for the interfacial redox reactions and not a more well-known selective contact, such as band bending. Inset: By varying the mass-transfer coefficient, as a velocity, for solution-phase species influx and efflux equally for all four species (i.e. $R^{n+}{}_{CB}$, $R^{m+}{}_{VB}$, $R^{n+}{}_{CB}(e^-)$, and $R^{m+}{}_{VB}(h^+)$) over a range of values, species flux as a function of thermodynamic driving force ($E_{F,e^-}$ and $E_{F,h^+}$ stand for quasi-Fermi levels of $e^-$ and $h^+$, respectively) was found to exhibit a photodiode-like relationship. *Image credit:* Shane Ardo.

Prashant Kamat discussed ways to increase the net yield for photoinduced charge separation in semiconductor quantum dot nanocrystals, which have strong and tunable light absorption and surface binding. In this case, electronic wavefunctions expand beyond the physical size of the nanocrystal such that it behaves more like a molecule with quantized energy levels — electron and hole transport and band-bending are generally irrelevant. In this regard, every step in photochemical energy conversion is a kinetic competition between a desired and undesired process and many operate in parallel to dictate complex steady-state behavior (Figure 5). There has been a lot of research into speeding up the rate of charge separation, generally under the assumption that the rate of competing exciton/electron-hole-pair recombination is fixed for a given system; there has been less focus on slowing down the rate of back-electron-transfer charge recombination, generally under the assumption that the rate of competing fuel-forming reactions/steps are fixed for a given system. Kinetics are often studied using photoluminescence spectroscopies (i.e. steady-state and time-resolved) and transient absorption spectroscopies. Moreover,

steady-state conditions must be considered when evaluating actual operational performance because back-electron-transfer can be fast and sacrificial reagents often transfer more than just one charge per photon absorbed, even though it sometimes takes quite some time for them to do so. It was recognized that facets play an important role, cocatalyst loading must be optimized and that even metallic cocatalysts do not generate band bending unless semiconductor doping is large. In addition, a figure-of-merit from the photography field could be of use to the photoelectrochemistry community, as the ratio of reaction product diffusion coefficient to interfacial charge transfer rate coefficient.[30]

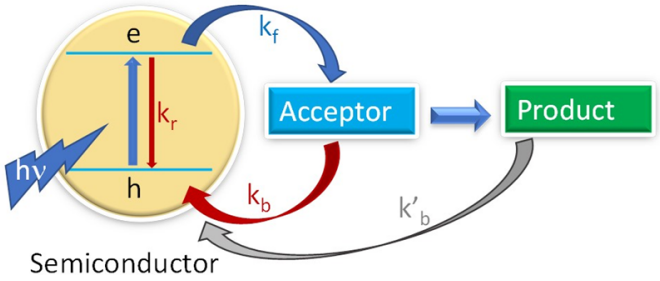



**Figure 5.** Back electron transfer processes control net product yield. *hv* represents the photon energy, where *h* is Planck's constant, *v* is frequency of the photon, *e* and *h* represent electron and hole, $k_r$ is the rate constant for radiative recombination, $k_f$ is the rate constant for electron transfer from the conduction band to the acceptor, $k_b$ is the rate constant for back electron transfer from the acceptor to the valence band. $k'_b$ is the rate constant for back electron transfer from the product to the valence band. *Image credit:* Prashant Kamat.

Erin Ratcliff discussed soft photoelectrochemical materials, whose optical, redox, and structural properties can be tuned using synthesis and are of use in applications beyond photochemistry, such as ion pumps, sensors, interfacing with biology, etc. Notably, conducting polymers mitigate shortcomings of crystalline inorganic semiconductors due to surface termination trap states, yet ions can often intercalate into soft photoelectrochemical materials from contacting liquid phases to alter transport properties and screen electrons and holes (Figure 6). Also, these mixed electronic–ionic conductors typically exhibit nanoscale heterogeneity that results in distributions of states (not bands) that can span a wide range of free energies. While it is facile to measure state densities as a function of free energy using spectroelectrochemistry, the exact nature of these states is complicated by the presence of semicrystalline-to-amorphous structures, coupled electronic–nuclear polaronic states, complex interphases, volumetric swelling, and dynamic metastable states that form with continued redox cycling. It was recognized that what are generally thought to be fixed properties in crystalline inorganic semiconductors can vary across orders-of-magnitude in space, time, and energy in ion-permeable soft materials, e.g. thermodynamics, rate coefficients, reorganization energy, permittivity, modulus, and other polymer properties that complicates analysis of experimental data with Marcus-Gerischer models.

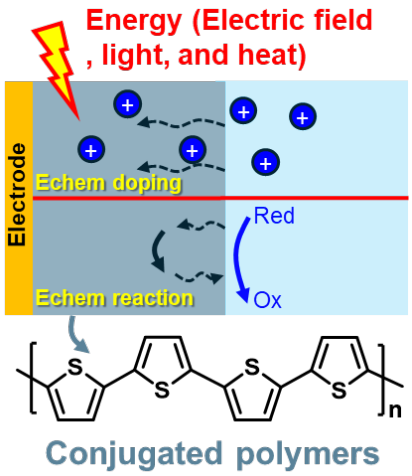



**Figure 6.** Mixed electronic–ionic conduction in soft materials allows for control of both carrier density via electrochemical doping and driving electrochemical redox reactions. *Image credit:* Erin Ratcliff.

**Summary of Scientific Session 4: Latest and Greatest from Early Career Researchers.** *Session Chair: Gary Moore (Arizona State University) Session Recorders: Asmita Jana (Lawrence Berkeley National Lab) & Marco Salvi (University of Bologna) Session Report Leaders: Claire Hallock (University of Texas), Avishek Banik (Colorado State University)*

This session allowed early career researchers to share outcomes from their ground-breaking research, build networks with senior researchers, and receive feedback. Camilla Tossi (University of Bremen) discussed utilization of photocatalysis/photoelectrochemistry for space applications, including manufacturing, life support ($O_2$ production) and energy storage.[31] While all valuable attributes that could one day be extended to use in space or on other planets, it is not known how gravity could drastically impact the progress of traditionally well-established electrochemical nanomaterial synthesis as compared to typical terrestrial laboratory conditions. She succeeded in optimizing new conditions for efficient use in microgravity and replicated the results commonly practiced on Earth. In the future, she aims to focus on using elements for nanomaterial synthesis abundantly available on Mars.

Oshnik Maurya (Institute of Chemical Technology, Mumbai) displayed photoelectrodes composed of earth-abundant materials ($TiO_2$, $Bi_2S_3/Se_3$ etc.).[32] His research focused on the impact of morphology on photoelectrochemical properties and showed that synthesis conditions can be used to control the density and size of nanotubes. Further utilizing a buried p-n heterojunction from $Bi_2S_3$ and $Bi_2Se_3$, he showed how charge separation can be improved for better photoelectrode performance.

Verena Streibel (Walter Schottky Institute, TU Munich) presented an overview of the work performed in Ian D. Sharp's and her groups on transition metal (oxy)nitride thin films for photoelectrochemical applications (Figure 7). Streibel noted that while this class of materials is

underexplored due to complex synthesis and substrate compatibility issues, the materials are abundant and offer significant band gap tunability. Streibel presented recent work showing that Ti doping in $Ta_3N_5$ thin film photoanodes enhances solar water splitting performance.[33] $Ti^{4+}$ ions substitute for $Ta^{5+}$ in the lattice, reducing detrimental deep-level defects such as nitrogen vacancies and $Ta^{3+}$ centers, which suppresses charge carrier recombination and improves photoconductivity and photocurrent generation. Similarly, they reported the synthesis and characterization of zirconium oxynitride thin films as a new class of semiconducting materials for PEC water splitting.[34] By optimizing nitrogen content and crystallinity, they demonstrate that zirconium oxynitride films exhibit visible light absorption and photocurrent generation, highlighting their potential as earth-abundant photoelectrode materials. In conclusion, even though the synthesis of (oxy)nitrides is challenging, there are several strategies to beneficially tune the transport properties and band gaps of the materials by altering the lattice constituents/elements, which pave a pathway for more exploration of such material as photoabsorbers.

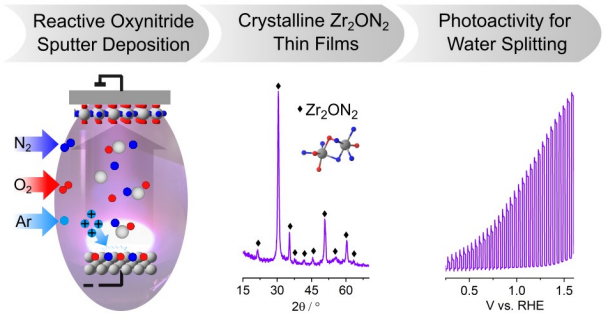



**Figure 7.** Overview of thin film preparation and characterization methods. Image reproduced from reference [34] under license CC-BY 4.0.

Claire Hallock described how covalent bonding of organic molecules to the surface of Si impacts surface states at energies in the forbidden band gap and inside the bands. Hallock's hypothesis was that increasing the concentration of states at the band edge energies would be beneficial for photoelectrochemical or electron transfer applications. However, electrochemical techniques to quantify the interfacial density of states (DOS) near the band edges presented a significant roadblock. By taking inspiration from a seminal paper by Gerischer on graphite which showed capacitance as a function of the DOS,[35] Hallock calculated the DOS of silicon and germanium from capacitance measurements utilizing Electrochemical Impedance technique (EIS; schematically shown in Figure 8).[36] She noted that similar EIS

analysis can be expanded to other materials such as quantum dots, 2D transition metal dichalcogenides, etc., for electrochemical DOS characterization.

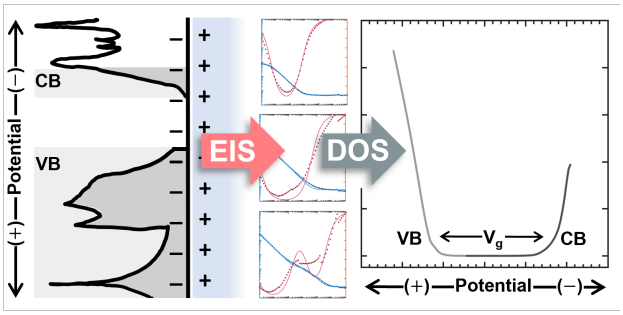



**Figure 8.** Electrochemical approach to determine the electronic DOS of semiconductor electrodes. CB and VB represent the conduction band and valence band. $V_g$ represents the energy level difference between CB and VB levels on the electrochemical scale. *Image credit:* Claire Hallock.

Judy Hart (UNSW, Sydney) spoke on computational tools to investigate the underlying mechanism of the oxygen evolution reaction (OER) on tungsten oxides with different dopants and ferroelectric polarization-induced photocurrent enhancement in multiferroic bismuth ferrite (BFO) and bismuth vanadate (BVO).[37] In the dopant studies done with Bosi Huang, she showed that catalysts with intermediate OH* and O* binding energies produce the best performance overall, and concluded that dopants in ternary oxides can shift the adsorption energies of different intermediates in water oxidation (Figure 9a). In the ferroelectric work, Hart demonstrated a BFO/BVO photoanode that achieves good performance in photoelectrochemical water splitting. She showed direct evidence that ferroelectric switching modulates the electronic structure and surface chemistry of the heterostructure, leading to photocurrent enhancement compared to non-poled conditions (Figure 9b-c). The findings reveal a complex interplay between band edge shifts, modulation of internal electric fields, and changes in BFO–adsorbate interactions, all of which vary with polarization direction.

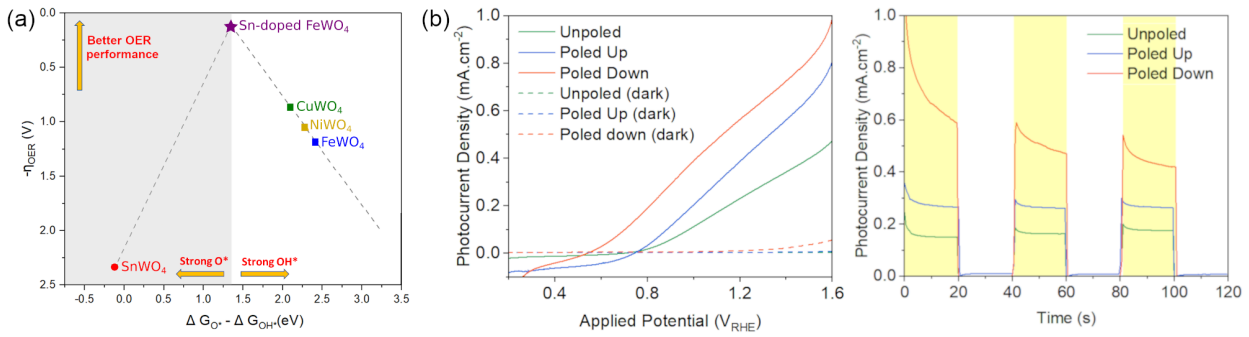



**Figure 9.** (a) Computational analysis of oxygen evolution reaction (OER) mechanisms on doped tungsten oxide catalysts, and (b) enhancement in photoelectrochemical water splitting performance using ferroelectric polarization switching, presented by Judy Hart. Figure reproduced with permission, © 2025 Wiley-VCH GmbH.

**Summary of Scientific Session 5: Catalysis, Interfacial fields, and Surface States.** *Session Chair: Roel van de Krol (Helmholtz-Zentrum Berlin), Session Recorders: Aaron Kaufman (University of Oregon) & Oshnik Maurya (Mumbai Institute of Chemical Technology), Session Report Leaders: Gary Moore (Arizona State University), Louise Berben (University of California, Davis)*

This session addressed topics in catalysis, interfacial fields, and surface states. The speakers collectively pointed to the need for a deeper understanding and control of interfacial processes to enhance the efficiency and selectivity of catalytic systems. Figure 10 illustrates the overall message of the session: (photo-)electrochemical solar energy conversion systems demand control of interfacial chemistry.

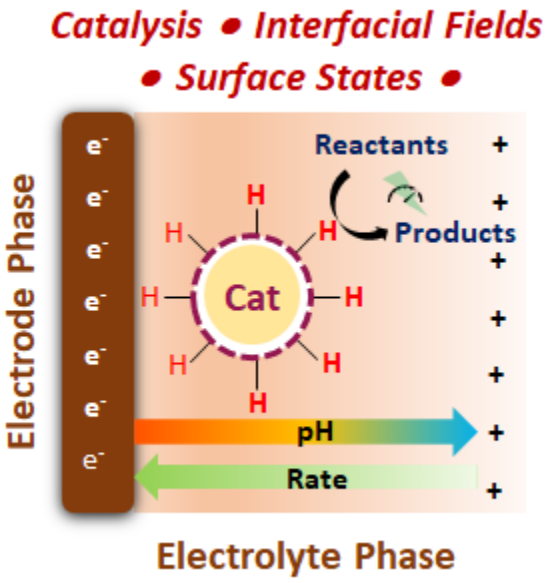



**Figure 10**. A schematic diagram/artistic depiction highlighting concepts and themes relevant to session five of the Gerischer-Lewerenz Symposium, including the role of delocalized electronic structures during chemical catalysis at electrified interfaces, control of surface hydride formation and hydride transfer, the role of polarization in driving

interfacial charge transfer, the impact of pH on reaction dynamics, as well as the interplay between catalytic reaction rates and pH gradients. Image credit: Humayra Begum.

In their joint presentation, James (Jim) Mayer and graduate student Sam Magpantay emphasized that metallic and semiconductor electrons often react by inner-sphere electron transfer. While electrodes are described to undergo pure electron transfer, polarization of interfaces often forms or breaks chemical bonds. For instance, when the interfacial redox energetics are pH-dependent, a proton-coupled electron transfer lens is important. Understanding the surface *chemically* – through the thermochemistry, stoichiometry, and reactivity of surface-H bonds – enables unique approaches for optimizing reactivity at the solid/solution interface. They highlighted Gerischer's papers stating that the Marcus-Gerischer model (used in many of the Figures above) applies only when specific adsorption is absent. This is critical as modern photo-electrocatalysis involves chemically complex and reactive electrodes and electrolytes, which in turn require perspectives that go beyond electron-only models.

Louise Berben discussed how metal clusters, with delocalized electronic structures, lower reorganization energies for electron and proton transfer. These clusters, such as an organometallic $Fe_4$ carbonyl cluster, significantly improved reaction kinetics and selectivity through multi-electron transfer processes, addressing critical challenges in solar fuel production.[38] She proposed that pre-equilibrium mechanisms could increase kinetic rates and reduce overpotential in these reactions. Berben also emphasized how solvent environments improve the direct conversion of captured $CO_2$ into liquid fuels, including how applications of protic solvents can enhance selective formate production.

Gary Moore introduced applications of extended electronic conjugation as a ligand-design motif for breaking scaling relationships in electrocatalysis and showcased results using binuclear Fe(III) fused porphyrins to demonstrate this.[39] He also presented diagnostic tools for characterizing photo-electrosynthetic reactions where chemical substrates, electrons, and protons are all reagents. Moore's investigations on the influence of light intensity highlighted electrode-potential-dependent and pH/light-responsive mechanisms relevant to solar photochemistry, including how buffering species can outcompete water as a proton donor.[40]

Yogesh Surendranath (Massachusetts Institute of Technology) highlighted the role of polarization in driving interfacial charge transfer. He challenged conference attendees with a proposal that "all interfacial reactions are inherently electrochemical," opening discussions on the role of non-Faradaic processes and thermal catalysis.[41] His insights into polarization-driven reactivity demonstrated the complex interplay between electrochemical potentials and reaction kinetics, suggesting that polarization is a crucial, yet often underexplored, factor in electrochemical and thermochemical reactions.

**Summary of Scientific Session 6: Electrode Stability and Passivation Layers:** *Session Chair: Shu Hu (Yale University). Session Recorders: Nathaniel Gomez (University of California, Irvine) & Colby Evans*

*(National Institutes of Standards and Technology) Session Report Leader: Dan Esposito (Columbia University), Dunwei Wang (Boston College)*

Long-term electrode stability and durability are critical to practical solar fuels devices. However, fundamental details of photoelectrode failure mechanisms are poorly understood, motivating this as the central theme of this session. Francesca Maria Toma (Lawrence Berkeley National Laboratory and the Helmholtz-Zentrum Hereon) reported on the stability of photoelectrodes, with a focus on water splitting. She highlighted the importance of understanding the chemical and physical changes in photoelectrode materials during operation, particularly with materials like $BiVO_4$. Techniques like Scanning Transmission X-ray Microscopy (STXM) and Kelvin Probe Force Microscopy reveal chemical heterogeneity, showing that grains and boundaries exhibit different spectral components.[42] Her research also investigates $Cu_2O$ and Cu-ternary oxides, showing that stability and catalytic products for $CO_2$ reduction differ based on materials composition and synthesis methods. Additionally, Toma's work on ZnTe photoelectrodes demonstrates that annealing temperature significantly influences photoelectrochemical activity and selectivity, with findings suggesting that smaller nanoparticles and surface diffusion of Zn at higher temperatures can improve $CO_2$ reduction activity, though with varying selectivity depending on the annealing conditions.

Sanghyun Bae (University of Zurich) presented work on enhancing the stability of $BiVO_4$ photoanodes for solar water oxidation using a hole-selective hybrid $TiO_2$ layer.[43] Despite its efficiency, $BiVO_4$ faces stability challenges due to ion leaching during electrochemical reactions. Bae's approach involves depositing a conformal $TiO_2$ layer via atomic layer deposition (ALD) to protect the surface, but with an innovative twist: first modifying the $BiVO_4$ surface with polyethylenimine (PEI). This surface modification enhances hole transfer through dipole effects and electron donation, making the $TiO_2$ layer more effective. Characterization techniques, including SEM, XPS, and TEM, confirm the successful incorporation of PEI and its impact on materials morphology and stability. The PEI-modified $BiVO_4/TiO_2$ photoanode exhibits improved water oxidation performance and stability, supported by 120 hours of photoelectrochemical analysis. The study concludes that the PEI layer not only provides hole selectivity but also improves photovoltage, contributing to the overall durability and efficiency of the photoanode.

Aiming to create highly efficient and durable photoelectrodes, graduate student Anna Kundman from NREL reported the potential of using $ZnTiN_2$ as a protective coating and carrier-selective heterojunction contact to p-type Si. This research approach aimed at co-designing materials that self-passivate, integrate with other materials, and maintain high performance. [44] $ZnTiN_2$, an experimentally underexplored ternary nitride with tunable properties like cation ordering and bandgap, and demonstrated self-limiting surface oxide formation under electrochemical bias, which is crucial for stability.[45] Kundman's ongoing synthesis development shows improved crystallinity and optoelectronic properties through heteroepitaxial growth. $ZnTiN_2$ forms an effective electron-selective layer on p-Si, maintaining stable photovoltage and

photocurrent even under varying pH conditions, highlighting its durability and potential in photoelectrochemical cells. Stability testing further supported $ZnTiN_2$'s robustness; it exhibited greater performance over extended periods compared to uncoated p-Si, making it a promising material for solar water oxidation applications.

Dan Esposito and William Stinson reported on the use of nanoscopic oxide coatings to enhance PEC stability and selectivity (Figure 11).[46,47] This research aims to addresses challenges of semiconductor corrosion and cocatalyst degradation, noting that stability issues arise from both thermodynamic and kinetic factors. They highlight the role of coatings in mitigating degradation by isolating the semiconductor from reactive environments, using "nanoemitter" designs (featuring passivating surfaces) and continuous tunneling films less than 1 nm thick. Their findings show that very thin (< 10 nm thick) silicon oxide coatings significantly improve stability and even increase current density, a counterintuitive result. Additionally, these coatings demonstrate selective transport properties, blocking undesirable reactions such as the poisoning of electrodes by solvated Cu ions while enhancing the $H_2$ evolution reaction at interfaces buried under silicon oxide coatings. Computational models support the effectiveness of these coatings, showing high energy barriers for unwanted Fe oxidation states. They also reported a micro-electrode technique to map defects in coatings. Overall, the work demonstrates how passivation layers can stabilize semiconductors and cocatalysts while enhancing reaction selectivity, improving the production of solar fuels.

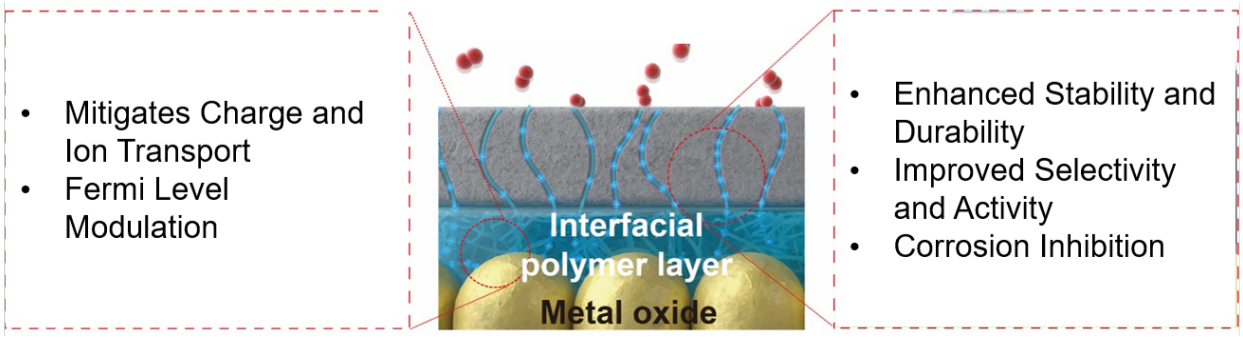



**Figure 11.** Schematic side-view of multi-functional protective layers applied to (photo)electrocatalysts and photoelectrodes. *Image credit*: Sanghyun Bae and Daniel Esposito.

**Summary of Scientific Session 7: New Frontiers in Electrode/Electrolyte Interface Measurements:** *Session Chair: Thomas Hannappel (Technical University of Ilmenau). Session Recorders: Sanghyun Bae (University of Zurich) & Sam Magpantay (Yale University) Session Report Leader: Scott Cushing (California Institute of Technology), Renato Neiva Sampaio (University of North Carolina, Chapel Hill)*

Emerging and cutting-edge techniques are under development that are expected to provide unprecedented insights into the dynamic processes of the semiconductor/electrolyte interface. Advanced

methodologies in electrochemistry, spectroscopy, and theory can elucidate critical information on the complexity of this interface, including electron-transfer rates, polaron dynamics, intermediates, and more.

Renato Neiva Sampaio demonstrated that chronoamperometry offers a straightforward, real-time method for assessing electron transfer kinetics at illuminated semiconductor/electrolyte interfaces (Figure 12).[48] This avoids the need for the more complex modeling required to extract kinetic data from cyclic voltammograms. By systematically varying the amplitude of potential steps in both the cathodic and anodic directions relative to the formal reduction potential, the resulting transient current and associated rates are controlled according to predictions of Marcus-Gerischer electron transfer framework. Additionally, time-resolved infrared spectroscopy, combined with electrochemical methods, was employed to quantify carrier recombination kinetics under applied bias conditions. The prolonged lifetime of electron-hole pairs measured at more negative potentials was attributed to the presence of an inversion layer at the p-Si surface.

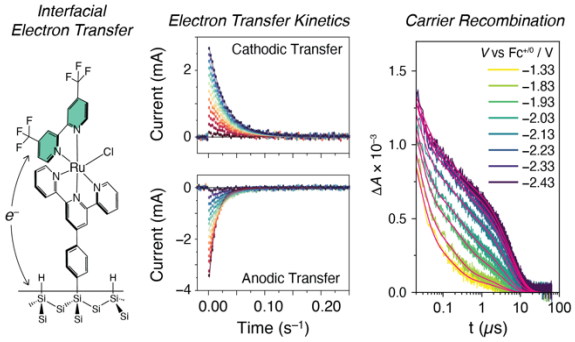



**Figure 12.** Overview of Renato Neiva Sampaio's talk describing the kinetics for interfacial electron transfer, using chronoamperometry, from an illuminated p-Si electrode to a surface-immobilized Ru complex after increasingly applied potential steps in both the cathodic and anodic directions. Time-resolved FTIR monitoring the recombination of photogenerated carriers, as a function of externally applied biases, in a H-terminated p-Si electrode after a pulsed laser excitation. *Image credit:* Renato Sampaio.

Tanja Cuk employed time-resolved optical spectroscopies to identify and track the dynamics of intermediate oxygen species during photoelectrochemical oxygen evolution catalysis (Figure 13).[49] She emphasized the significance of these techniques in addressing key challenges related to extracting molecular-level details and kinetic pathways of elementary reaction steps. For the $TiO_2$ interface, hole-polarons—whereby the lattice reorganizes around a trapped hole on predominantly an oxygen site—are predicted to occur by density function theory calculations. Recent work connected a below bandgap excited-state absorption that redshifted by ~1 eV between a rutile $TiO_2$ (100) and a perovskite $SrTiO_3$ (100) surface to theoretical predictions. The optical dipole calculated by time-dependent density function theory is bright for the terminal oxyl and lateral hole-polaron configuration, respectively, in $TiO_2$ and $SrTiO_3$.

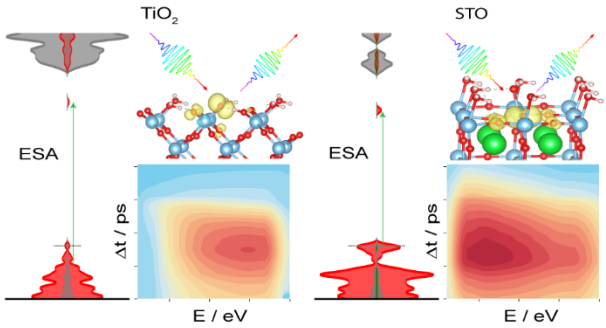



**Figure 13.** Time-resolved spectroscopy and assignment of reactive intermediates on metal oxide photoelectrode surfaces. *Image credit:* Tanja Cuk.

Roel van de Krol and Jonathan Diederich discussed how recent advances in surface science and ultrafast spectroscopies, such as X-ray photoelectron spectroscopy and time-resolved two-photon photoemission (Figure 14), improves the characterization of surface states at and near the semiconductor/electrolyte interface, including their chemical nature and occupancy.[50] They also stressed that selective contacts,[51] even in the absence of an electric field, can drive interfacial charge separation in photoelectrochemical systems without an applied bias. Lastly, van de Krol emphasized the importance of creating buried junctions to enhance charge separation and to effectively passivate surface states.

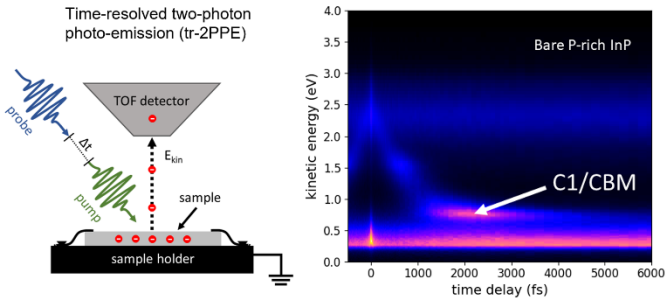



**Figure 14.** Time-resolved two-photon photoemission studies of an InP photoelectrode discussed by Roel van de Krol and Jonathan Diederich. Counts of photoemitted electrons are given as a function of delay time between pump and probe and kinetic energy of emitted electrons. Image reproduced from reference [50] under license CC-BY 4.0.

Graduate student Sa Suo proposed a novel contactless spectroscopic method for accurately determining the quasi-Fermi level of metal–insulator–semiconductor (MIS) junctions (Figure 15). Utilizing surface-enhanced Raman spectroscopy, she demonstrated how the vibrational Stark shift of a molecular probe was directly correlated with changes in the Fermi level of a metal cocatalyst induced by an applied electrode bias and illumination conditions. Suo further showed how this SERS approach can be applied to investigate Fermi level alignment and electron-transfer mechanisms in a semiconductor-redox polymer-metal hybrid photocathode.[52]

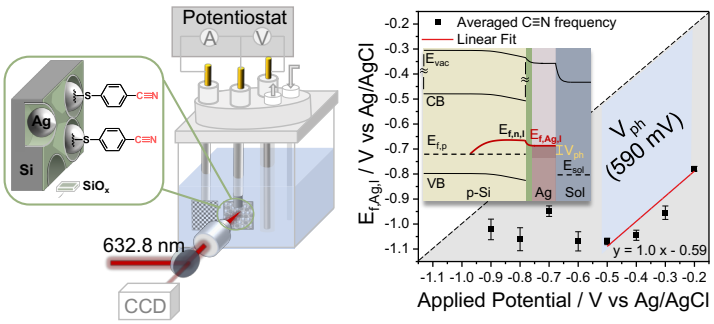



**Figure 15.** Quantifying energy level aligned at semiconductor/electrolyte interfaces using *in situ* spectroscopy. *Image credit:* Sa Suo.

Borrowing concepts from correlated quantum materials can pave the way for developing photoelectrochemical materials, as demonstrated by Scott Cushing and graduate student Jocelyn Mendes on photoexcited polaron effects. His group introduced the Hubbard-Holstein model as a good descriptor of excited-state polaron dynamics, where different materials can be plotted to determine what kinds of regimes (polaron strength vs. polaron/electron hopping) they are in. By recognizing the different properties of polarons, and mapping them using a quantum model, this approach can increase polaron lifetimes and mobilities by orders of magnitude, particularly through utilizing electron and spin correlations.

An outlook-oriented question for the field that emerged during this session is: "*As advancements in surface science and interface characterization continue to provide important insights into the physical properties of bulk materials and interfaces, what advancements in theory or experimentation are needed to better understand the chemical nature of interfaces and surface states*?"

**Summary of Scientific Session 8: The Impact of Ultrathin 2D Materials on Semiconductor Electrochemistry:** *Session Chair: Justin Sambur (Colorado State University) Session Recorders: Jeremy Brinker (University of Texas at Austin) & Colby Evans (National Institutes of Standards and Technology) Session Report Leaders: Jao van de Lagemaat (National Renewable Energy Laboratory) & Justin Sambur (Colorado State University)*

Justin Sambur introduced this session stressing that 3-atom thick semiconductors such as monolayer transition metal dichalcogenides, e.g., $MoS_2$, $WSe_2$, challenge traditional assumptions such as the depletion approximation. Sambur shared that a remarkable phenomenon occurs upon applying a bias to, or illuminating, a 2D semiconductor electrode such as monolayer $MoS_2$: the electronic bandgap changes by almost 1 eV! This bandgap renormalization effect induces significant changes in band edge energetics (0.2–0.5 eV) over a narrow range of applied potentials (0.2–0.3 V). Such large band edge shifts could change electron-transfer rate constants ($k_{ET}$) by a factor of 10–100, which has important consequences for practical solar energy conversion applications. On the practical side, Sambur reminded conference attendees that

Gerischer,[53] Lewerenz,[54] Tributsch,[55] Tenne,[56] and Parkinson[57] constructed arguably the most efficient and stable photoelectrochemical solar cells based on the group VI transition metal dichalcogenides. Sambur noted one issue that remains to be solved in this materials class: doping heterogeneity. Lewerenz previously reported efficiency losses in bulk transition metal dichalcogenide solar cells due to carrier type heterogeneity, or the coexistence of n-type and p-type domains in the same crystal.[58] Recent photocurrent mapping and molecular reaction imaging measurements in Sambur's lab defined the n- and p-type domain sizes and explained the surface recombination reaction responsible for efficiency losses. An open challenge for the materials chemistry community is reliably and uniformly doping n-type and p-type transition metal dichalcogenides. Sambur pitched ultrathin monlayer transition metal dichalcogenides as efficient and stable photoelectrodes because (1) hot carrier extraction is possible[59] and efficient because photo-excitation produces hot carriers *immediately* at an interface, which opens the possibility of driving thermodynamically "uphill" reactions with high energy hot carriers; and (2) monolayer transition metal dichalcogenides resist anodic dissolution under water oxidation conditions;[60] bulk transition metal dichalcogenides corrode under the same conditions. The key point of Sambur's introduction is that monolayer transition metal dichalcogenides are potentially transformative photo-absorbers for photocatalytic applications, and there are opportunities to harness the unique interfacial energetics of the 2D semiconductor/electrolyte interface to control electron-transfer kinetics from the semiconductor absorber to reactants in solution.

Andrés Montoya-Castillo (University of Colorado, Boulder), postdoc Thomas Sayer (University of Colorado, Boulder), and graduate student Rafael Almaraz (Colorado State University) shared the interfacial energetics and hot carrier (high energy exciton) dynamics in 2D semiconductor photoelectrodes, focusing on the unique properties that arise from their atomic thinness. The transition from bulk to monolayer in 2D materials leads to significant changes, such as an indirect to direct bandgap transition, and the potential to prevent thermalization losses due to the interface's reactivity. The team studied hot carrier generation and extraction dynamics in a working photoelectrochemical cell using a combination of steady state photocurrent spectroscopy and *in situ* transient absorption spectroscopy.[59] Sayer's modeling of Fermi-polaron interactions helps explain observed shifts in exciton and trion behavior,[61] revealing the complex interplay of electronic structure and environmental factors. Almaraz investigates how the introduction of redox-active molecules alters the electronic structure, particularly the equilibration of the Fermi level with a redox couple, influencing the bandgap and exciton dynamics. The study underscored the potential to extract hot carriers in 2D systems, highlighting the need for advancements in theory, spectroscopy, and method development to fully harness these capabilities.

Dan Frisbie (University of Minnesota) reported the use of backside gates to control electrochemical potentials and reaction rates on 2D semiconductor electrodes. By constructing a 2D material device as a thin-film capacitor, Frisbie demonstrates how the gate voltage can independently tune charge carriers in the

material, effectively manipulating the Fermi level in the density of states. This tuning allows for precise control over electrochemical reactions, such as the $H_2$ evolution reaction,[62] by optimizing the binding energy of reactants at the electrode surface. For instance, using a gate voltage in a ZnO field effect transistor setup, Frisbie showed how the conductance and catalytic efficiency can be significantly improved. He further extended this concept to $MoS_2$, where applying gate voltage alters semiconductor band edges, enabling a transition from irreversible to reversible electrochemistry and reducing the overpotential for catalytic reactions. By charging defect states in the semiconductor, the gate voltage enhances the electrochemical interface, facilitating targeted reactions. This gated approach offers a powerful tool for advancing semiconductor-based catalysis.

Jao van de Lagemaat reported the role of strongly-coupled plasmon-exciton polaritons in light-driven chemistry, particularly in enhancing hot carrier effects in 2D materials. He discussed how plasmonic interactions, such as those in $MoSe_2$ sheets with gold nanoparticles, can extend excited-state lifetimes and enable processes like water splitting, even though gold nanoparticles alone are not typically photocatalytic. Their transient absorption spectroscopy data revealed long-lived hot polariton states, suggesting a mixture of plasmon and polariton behavior, which is tunable by adjusting the photonic cavity. Jeiwan Tan then delved into the use of chiral surfaces in electrochemistry, particularly for $CO_2$ reduction reactions. Tan highlighted how chiral copper surfaces, created through electrodeposition with chiral agents, can selectively produce formate while suppressing $H_2$ evolution, driven by spin-aligned hydrides on the surface. This spin alignment, potentially caused by a spin Hall effect, significantly influences product formation and is a key area for further research in understanding and harnessing spin polarization in catalytic processes. The work underscores the potential of combining plasmonics, chirality, and spin effects to stabilize hot excited states and control reaction pathways in photoelectrochemical systems.

**Summary of Scientific Session 9: Photoelectrochemical Cells in Action 2:** *Session Chair: Todd Deutsch (National Renewable Energy Laboratory) Session Recorders: Jeremy Brinker (University of Texas at Austin) & Sanghyun Bae (University of Zurich) Session Report Leaders: Robert Coridan (University of Arkansas) & Kyoung-Shin Choi (University of Wisconsin, Madison)*

Photoelectrochemical system implementation requires optimizing multiple parameters and processes simultaneously. Dunwei Wang reminded conference attendees that the fundamental Gerischer model relies on having a simple outer-sphere redox couple in solution, which isn't the case for most interesting reaction chemistries, especially multi-electron-transfer reactions. Wang showed that, counterintuitively, *both* increasing and decreasing catalyst loading led to enhanced PEC performance and explained that both chemical kinetics and semiconductor hole density led to these competing effects.[63] The

key takeaway from this effort was to remember that in complex systems, several competing effects are often present, and work should focus on optimizing these trade-offs.

Robert Coridan presented insights on enhanced light trapping and carrier collection yields in semiconductor photoelectrodes, using photonic glasses as structural templates for earth abundant, thin film semiconductor photoelectrodes.[64] The photonic glass structure can generate a "slow light" effect like what is observed in more commonly used photonic crystal light trapping structures. In photonic crystals, the propagation of light through the material is slowed near the edges of the photonic stop band. Coridan showed in simulation data that a disordered colloidal structure could also slow the propagation of light, enhancing the absorption in the photoelectrode. This offers an advantage as a light-trapping strategy over the conventional photonic crystal structures due to the disorder tolerance of the template. Graduate researcher Ashlyn DesCarpentrie summarized experimental work in photoelectrodes based on nanometer-thin films of anatase $TiO_2$ that used this slow light effect in a photonic glass electrode structure to improve light absorption near the absorption edge.[64] The improved absorption and open photoelectrode structure provided significant external quantum yields for photoelectrochemical reactions such as ferrocyanide oxidation and water oxidation.

Kyoung-Shin Choi presented on the impact of photoelectrode surfaces and interfaces on the overall performance of photoelectrodes. Choi showed that for the same $BiVO_4$ photoanode, variation of the surface composition in the outermost layer and the bonding nature between the photoanode and an $O_2$ evolution catalyst impact interfacial energetics strikingly. These results show that understanding the effects of surfaces and interfaces is as important as understanding bulk photoelectrode properties. She concluded her talk with an outlook towards using PEC devices to synthesize both fuels and value-added chemicals at the same time, sharing her perspective that this would increase the widespread implementation of PEC devices. As the PEC field comes into maturity, the question remains: "*In practical devices, how will fundamental principles inform both photoinduced generation, separation, and transport of electronic charge carriers and catalytic activity*?"

The 2nd Gerischer Electrochemistry Today meeting brought together graduate students, postdoctoral researchers, industry professionals, and academics to explore the rich chemistry, materials science, and photophysics at semiconductor/electrolyte interfaces, establishing a dedicated disciplinary home for the semiconductor photoelectrochemistry community. The fundamental insights gained at this interface span multiple disciplines.

Discussions throughout the Gerischer Symposium revealed several cross-cutting knowledge gaps that currently limit progress in semiconductor electrochemistry and interfacial catalysis. With regards to mechanisms of charge carrier separation, there is a need to clarify and distinguish between charge separation mechanisms, particularly the role of electric fields and band bending versus reaction selectivity at

nanostructured semiconductor/electrolyte junctions where conventional bulk models may not apply. Researchers often lack a clear understanding of how interfacial electric fields form and evolve during photoelectrochemical operation. The influence of surface terminations, adsorbates, and passivating layers on interfacial charge transfer and catalysis is not yet fully understood and go beyond the "Gerischer view" in Figure 1. New experimental tools are needed to simultaneously measure structure, electric field strength, and local reactivity under operando or in situ conditions.

Existing models often fail to capture the effects of real-world features such as non-ideal defect distributions, complex interfacial water structures, and electrolyte dynamics. Quantitative descriptors that link defect density or chemistry to electrochemical behavior are scarce, making it difficult to compare materials or predict outcomes.

Performance metrics are inconsistently reported, with most studies focusing on best-case data rather than statistical distributions across particles or batches. Insights from single-particle or nanoscale studies are not always translated to larger-scale or device-relevant conditions, limiting practical impact. Long-term stability and durability under operating conditions remain underexplored. Materials discovery efforts are often decoupled from system-level modeling, creating barriers to scalable implementation.

The field faces an urgent challenge: demonstrating the tangible impact of these systems in real-world applications. Can these interfaces be leveraged to produce solar fuels and value-added chemicals in resource-limited settings? Can we harness light to drive transformations that are otherwise unattainable under traditional electrochemical conditions? The enthusiasm, interdisciplinary collaborations, and scientific momentum from this meeting leave us optimistic for what lies ahead. We eagerly anticipate the 3rd Gerischer meeting, to be held in Berlin in 2027, organized by Roel van de Krol and Francesca Toma, which will continue to shape the future of this exciting and impactful field.

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