Analytical Methods

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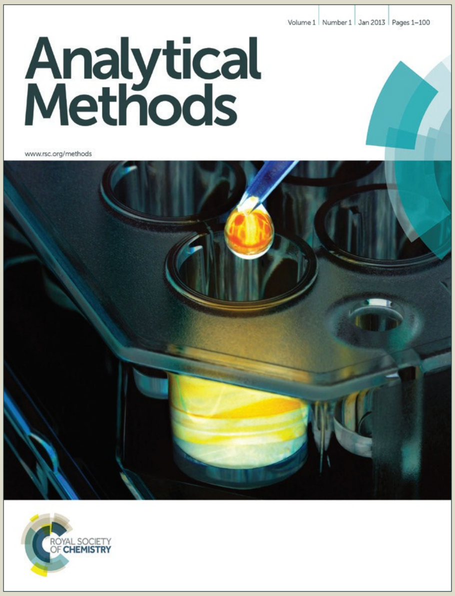

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Emerging Techniques for the In Situ Analysis of Reaction Intermediates on Photo-Electrochemical Interfaces

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Using light excitation to perform uphill chemical reactions is an attractive strategy for powering alternative energy sources, producing renewable fuels, and providing efficient methods for environmental remediation. In particular, photoelectrochemical reactions at wide-bandgap semiconducting electrodes and their colloidal particles have been thoroughly studied for the last 40 years. Although materials such as TiO_2, $SrTiO_3$, and ZnO among others have found a myriad of applications, from dye-sensitized solar cells to formulations for self-cleaning street pavement, many questions still remain regarding their surface reaction mechanisms. The need to understand these systems in situ and in operando schemes has become invigorated by the interest in plasmonics, co-catalysts, and bandgap engineering for enhancing their performance. Thus, elucidating the impact of these technologies on the photogenerated surface chemical intermediates can reveal relevant mechanistic differences. Do the reactivities and properties of Reactive Oxygen Species depend on the wavelength of excitation on engineered materials? What is the impact of metal deposits and defects on the formation and properties of surface species? Are there any recent developments in techniques that could shed new light on new materials interactions at the nanoscale? In this review, we seek to provide a fresh perspective on existing and emerging in situ analytical methods applied to semiconducting photocatalysts for answering these and other modern aspects of surface intermediates.

1 Introduction

Photo-assisted electron transfer at the semiconductor-electrolyte interface starts with the rapid photophysics of light absorption but it is only enabled by temporally-, energetically- and spatially- distributed surface processes. [1-3]The chemistry at photoactive surfaces, as in many heterogeneous catalytic systems, depends on surface intermediates.[4-6] For instance, electrocatalytic metals and metal oxides generate species which lower the activation barriers for multi-electron reactions,[6] such as in small organic molecule oxidations[7, 8] and the water splitting reaction. [5, 9] Photoactive and photoelectrocatalytic (PEC) surfaces are of special interest because the driving force for chemical processes comes from absorbed light. Absorption of light generates photogenerated charge carriers, such as the hole (h^+) and the electron (e^-), which eventually interact with the medium to form reactive oxygen species (ROS) in aqueous electrolytes. These intermediates interact with surface features and deposited (electro)catalysts to further decrease the activation energy of a reaction. [2, 10-13]

The prospects of converting light and electrical energy into chemical energy has produced a wealth of literature dedicated to photocatalyst chemistry. These studies include reactions for splitting water into oxygen and hydrogen gases,[14, 15] photo-initiated polymerization reactions,[16] the modification of surface properties such as wetting and self-cleaning,[17, 18] and the photodecomposition of many organic[19-21] and inorganic compounds. [22] Clearly, elucidating PEC dynamics in detail is implicit in the societal importance of their applications: environmental remediation,[21, 23-26] surface engineering and functional surfaces,[3, 17, 23, 27-30] and fuel and chemical synthesis,[11, 16, 19, 23] including approaches to solar energy conversion.[1, 31-33]

The complex chemical environment at the semiconductor-electrolyte interface presents significant challenges for understanding reaction mechanisms. Both ROS and "trapped" charge carriers are chemically active during a series of events that evolve over time.[2] Thus, detecting and differentiating the reactivity of each species is critical to understanding its mechanisms and enhancing their reactivity for a given purpose. [3, 34] For instance, photoanodic oxidations of pollutants in solution via ROS could yield different products from those generated by direct decomposition via holes. The creation of mid-bandgap states by using strategies designed to align the material to the solar spectrum can change the fraction of ROS generated,[35] Likewise, the advent of new concepts based on plasmonics [36] – hot carrier generation,[37] emerging materials interactions based on hetero-interfaces,[38] and spillover from metal and metal oxide deposits,[12] make the task of understanding reaction mechanisms

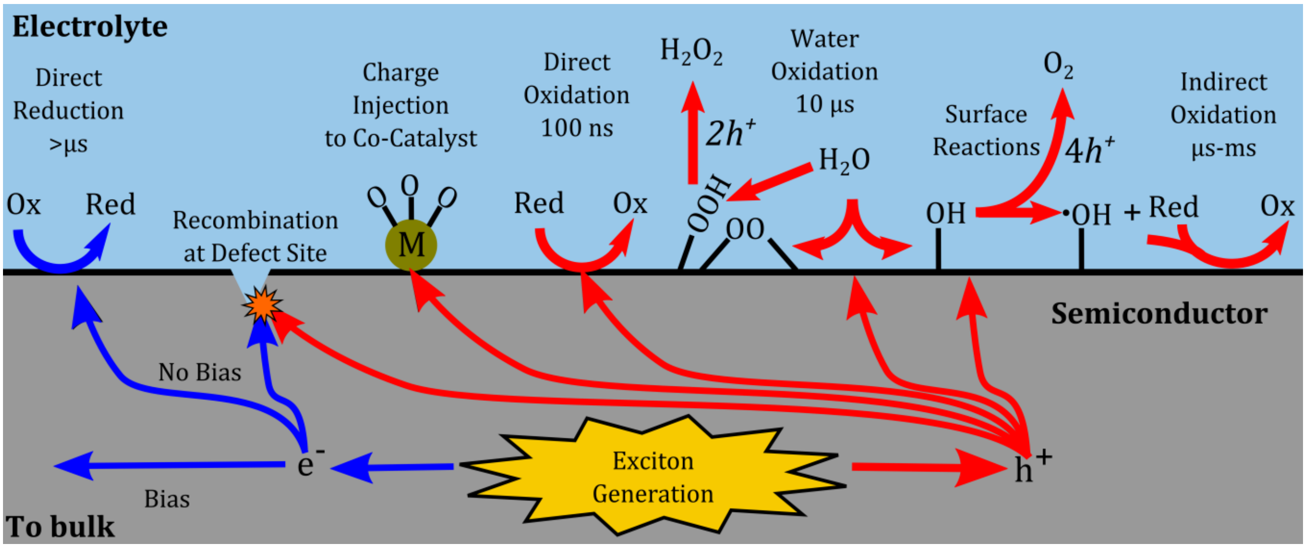

Figure 1) The TiO_2/water exemplifies the many processes occurring simultaneously at the semiconductor/electrolyte interface, each with a characteristic time scale.

a modern endeavour. Fundamental questions are emerging concerning how these materials discoveries modify the identity, reactivities, and surface coverage and dynamics of intermediates at novel PEC interfaces.

Mechanisms of charge transfer at the PEC interface can broadly be divided into direct or indirect routes, and their fates are summarized in Figure 1. Direct charge transfers occur when a free or trapped charge carrier tunnels directly to a solution phase molecule.[10] Indirect charge transfers happens through a photogenerated surface chemical intermediate. In aqueous PEC systems, commonly proposed reactive surface groups include hydroxyl radicals (•OH), peroxo groups (OO), and hydroperoxo groups (OOH).[3] These ROS have been implicated in many processes, especially those occurring in ambient conditions.[21] In contrast, direct mechanisms are often studied under vacuum conditions, although the chemical nature of trapped holes is not an entirely settled subject.[39] Better understanding of the PEC interface will require measurements that unambiguously identify species.

A common referent for exploring the electrochemistry of surface-bound species is the use of current-potential experiments. Voltammetry for instance, provides detailed information about intermediate formation on metal electrodes, including the formation of hydrides, oxides, and many other carbon-containing molecules. On noble metal electrodes, these intermediates show well-defined voltammetric waves that allow experimenters to estimate details of their surface coverages and predominance under different reaction conditions.[40] However, for a great majority of doped semiconductor electrodes, the constraints imposed by the concentration and type of dopants, as well as their different behaviour in the dark versus illuminated conditions significantly obscure their voltammetric response.[2] Photocurrent transients can often provide information about the fate of some intermediates, but in general, current-time and current-potential techniques have limited information to offer regarding mechanistic electrochemistry at the PEC interface.

A desirable analytical method for studying the PEC interface would provide high spatial and temporal resolution, as well as the capability of analysing the material in its operating medium. Surface photochemical processes span a wide range of time scales, thus leading to instrumental challenges.[41] Some processes, such as charge carrier generation, occur within femtoseconds, while charge transfers across the interface may show characteristic times lasting several microseconds.[3] Spatial heterogeneities may result from processes occurring on surface features on the nanometer scale, but may eventually impact reactivity on the micron scale or larger. Analytical techniques need to either simultaneously address a range of length and time scales spanning several orders of magnitude or must be flexible enough to adapt to many scales. *In situ* techniques are ideal for studying surface intermediates in the medium in which they are formed. By measuring under native conditions, we avoid extrapolation from conditions that bear little relevance to the operation medium, as is a common concern in studies performed in ultra-high vacuum (UHV). Despite the amount of work done on photoelectrochemical interfaces, we still lack a technique that fulfils all of the criteria for species selectivity, and time and space resolution, but new methods or their combinations will continue to develop our working understanding of PEC systems.

In this review, we will focus on techniques that have been employed to produce our current understanding of the PEC interface, as well as those emerging techniques that are finding an application.[3] Intermediate species identity is always of primary importance, but is often the most difficult to directly determine. After this, the reactivity of the intermediates is especially useful for elucidating mechanisms. In addition, understanding the distributions of surface species in space and time is critical for correlating performance with material properties. Typically, gathering all this information requires data from multiple techniques. We will cite examples of measurements related to water splitting on wide-bandgap semiconductors such as TiO_2 and $SrTiO_3$ in order to maximize the consistency and comparisons between techniques. At the cutting edge, we will highlight techniques yet to be used at PEC interfaces that we believe represent the future of this field.

2 Spectroscopic methods

2.1 Electron Paramagnetic Resonance

Electron paramagnetic resonance (EPR) was the first technique used to identify reactive intermediates at a PEC interface.[42] EPR detects the energy level splitting of unpaired electrons in an applied magnetic field by exciting transitions between electronic spin states. This is often used to detect the unpaired electrons present in radical species. This was initially used to confirm the proposed mechanism for photocatalytic decomposition of carboxylic acids by TiO_2, which involved radicals similar to those in a Kolbe reaction. [43, 44] On platinized TiO_2 particles, this "photo-Kolbe" reaction was initiated using UV light, generating carbon radicals that were directly identified.[45]

EPR experiments often use spin trapping reagents to detect short-lived intermediates. These spin traps react with intermediate radicals to form stable radical species that accumulate in high enough concentration for detection. Although these probes were used to provide early evidence for the formation of •OH and HO_2• during water decomposition on platinized TiO_2 particles, identification of the trapped radical is not always straightforward.[46] More recent work comparing results from spin trapping methods with fluorescence techniques indicated photogenerated holes may oxidize the spin traps, thus rendering them less effective for distinguishing mechanistic pathways.[47] Highly reactive surface species will rarely be present in sufficiently high volumetric concentrations for EPR detection, making spin traps necessary. This eliminates much of the chemical information normally encoded within an EPR spectrum. While EPR imaging techniques are under development, currently EPR lacks the sufficient spatial resolution to probe sub-mm features,[48, 49] limiting its application to homogeneous samples. EPR can be coupled to electron microscopy to understand connections between structure and mechanisms, however this does not spatially resolve its signal.[50] Development of a super- resolution EPR technique would be a very exciting development, but this still seems to be beyond the horizon.

2.2 Vibrational Spectroscopies

Infrared (IR) and Raman spectroscopies provide detailed chemical information because they generate signals by exciting vibrational modes of chemical bonds. While application of IR spectroscopy is typically obscured in aqueous systems by the strong IR absorption of water, multiple internal reflectance IR, allows *in situ* spectroscopy of PEC surfaces.[51] In this configuration, the photocatalyst is deposited on top of a prism on which a laser is reflected multiple times. This effectively increases the path length through the sample and avoids illumination through water. Nakamura, et al. used this configuration to study photocatalytic water oxidation on nanocrystalline rutile TiO_2 and observed the formation of bridging surface peroxo species Ti-O-O-Ti at 812 cm^{-1} under alkaline conditions, but observed the presence of a surface bound hydroperoxo species TiOOH at 838 cm^{-1} under acidic conditions.[51] They used this information to support an oxygen evolution mechanism where a bridging peroxo group is formed on the surface, which then undergoes acid-catalysed hydrolysis into a hydroperoxo and hydroxyl groups. This direct chemical information is clearly invaluable in better understanding mechanisms.

Because Raman spectroscopy relies on a wavelength shift from Stokes scattering, signal degradation can be minimized through proper excitation wavelength selection. Raman spectroscopy is often used *in situ* to identify intermediates on several classes of catalysts.[52-54] It has been used to detect the presence of many species known to participate in water splitting, including surface peroxides.[55] Recently, this was employed to detect the intermediate Ti-peroxide species formed during photoelectrocatalytic aqueous oxygen reduction. Figure 2A

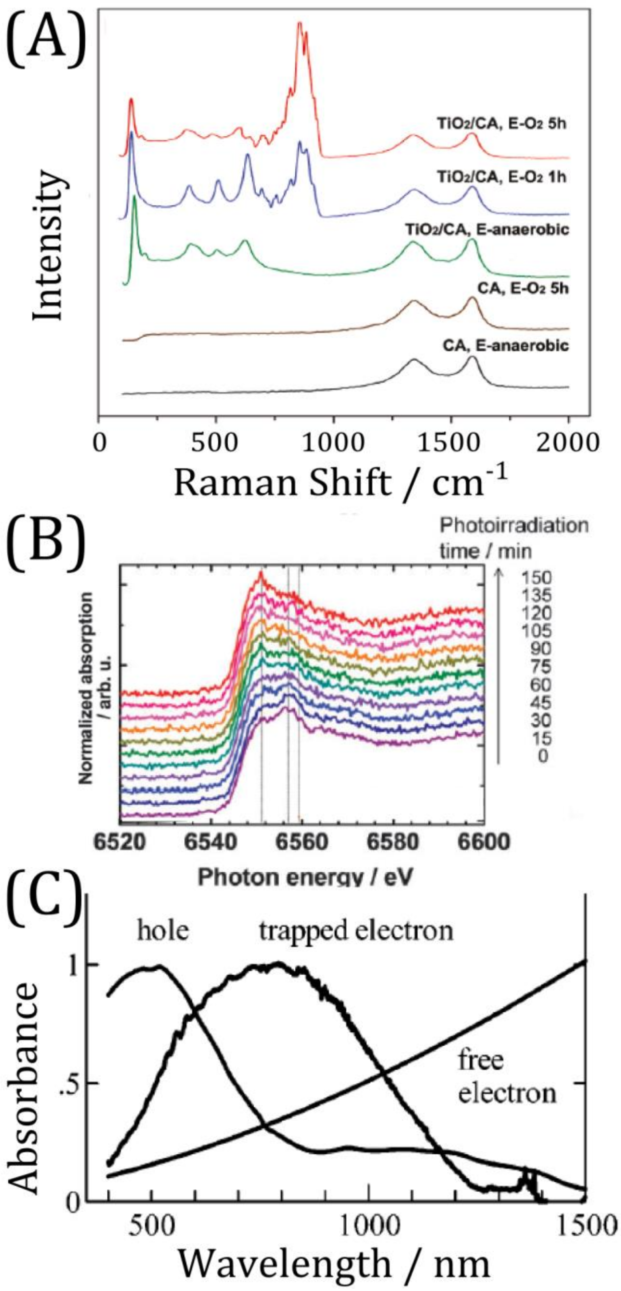

Figure 2A) Raman spectra of TiO_2 particles supported on a carbon aerogel (CA) showing formation of surface H_2O_2 during the oxygen reduction reaction. Reprinted with permission from Y. N. Jin, G. H. Zhao, M. F. Wu, Y. Z. Lei, M. F. Li and X. P. Jin, Journal of Physical Chemistry C, 2011, ***115****, 9917-9925. Copyright 2011 American Chemical Society. B) Sequential X-ray absorption spectra of a sample of Nb doped $SrTiO_3$ with Mn-oxide nanoparticles used as co-catalysts. UV photo-irradiation under +1.0 V potential shifts the peak at 6556.9 eV to 6559.6 eV, indicating conversion of Mn^{3+} to Mn^{4+} by the migration of photoexcited holes from the $SrTiO_3$ to the Mn-oxide. The appearance of the low energy peak at 6550.9 eV that gradually grows with irradiation time indicates that UV light induced some of the Mn^{3+} to change to Mn^{2+}. Reproduced from M. Yoshida, T. Yomogida, T. Mineo, K. Nitta, K. Kato, T. Masuda, H. Nitani, H. Abe, S. Takakusagi, T. Uruga, K. Asakura, K. Uosaki and H. Kondoh, Chemical Communications, 2013,* ***49****, 7848-7850 with permission of The Royal Society of Chemistry. C) Absorbance spectra of charge carriers detected using TAS. Reprinted with permission from T. Yoshihara, R. Katoh, A. Furube, Y. Tamaki, M. Murai, K. Hara, S. Murata, H. Arakawa and M. Tachiya, Journal of Physical Chemistry B, 2004,* ***108****, 3817-3823. Copyright 2004 American Chemical Society* shows this analysis on carbon aerogel supported nanocrystalline films of TiO_2.[56] The presence of surface peroxides suggested a mechanism of Rhodamine 6G degradation in which surface H_2O_2 was formed electrochemically, then photo oxidized by holes to produce •OOH and eventually •OH. Raman is a useful technique for the detection of O-H bonds that might be obscured in other spectroscopies by the presence of water.

IR and Raman spectroscopies exceed all other techniques available in their ability to provide chemical information about intermediate species. Not only do they identify specific bonds, they also provide details about the chemical environment near those bonds.[54] Understanding the influence of heterogeneities and defects on the spatial distribution of surface species is of primary concern. Light can only be focused to a wavelength-dependent spot size described by the Abbe diffraction limit ($d \equiv \lambda/2n\sin\theta$). Spatial resolution is limited to this spot size when using traditional measurement schemes, so none of these techniques really probe the effects of nanoscale heterogeneities.

Breaking the diffraction limit using super- resolution techniques should help answer questions regarding localized effects. Recent work with near-field scanning optical microscopy (NSOM) overcomes the diffraction limit on many surfaces[57] and may be broadly adapted to vibrational spectroscopy on photocatalytic systems.[58] Tip or surface enhanced Raman spectroscopy (TERS/SERS) rely on large local electric field enhancements from metal nanostructures to improve sensitivity of Raman signals.[36, 59, 60] Using SERS, the activity of single nanoparticles can be monitored, although experiments reaching this level of sensitivity have relied on both surface enhancement and a reactant species that provided strong Raman resonance effect.[36] TERS uses a metal tip to give super-resolution images of Raman signals from individual adsorbates [61] and surface states.[62] Single molecules can be probed with TERS, which allows addressing of charge transfer events occurring at individual sites.[61] The addition of these sophisticated methods pushes toward probing individual catalytic sites for chemical identity, certainly a desirable capability for investigating PEC mechanisms.

2.3 X-ray techniques

X-ray based techniques are ubiquitous in the field of materials characterization because they provide structural or chemical information. However, many X-ray techniques lack surface sensitivity because X-rays penetrate too deeply into materials to separate surface and bulk contributions. X-ray photoelectron spectroscopy (XPS) overcomes this by looking at core electrons ejected from atoms under X-ray illumination. Electrons interact strongly with matter, so only electrons ejected from atoms less than 10 nanometers from the surface are typically detected.[63] The ejected electrons have energies characteristic of the orbital from which they were ejected, so XPS is most commonly used in the study of PEC materials to identify atomic species present near the surface.[64, 65] It has been used to follow the formation and healing of oxygen vacancies sites on TiO_2 to study the binding of O_2 on the surface.[66] Although XPS is a powerful technique, it is typically limited to UHV conditions because electrons interact too strongly with matter to be detected through a solution. Under carefully controlled conditions, it is possible however to obtain information about chemical speciation after photochemistry. Ohtsu et al. used a proxy in situ method via a transfer line approach for minimizing the adsorption of atmospheric gases on samples of TiO_2 produced through electrochemical anodization.[67] Their results pointed out to the removal of carbon contaminations and the formation of surface hydroxyl species exclusively after UV irradiation. Although strictly lacking an electrolytic medium, these studies are important for understanding the properties of functional surfaces and the observed super-hydrophillicity in wide-bandgap semiconductors [28, 68]

A recent explosion of ambient pressure XPS for the study of solids has been driven by the development of better optical elements for both electrons and X-rays, and further advances might allow *in situ* observation of surface intermediates by XPS.[63] At present, ambient pressure XPS measurements easily identify surface species generated during catalytic reaction at gas/solid interfaces.[69, 70] These measurements can detect species often implicated in PEC mechanisms, such as surface hydroxyls.[71] *In situ* imaging of changing cerium oxidation state distributions in electrochemical systems has even been performed for solid oxide fuel cells.[72] Conceivably, a similar technique could reveal changing adsorbate coverages on a photoelectrocatalyst surface if XPS at the solid/liquid interface could be achieved, but this leap has yet to be made.

While lacking the surface sensitivity of XPS, X-ray absorption spectroscopy (XAS) is rising as a versatile tool for understanding electrochemical reactivity. In particular for manganese oxide deposits on Nb-doped $SrTiO_3$ photoanodes, Yoshida et al. have shown the possibility of observing photogenerated hole transfers from the bulk of the $SrTiO_3$ electrode to Mn oxide surface films and deposits. This was performed by observing Mn K-edge signals from the surface features.[73] By examining the changes in oxidation states as obtained by shifts in the absorption energies, their experiment showed that thin films exhibited uniform displacements throughout the film, but that in the case of nano-deposits, two populations of Mn species, reduced and oxidized, co-existed on the surface. XAS thus provides indirect information about the fates of charge carriers, their chemical transformation, and their localization. Other approaches to obtaining chemical speciation are available, such as the recently introduced Fixed Energy X-ray Absorption Voltammetry[74], which similarly uses XAS performed "in real time" as cyclic voltammetry is performed. This technique has been applied recently to determine the disproportionation of Ir species during the water oxidation reaction, and could be further applied to high surface area photocatalysts in the near future.

2.4 Fluorescent Probes

Most surface species found on PEC surfaces are not natively fluorescent, however, many of the formed ROS can activate chemiluminescence processes.[75, 76] Cathodoluminescence has been used to understand the energies of charge carriers generated by excitation in mid-bandgap states.[77] However, recent developments using visible-light emitting probes are also shedding light on the formation of ROS on the surface and electrolyte layer near the surface of active materials. By using probe molecules that are converted to a fluorescent form by reacting with specific intermediates, the formation of surface species can be quantified. Coumarin and terephthalic acid form fluorescent products by reaction with •OH and can be employed to quantify this species.[78-80] By comparing photocatalytic conversion efficiencies of non-adsorbing probe molecules with adsorbing probe molecules, fluorescence measurements recently showed evidence that anatase and rutile TiO_2 structures produce •OH through different mechanisms.[81, 82] Rutile TiO_2 reacts preferentially with adsorbed species because it only forms surface bound •OH, while anatase TiO_2 produces the free form.

An 80% anatase powder produced enough •OH to give a concentration of 3.2 nM near the surface, while a 100% rutile powder released very little of it. This observation suggests that •OH formation on rutile requires a peroxy intermediate, but it does not on anataste.

Fluorescence techniques have very low limits of detection, typically in the nanomolar range[83]. However, these measurements rely on external calibrations for quantification. As with spin trapping reagents in EPR, use of reactive fluorescent probes means that obtaining accurate chemical information relies on the selectivity of the probe. With the appropriate setup, fluorescence measurements can also achieve spatial resolution.[82] Super-resolution imaging by following a single molecule has been used to track available reactive[84] and adsorption[85] sites on TiO_2 nanoparticles. In these studies, the fluorescent probes were tailored derivatives of boron-dipyrromethane that became fluorescent either upon adsorbing or reacting. This demonstrates one interesting strategy for gleaning more information from fluorescence, and highlights how chemical synthesis may play a key role in improving analytical utility of fluorescent probes.

2.5 Transient Spectroscopies

Spectroscopic techniques can probe the dynamics of charge carriers in PEC materials with time resolution in the femtosecond regime across several spectral bandwidths. Trapped electrons and holes absorb light in the visible and near-IR ranges, while free electrons absorb light in the IR and microwave ranges. This makes them suitable for observation by means of transient absorption spectroscopy (TAS), transient diffuse reflection, and time-resolved microwave conductivity measurements. These techniques monitor the generation of charge carriers on the fs scale, but can be extended to μs or ms to measure their decay due to recombination and charge transfer across the interface. Some of the earliest TAS experiments investigated the bulk trapping of charge carriers on TiO_2 in the ps to ns regimes.[86] Later works focused on using transient spectroscopies to correlate the decay of charge carriers to reactivity with surface species and adsorbates,[87-90] carrier injection kinetics into co-catalysts,[88, 91] influence of bias on recombination kinetics,[92] and even assign chemical identity of trapped charge carriers.[93] Historically, transient spectroscopies contributed greatly to knowledge about the timescales relevant to PEC processes.

As of yet, transient spectroscopies have been limited to colloids and nanocrystalline films. Absorbance spectra of these carriers are typically broad and have spectral overlap, as shown in Fig. 2C, so delays after pulsed excitation are used to differentiate species. This differs considerably from operating photocatalysts, where carriers accumulate, changing their recombination kinetics[94] and their effective electrochemical potential at the semiconductor surface.[95]

As in the case of vibrational spectroscopies, recently NSOM has offered an alternative super-resolution platform capable of deploying ultrafast optical spectroscopy with nanoscale spatial resolution for tracking local charge carrier dynamics.[96, 97] For PEC interfaces, most of the work has focused on studying behaviour of charge carriers in nanostructures. Work by Emiliani, et. al. used near-field femtosecond spectroscopy to directly observe photogenerated carrier transport in 50 nm wide GaAs nanowires.[98] In this study, sections of wire up to 50 cm long were imaged with 200 nm resolution, and showed that although charge transport in the GaAs bulk was governed by holes, transport along the nanowires was primarily by electrons. These techniques present an opportunity to better understand carrier dynamics at heterogeneities in larger crystals.

3 Scanned Probe Microscopy

3.1 Scanning Tunnelling Microscopy

Scanning tunnelling microscopy (STM) measures tunnelling current at an applied bias between a conductive substrate and a small metal tip rastered above the substrate. It is sensitive to the local electronic structure, including perturbations generated by chemical species. Under UHV conditions, atomically-resolved images can be produced, and is often used for *ex situ* evaluation of PEC materials.[99] Much of this work has focused on where and how species adsorb to the surface. In one example shown in figure 3A, adsorption of water on the TiO_2 (110) surface was seen to occur at surface oxygen vacancies (site I in Fig 3A) when water vapor was introduced into the UHV environment.[100, 101] Water decomposition formed bridging hydroxyls (site II in Fig 3A) by dissociative adsorption. These experiments corrected misconceptions about ad-atom identities on these surfaces,[102] but *in situ* measurements are needed to form a dynamic picture of reactivity at the interface. Ultimately, STM becomes more difficult to perform when removed from UHV, but STM helps identify how structural heterogeneities can impact surface reactivity.

Atomic resolution can be achieved with *in situ* STM,[103] but STM on semiconductors can present other challenges. Controlling the tip-substrate bias conditions to a semiconductor is not an easy task. Surface defects can change nearby electronic structure, leading to difficulty understanding the meaning of images.[4] There has even been debate as to whether oxygen or metal atoms on TiO_2 are the darker sites in images, though this may be dependent on tip height. STM tips can remove surface oxygens as they scan, leaving vacancies in their wake. Despite this, *in situ* STM shows great utility because it can atomically resolve adsorbates, showing how they align on the surface.[104] If STM could be effectively applied at an operating photocatalyst to do the same, it could provide excellent information about how adsorbates interact with photocatalytic sites.

3.2 Atomic Force Microscopy

Atomic force microscopy (AFM) is another useful tool to relate structure and reactivity of PEC interfaces. Because AFM measures the force of interaction between the substrate and a tip, it primarily serves to image morphology of surfaces. Changes on the surface can be correlated to processes measured by other techniques. In one recent study on TiO_2, shown in Figure 3B, AFM was used to monitor roughening of single-crystal rutile TiO_2 during PEC water oxidation.[105] Roughening induced a drop in the onset potential of water oxidation in acidic solutions, attributed to more thermodynamically favorable formation of peroxo species that would otherwise be hindered by lattice strain.

AFM is primarily a supporting technique for studying catalytic mechanisms, but recent advances have broadened its applications. Tip enhanced Raman Spectroscopy discussed in Section 2.4 typically uses an AFM probe as the metal tip while simultaneously recording morphology information. In addition, AFM tips can be used to sense excitation of IR vibrational modes through the deflection of the tip.[106] A Fourier transform of the tip deflection gives sub-wavelength spectral resolution, and the precise tip positioning gives excellent spatial resolution for chemical mapping.[107] While this has only been demonstrated for biological or polymeric systems, it could be a future strategy for identifying intermediates generated at PEC interfaces. While STM and AFM provide the spatial resolution required for

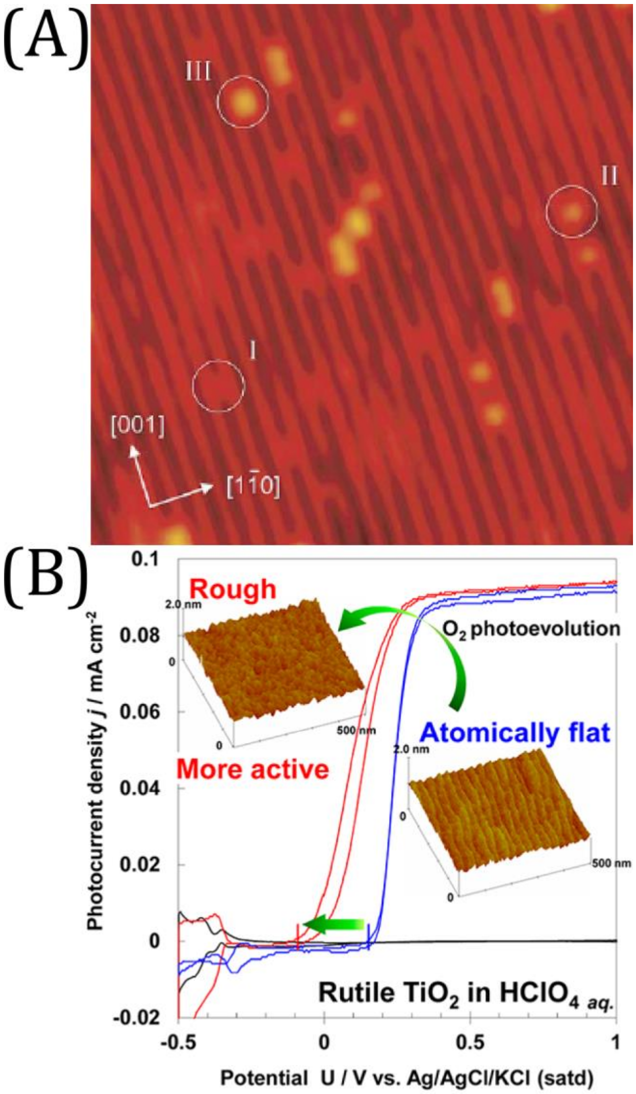

Figure 3A) STM image of TiO_2 (110) showing Type I, II, and III defects attributed to lattice oxygen vacancies, bridging hydroxyl groups, and paired hydroxyls, respectively. Reprinted from Surface Science, 598, S. Wendt,R. Schaub, J. Matthiesen, E.K. Vestergaard, E. Wahlström, M.D. Rasmussen, P. Thostrup, L.M. Molina, E. Lægsgaard, I. Stensgaard, B. Hammer, F. Besenbacher, Oxygen vacancies on TiO_2(110) and their interaction with H_2O and O_2: A combined high-resolution STM and DFT study, 226-245, Copyright 2005, with permission from Elsevier B) AFM images and corresponding photocurrent-potential curves demonstrating the enhancement of photocatalytic activity of rutile TiO_2 caused by roughening during catalytic operation. Reprinted with permission from E. Tsuji, K. Fukui and A. Imanishi, *Journal of Physical Chemistry C*, 2014, **118**, 5406-5413. Copyright 2014 American Chemical Society.

exploring the atomic aspects of surface photocatalysis, it seems that their implementation as stand-alone techniques for in situ analysis is challenging and it only offers limited information about reacting systems. However, as discussed in the previous sections, the coupling of AFM with other spectroscopic means of analysis such as TERS and NSOM promises to provide unprecedented detail in spatial resolution and chemical information for photogenerated surface intermediates, although the ultimate performance of these coupled techniques under dynamic conditions, i.e. during oxygen evolution, has yet to be tested.

4 Electrochemical Characterization

4.1 Transient Photocurrent

Electrochemical techniques by nature are interfacial and can be applied to the native PEC system. Although details are often obscured in voltammetry at semiconductor-electrolyte interface, bulk electrochemical techniques can still provide information through kinetic analysis of current transients. These techniques provided some of the earliest information about mechanisms occurring at PEC interfaces. In one study shown in Figure 4A, Salvador studied the ratio of the steady state photocurrent to the anodic transient rising photocurrent ($I_{ph} = i_{st}/i_{in}$) to better characterize the formation of surface-bound H_2O_2 and •OH during basic photoelectrolysis on single crystal n-TiO_2.[108] This study used a kinetic analysis that took into account the many involved reactions at the surface which described the transient behaviour of I_{ph}. The resulting equations were then used to extract the potential-dependent surface coverage of both •OH and H_2O_2 as well as the rate constants for the included reactions. Limiting coverages for •OH and H_2O_2 were calculated to be 10^{13} and 10^{14} cm^{-2}, respectively. Kinetic analysis of transient photocurrent provided an approach to quantifying the surface coverage and reactivity of intermediate species, but the method of detection was overall indirect. It also seemed too cumbersome to be used to identify unknown intermediates and it cannot exclude the presence of side reactions. However, the importance of a technique that can quantify surface coverage in such a complex environment should not be discounted for well-established experimental systems such as TiO_2.

4.2 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) techniques model electrochemical cells as circuit elements composed of resistors and capacitors and measure these using an alternating current at different frequencies. Typically, interfacial charge transfer events act as resistors, while formation of the electrical double layer is the primary source of capacitance. By modelling how formation of surface intermediates influence both of these properties, surface species can be quantified and their effect on interfacial reactivity can be understood.[109] This technique is widely used to study corrosion processes and identify the contributions of branching reaction mechanisms.[110, 111] As with measurement of transient photocurrents, the need to develop a detailed kinetic model of the system hinders application of EIS in systems where some paths are unknown.

EIS is commonly employed to study the impact of charge carrier transport and distribution properties on PEC performance.[112] EIS is often used to take Mott- Schottky measurements to determine dopant type and density by analysing the potential dependence of the interfacial capacitance.[113] While it is less commonly employed to identify intermediates, many works have developed its use for this purpose. EIS can demonstrate when reactions proceed through one simple step versus multi-step mechanisms.[114] When coupled to a thorough kinetic analysis, it can even be used to determine coverages of multiple intermediates from parallel reactions.[115] The capability to sense changes from so many sources complicates use of EIS, as all of these contribtions must be modelled as separate elements. Without supporting techniques or a solid theoretical foundation, EIS will not provide conclusive evidence for intermediate identification, especially in complex systems. However, its coupling to electrochemical microscopy (section 5)

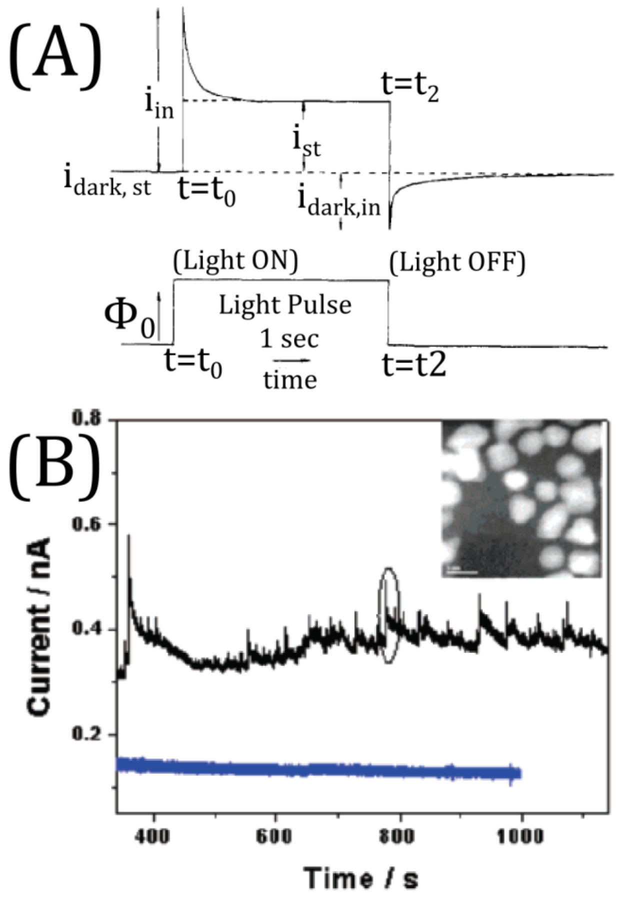

*Figure 4A) Transient photoresponse of a n-TiO_2 single crystal in aqueous 1 M Na_2SO_4 (pH 11) to a square wave light pulse of band-gap light. Reprinted with permission from P. Salvador, Journal of Physical Chemistry, 1985, **89**, 3863-3869. Copyright 1985 American Chemical Society. B) Current transients from single nanoparticle collisions include charging current, and an increase in the steady state current when particles stick to the UME after colliding (black), which does not occur in the absence of nanoparticles (blue). The inset transmission electron micrograph shows that the nanoparticles range from 2 to 6 nm in diameter. Reprinted with permission from X. Y. Xiao and A. J. Bard, Journal of the American Chemical Society, 2007, **129**, 9610-9612. Copyright 2007 American Chemical Society.*

may yield localized information about surface adsorbates in situ.[116]

4.3 Single Nanoparticle amperometry

The use of single nanoparticle collisions at an ultramicroelectrode (UME) to study electrocatalytic reactions was first introduced in 2008 by the Bard group and applied first to proton and H_2O_2 reduction on platinum nanoparticles.[117] In these experiments, a catalytically inactive electrode in a colloidal suspension is biased to a potential able to activate the nanoparticles. As nanoparticles collide with the electrode, they create current spikes Faradaic catalytic enhancement, as well as double layer charging (Fig 4B).[118] This technique has been used to study nanoscale kinetic enhancements,[119] active site blocking by nonreactive adsorbates,[120] and kinetic effects of active surface species.[121]

The use of nanoparticle collisions recently extended to PEC systems with experiments by Fernando et al. demonstrating transient currents of PEC methanol oxidation on anatase TiO_2.[122] Although this study focused on proof-of-concept, future works can use nanoparticle collisions to better characterize PEC mechanisms. With a technique sensitive to individual nanoparticles, it can provide excellent information about how particle morphology influences surface species. Although it is only usable to characterize colloid suspensions, it helps us understand how nanoparticles adsorbed to a surface act individually, rather than as an ensemble. The main limitations on temporal resolution come from charging current of the nanoparticle, but this is primarily dependent on particle size and is an unavoidable physical limitation.[117] No other technique thus far directly probes reactivity of single nanoparticles, so similarcollision experiments could produce very interesting information in the near future.

5 Scanning Electrochemical Microscopy

5.1 Steady-State Feedback and Transient Collection

Scanning electrochemical microscopy (SECM) techniques are ideal for studying heterogeneous catalysis because they combine the spatial resolution of scanned probe microscopy with the *in situ* operation of electrochemical techniques. As shown in Fig. 5A, these techniques detect interfacial reactivity using probe molecules generated by an UME positioned near a substrate. Steady-state positive feedback measurements are used to characterize localized electron transfer rates at semiconductor surfaces, [123] and even PEC processes,[124, 125] but differentiating contributions from multiple reactive species is challenging.

Chemically selective electrodes allow indirect evidence to be gathered to build reaction mechanisms. TiO_2 in oxygenated aqueous solutions can produce H_2O_2 either through reduction of oxygen or oxidation of water. Using a horseradish peroxidase modified UME, Sakai, et al. collected H_2O_2 above a photoelectrocatalytic surface with discrete oxidative and reductive domains.[126] The reductive domain showed far less efficient formation of H_2O_2, providing evidence for the breakdown of H_2O_2 to •OH by photogenerated holes on the oxidative surface. More recent collection experiments have replaced the traditional SECM tip with a fiber optic surrounded by a ring electrode.[127] This allows localized delivery of light, so the origin of any collected products is known. Decoupling bulk properties from local properties should be useful for studying how surface features impact PEC mechanisms, but this has only been infrequently employed. While such experiments do not directly measure the presence of surface species, they can quantify product generation and help describe mechanisms.

Combinations of feedback and collection modes can be employed together. They provide spatial resolution only limited by the tip size and can resolve extremely fast kinetics.[128, 129] However, they have been useful only in some cases, such as measuring surface diffusion rates of species adsorbed to graphene.[130] Increasing the spatial resolution of SECM to the nm level is an active area of research, and will permit to implement both feedback and collection schemes to evaluate the reactivity of individual surface features. [128,131] Still, in systems as complex as PEC interfaces, techniques specifically sensitive to adsorbed species are needed.

5.2 Surface Interrogation SECM

Recently, surface interrogation (SI-) SECM was introduced to quantify the absolute surface coverage of reactive surface species, thus providing a powerful addition to the identification

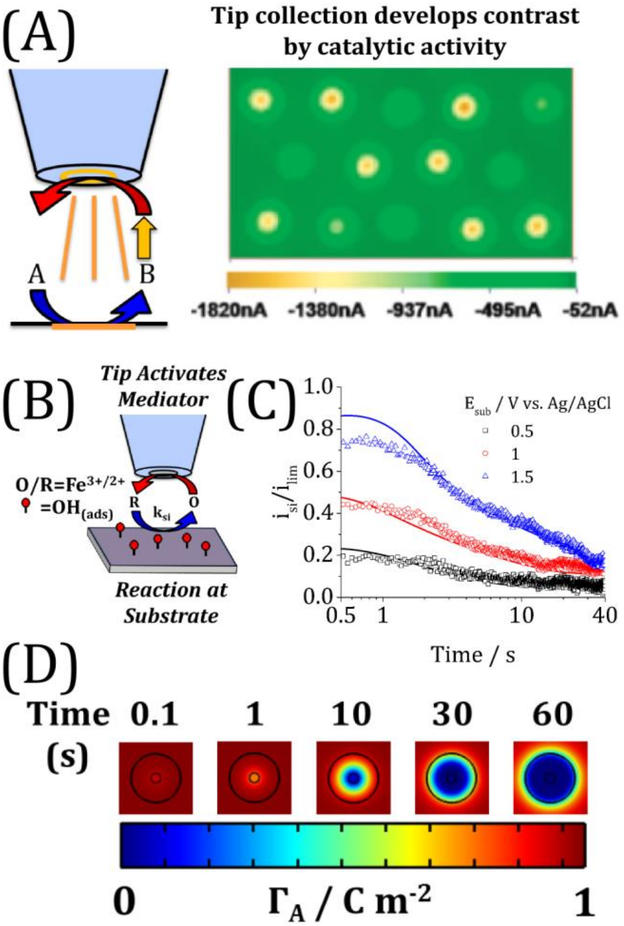

Figure 5A) Replacing a traditional SECM tip with an optical fiber supporting a ring electrode, localized PEC activity can be measured. Using this setup, PEC performance of $BiVO_4$ catalysts with different levels of W dopants was evaluated. Reprinted with permission from J. W. Lee, H. C. Ye, S. L. Pan and A. J. Bard, Analytical Chemistry, 2008, ***80****, 7445-7450. Copyright 2008 American Chemical Society. B) Schematic showing in situ reactive titration of surface species by a probe species generated at the UME. C) SI-SECM transients on doped $SrTiO_3$ photoanodes detect an increase in the presence of oxidizing surface species as the substrate bias potential is increased during illumination. D) Simulation demonstrating the expansion of the titrated surface area during SI-SECM. By constraining the length of surface interrogations, SI-SECM can be used as a platform for imaging heterogeneous surfaces. Adapted from B. H. Simpson and J. Rodriguez-Lopez, Electrochimica Acta, 2015,* ***In press****, DOI:10.16/j.electacta.2015.04.128*

capabilities that the methods discussed so far can provide. As shown in Fig. 5B, this technique titrates in situ adsorbate species left after a catalytic step using a species generated electrochemically, and it can be applied under open circuit conditions and on free-standing samples. It was first demonstrated as a tool to quantify metal oxides formed on noble metal substrates during anodic operation in aqueous systems.[132] SI-SECM detected the presence of “incipient oxides” on Au and Pt that are not accounted for in the oxide reduction peak recorded during voltammetry. Later SI-SECM experiments with this same system measured the bimolecular rate constant for the reaction of several titrants with Pt oxides, facilitated by the use of simulations using the finite element method.[133] When connected to steady-state feedback measurements, this study showed evidence that the oxides only mediated electron transfer to $[Fe(II)EDTA]^{2-}$, but not methyl viologen or ferricyanide, suggesting different mechanisms for these electron transfers. It has since been applied to study adsorbate formation during several electrocatalytic processes.[134-136] Because SI-SECM probes reaction kinetics, it might be used in the near future to answer fundamental questions about the chemical reactivity of adsorbates formed under different illumination conditions, or through co-catalytic or plasmonic schemes.

SI-SECM quantifies intermediates formed during PEC reactions equally well. Using the $IrCl_6^{3-/4-}$ probe, Zigah, et al. studied the formation of •OH on nanostructured TiO_2 during open circuit water oxidation and measured both its limiting surface coverage and dimerization rate to H_2O_2.[137] A similar study on $BiVO_4$ photoanode extended this technique to measure the conversion efficiency of photons to •OH as 6%.[138]While it is a relatively new technique, SI-SECM has much promise for studying photoelectrocatalysts. SI-SECM on metal electrodes displays the limitation of having to use a tip of a similar size as the substrate under study due to the difficulty in decoupling the role of the background electrode over that of the intermediate species. Our group has recently overcome that limitation on lightly n-doped $SrTiO_3$ samples and reported on the detection of adsorbed ROS on an extended surface, as shown in the transient in Figure 5C. In this case, by careful choice of the titration parameters, e.g. redox mediator concentration and the titration time, it is possible to estimate the surface density of adsorbed ROS on $SrTiO_3$ to be 2.5×10^{13} and 3.1×10^{14} m^{-2} with applied biases of 0.5 and 1.5 V, respectively. This surface coverage is in good agreement with results obtained through photocurrent transients (section 4.1) by Salvador [108]but the application of SI-SECM is attractive because it addresses *local* surface coverage.

Already, SI-SECM has been used to detect surface species not seen through direct voltammetry, directly quantify intermediate coverage, and measure kinetics of adsorbate reactions across several orders of magnitude. Clearly, it addresses the need for a direct probe of adsorbate reactivity, but it was not until recently that our group developed SI-SECM into a technique with the prospect of evaluating adsorbate coverage with spatial resolution on a photo-activated surface. This capability could be used to titrate species formed in situ on different surface features, such as defects, metal deposits and portions of native crystals. Recent work in our lab has focused on understanding the transient behaviour of SI-SECM in preparation for imaging experiments. Using numerical simulations, we studied the titration area where reactive adsorbates are depleted.[139] The growth of this region is governed by the ratio of generated titrant to available analyte. The advancing titiration below a 1 μm tip is shown in Fig. 5D, which clearly shows that spatial resolution of SI-SECM can be controlled by limiting titration times. In combination with numerical simulations that predict transient response, this demonstrates that SI-SECM is poised to become a powerful technique for quantitatively imaging reactive adsorbates on PEC surfaces. Further combination with spectroscopic methods such as Raman, IR or chemiluminescence pursued in our laboratory might offer an unprecedented view of total adsorbate identification and quantification for advancing our knowledge on PEC surface reactivity.

6 Conclusions

Surface species mediate reactivity at many solid-liquid interfaces, especially as intermediates that facilitate inner-sphere electron transfer reactions.[140] While in situ identification and quantification of these species at PEC interfaces presents some unique challenges due to the broad distribution of process that lead to their formation, techniques are rapidly being adapted from other fields to help identify photogenerated intermediates. For several techniques, in addition to the constraints posed by analysis of an interface immersed in electrolyte, one immediate goal is developing the ability to address nanoscale domains. Developments of super-resolution methods are allowing spectroscopies to approach these levels, which should provide important details about reaction dynamics at individual sites. Although many scanning probe techniques could already access these length scales, adding new detection modalities is allowing more direct information to be extracted with these methods. Tailor-made for quantification of surface intermediates, SI-SECM is a new modality that will soon provide imaging capabilities that decouple electrode and adsorbate reactivity.

Techniques that measure the presence of surface intermediates can provide direct mechanistic information about PEC reactions. Often, multiple species are present on these surfaces, generated as intermediates within distinct reaction paths. [3, 4, 41] The similarity in the reactivity of the photogenerated products limits several techniques because they lack sufficiently selective probes. Synthetic methods may play a key role in strategies to improve the capabilities of all of the techniques like EPR and fluorescence microscopy which require chemical probes. Chemical mapping of biological systems often employs similar methods, and borrowing knowledge from others will allow old tools to break new ground. Incipient methods in spectroscopic X-ray analysis will likely shed some light in the near future about the nature of the species formed on metallic deposits used as co-catalysts.

Surface species play key roles in many societally important chemistries, and knowledge can be transferred from other fields of electrochemistry onto PEC and vice-versa. For instance, the formation[141-143] and breakdown[41, 144-146] of passive layers on metals often require surface intermediates. Corrosion often occurs through multiple mechanisms simultaneously that each rely on distinct surface intermediates, and its prevention is a topic of extensive research. [111, 147] New discoveries developed to identify photogenerated surface species may find application in these related fields. Although options for future research are already clear, the diverse nature of PEC systems means that a wide array of techniques will always be needed so that methods can be tailored to specific systems. The near future promises to be an exciting time, as interest in new plasmonic interactions and the use of solar energy conversion schemes will likely present yet unexplored chemistries. Emerging in-situ analytical techniques will play a decisive role in understanding their reaction mechanisms.

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