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Important Considerations in Plasmon-Enhanced Electrochemical Conversion at Voltage-Biased Electrodes

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Introduction

Plasmon-enhanced electrochemical conversion (PEEC) is performed by illuminating the surface of a plasmonic electrode while applying a potential to reduce or oxidize a reactant. This underexplored field presents new opportunities for sustainable production of fuels and value-added chemicals. PEEC is related to the established field of photoelectrochemistry (PEC) where solar light is converted to electron-hole pairs at a biased or unbiased semiconductor photoelectrode to drive an electrochemical reaction, typically water splitting. In this perspective we compare PEEC to PEC and discuss how standards developed in the field of PEC regarding temperature control, light flux measurement, and electrode stability characterization relate to the study of PEEC.

The origins of PEC and PEEC can be traced to the discovery of the photoelectric effect by Becquerel (1839), with pioneering advancements made on illuminated metal electrodes by Gerischer and Delahay (1961). The first reported PEC reaction was water splitting at an illuminated TiO_2 anode (Boddy, 1968; Fujishima and Honda, 1972). PEC water splitting has been extensively explored and reviewed (Gratzel, 2001; Bak et al.; Kudo and Miseki, 2009) and, to a lesser extent, other PEC reactions like carbon dioxide (CO_2) reduction (Ganesh, 2011; Kumar et al., 2012; Zhao et al., 2014) and oxidation of organics (Lianos, 2011; Georgieva et al., 2012). The first report of PEEC was the extraction of plasmonically excited hot electrons and holes at a silver electrode (Sass et al., 1974). Despite the comparable age, PEEC has been the subject of many fewer studies than PEC. Reported PEEC reactions include CO_2 reduction (Kostecki and Augustynski, 1994; Creel et al., 2019), oxygen (O_2) reduction (Zheng et al., 2017; Shi et al., 2019), and hydrogen (H_2) evolution (Zhang et al., 2018; Guo et al., 2018; Wilson et al., 2019).

The goal in PEC is to completely drive the reaction with sunlight, although an external potential bias is often needed to overcome the reaction activation barrier. In most

semiconductor-driven PEC, there is little to no electrochemical activity observed under dark conditions. In contrast, the aim in PEEC is to couple illumination with an applied voltage to influence the catalyst selectivity and activity. In other words, in PEEC there will be electrochemical activity without illumination, and it is important to compare light and dark performance to discern the impact of the light. In PEEC the total photocurrent can be distinguished from overall activity (often by chopped light experiments), but it can be difficult to precisely quantify how individual product formation changes upon illumination if products are formed in the dark and the light. The dark current may be quite high compared to the photocurrent which can make it challenging to detect subtle changes in product selectivity that are driven by the light. This need in PEEC to precisely compare dark and light performance motivates the essential use of temperature control.

Temperature Control

In PEC, temperature control is recommended (Chen et al., 2013) to ensure that experiments performed at room temperature are comparable between labs. PEC cells must be designed to withstand heating from a 100 mW cm^{-2} solar simulator, but PEEC cells are often exposed to higher intensity light sources to maximize photocurrent. Continuous illumination of a PEEC cell can lead to dramatic heating of the electrolyte, as shown in Figure 1A. The uncontrolled temperature of the electrolyte in this cell (Corson et al., 2018), which was designed to have a low electrolyte volume to allow sensitive liquid product analysis specifically for CO_2 reduction, rose by 12 K in 20 minutes—and would have continued to rise had the experiment not been terminated—under constant illumination by a 170 mW cm^{-2} 365 nm light-emitting diode (LED). This temperature rise demonstrates that PEEC cells are susceptible to heating whether the light source is a broadband incandescent bulb or a monochromatic beam. This heating can be caused by light absorption of the cell components, electrolyte, and plasmonic electrode. Light absorption of water, which can vary with ion concentration, is low at ultraviolet (UV) and visible wavelengths and highest at infrared (IR) wavelengths, and increases

with increasing water path length (Xiang et al., 2019; Döscher et al., 2014). Commonly used electrolyte salts such as potassium bicarbonate (KHCO_3) and sulfuric acid (H_2SO_4) absorb strongly in the near-UV, as shown in Figure 2B.

Increasing the electrolyte temperature typically causes the solubility of gases to decrease exponentially, as described by the van't Hoff equation. This can greatly decrease the reactant concentration for PEEC systems where the reactant is a gas, as in CO_2 reduction or nitrogen (N_2) reduction. At the same time, the Arrhenius equation predicts that reaction rate constants depend exponentially on temperature. As current is directly related to the reaction rate, we expect the current to increase with increasing temperature at a plasmonic electrode. However, as each elementary reaction has a different temperature dependence, increasing the temperature may change the product distribution. In PEC the reaction kinetics will be similarly influenced, but this effect may be counteracted by a decrease in the photovoltage because the semiconductor bandgap decreases with increasing temperature (Haussener et al., 2013). In contrast, the rate of hot carrier generation is expected to increase with temperature in metal PEEC systems due to the increase in phonon-assisted electronic transitions (Brown et al., 2016).

How the current is affected by changes in temperature can be seen in Figure 1B where linear sweep voltammetry is performed at a plasmonic silver cathode where CO_2 reduction and H_2 evolution are occurring. The magnitude of the current density increases at each potential as the electrolyte temperature is increased from 14°C to 24°C . At -1.0 V versus the reversible hydrogen electrode (V_{RHE}) there is a 30% difference between the highest and lowest current densities across this modest 10 K temperature range, a range we have shown can easily be exceeded in an illuminated PEEC cell when the temperature is not controlled (Figure 1A).

If there are multiple reactions, changing the electrolyte temperature can significantly alter the product distribution as the individual reaction rates change according to their respective activation energies and pre-exponential factors (Corson et al., 2018). As shown in Figure 1B,

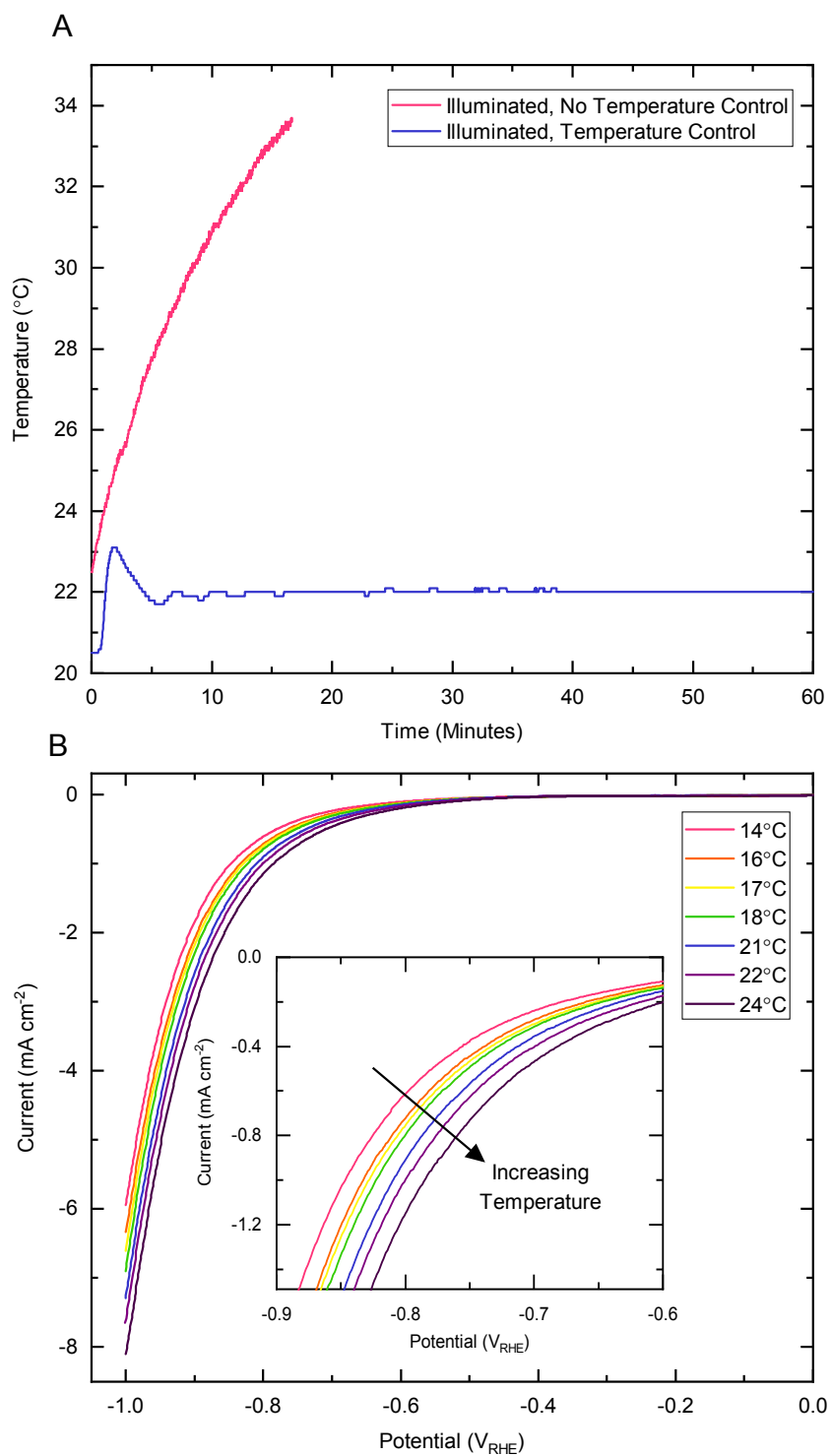


Figure 1: (A) Electrolyte temperature in a low-volume PEEC cell (Corson et al., 2018) over time with and without temperature control when illuminated with a 365 nm 2.5 W LED. (B) Linear sweep voltammetry at 100 mV s^{-1} at a plasmonic silver cathode in CO_2 -saturated 0.5 M potassium carbonate (K_2CO_3) electrolyte at various electrolyte temperatures. CO_2 flows continuously through the cell at 5 sccm. Inset is the same data in a smaller potential range to demonstrate activity increase with increasing temperature.

the current can change when the temperature is varied by just 1 or 2 K. It is thus imperative in PEEC to use a temperature-controlled cell with precision of at least 1 K, especially when comparing illuminated and unilluminated activity and product distributions.

Effective cell temperature control requires incorporation of a temperature probe in contact with the electrolyte, ideally as close to the working electrode as possible, a cooling method, and a proportional-integral-derivative (PID) controller. The selection and sizing of the cooling method depends on the cell geometry and the maximum light intensity desired, as this will define the maximum heat removal needs of the system. One cooling method is a solid-state Peltier element with a heatsink and fan (Corson et al., 2018). While complete cell submersion in a water bath would make light incorporation difficult, a circulating bath connected to a cooling jacket or integrated heat-transfer channels within the cell can be designed to allow electrode illumination (Zavarine and Kubiak, 2001).

Light Flux at the Electrode

An important figure of merit in PEC water splitting is the solar-to-hydrogen (STH) efficiency. While STH is not relevant for PEEC studies that use a non-solar light source or investigate reactions other than H₂ evolution, there are efficiency standards from the field of PEC that can be used in PEEC. The most applicable are the two ways to measure the quantum efficiency of light utilization for a given electrode: external quantum efficiency (EQE) and internal quantum efficiency (IQE) (Chen et al., 2010).

$$\text{EQE} = \frac{\text{photogenerated electrons/s}}{\text{incident photons/s}} \tag{1a}$$

$$\text{IQE} = \frac{\text{photogenerated electrons/s}}{\text{absorbed photons/s}} \tag{1b}$$

EQE is the ratio of photogenerated electrons to *incident* photons. In PEC, typical EQE values are greater than 10% and can approach 100% for wavelengths above the bandgap (Shi et al., 2015). In contrast, PEEC systems without semiconductor or molecular co-absorbers

typically have EQE values below 1% at the plasmon resonance wavelength (Robatjazi et al., 2015; Kim et al., 2018). For example, if we compare PEC to PEEC for CO₂ reduction at -0.9 V_{RHE} in neutral electrolyte under 360 nm illumination, a ZnTe photocathode has an EQE of 80% (Jang et al., 2014) while a plasmonic silver cathode has an EQE of 0.45% (Kim et al., 2018).

IQE is the ratio of photogenerated electrons to *absorbed* photons. IQE is generally higher than EQE for both PEC and PEEC materials due to the exclusion of losses from photons that are transmitted or reflected. However, the difference in order of magnitude between PEC and PEEC electrodes found in EQE still exists for IQE. From the previous CO₂ reduction example, the semiconductor IQE is 100% (Jang et al., 2014) while the plasmonic metal IQE is 1.2% (Kim et al., 2018).

One key difference between PEC and PEEC is carrier lifetime. Photoexcited electrons and holes in semiconductors can have lifetimes on the order of nanoseconds (Abdi et al., 2013) while excited carriers in plasmonic metals exist for less than a picosecond (Boerigter et al., 2016) due to the high density of electronic states in metals and other conductive media. Due to their brief existence, plasmonically-generated excited carriers must be co-located with the charge-accepting species. In contrast, photoexcited carriers in semiconducting materials have time to diffuse to the solid-liquid interface and can have diffusion lengths on the order of tens of nanometers (Abdi et al., 2013). These differences in carrier lifetime and diffusion length help explain why the EQE and IQE of plasmonic metals used in PEEC is much lower than that of semiconducting materials used in PEC.

Just as in PEC, reporting the EQE and IQE in PEEC will deconvolute a material's ability to separate and collect photoexcited electrons and holes from its optical absorption. This provides insight for further optimization of the material's optical absorption or extraction of charge carriers.

Measuring the incident light intensity is necessary for calculating EQE and IQE. It is important to measure the light *at the electrode surface*, especially in studies that focus on catalyst performance and mechanism rather than overall device efficiency. Glass, quartz, water, common electrolytes, and gas bubbles can all have significant reflection or absorption, making the light intensity incident on the plasmonic electrode significantly less than the light intensity incident on the PEEC cell (Figure 2). For example, Figure 2 shows that the transmission of light through glass is reduced by 50% at a wavelength of 350 nm and is completely blocked for wavelengths below 300 nm. This means that if the light intensity were measured before the light passed through the glass the reported EQE and IQE values for the photoelectrode would be half of the actual value at 350 nm.

Researchers should also bear in mind that the optical properties of all materials are temperature-dependent (Xiang et al., 2019). While full device research incorporates short path lengths through electrolyte and anti-reflective coatings on cell windows (Xiang et al., 2019), most laboratory-scale PEEC cells are not designed with maximum light transmission to the plasmonic electrode in mind. Thus, the light attenuation may be significant. Low light intensity may impact the signal to noise ratio between the photocurrent and background “dark” current as plasmonic photoactivity increases with light intensity. Additionally, it may be difficult to control the temperature of electrochemical cells that are not designed for high light transmission due to the high light intensity needed to achieve a measurable photocurrent.

The light attenuation through the electrochemical cell walls and electrolyte becomes especially important with broad-spectrum illumination because the light transmission of cell components is wavelength dependent and often has especially low transmission in the UV or IR regions of the spectrum (Figure 2B). While glass is often replaced with quartz for UV transmission, the effect of the absorption of water (Döscher et al., 2014) or the electrolyte salt is not commonly accounted for.

Light power incident on the cell can be measured with a power meter, thermopile, or pho-

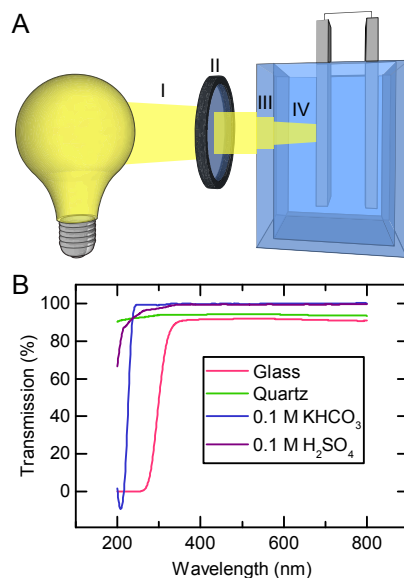


Figure 2: Light intensity attenuation from the light source to the plasmonic electrode surface. (A) Light intensity per unit area decreases (I) as a function of distance from a non-collimated source, (II) when passing through optical lenses or filters, (III) when passing through electrochemical cell walls, and (IV) when passing through electrolyte. (B) Transmission spectra of a 1 mm thick glass slide, 2 mm thick quartz window, 1 cm path length through 0.1 M KHCO₃, and 1 cm path length of 0.1 M H₂SO₄. Transmission spectra of glass and quartz are measured relative to air. Transmission spectra of salt solutions are measured in a quartz cuvette relative to a quartz cuvette filled with ultrapure water.

todiode then corrected to find the light power incident on the plasmonic electrode using the transmission of the cell components. For broad-spectrum illumination, it is important to measure the light spectrum rather than just the light intensity because of the wavelength dependence of the photoactivity (Tian and Tatsuma, 2004) and the wavelength dependence of the optical properties of the cell components. The method for correcting spectral mismatch between a lamp and solar irradiance (Döscher et al., 2014) is also suitable for correcting for decreased transmission of cell components.

Standards for calibrating light sources to closely match the AM 1.5 G spectrum have been well-defined within the field of PEC (van de Krol and Grätzel, 2012; Chen et al., 2013; Döscher et al., 2016; May et al., 2017). While these standards can be directly applied to PEEC systems for broad-spectrum illumination studies, they are not relevant for single-wavelength light experiments that are commonly used in the field of PEEC. High-intensity single-wavelength illumination at the plasmon resonance wavelength can help increase the

photocurrent for PEEC systems, improving the signal-to-noise ratio and enhancing the difference in product distribution between light and dark conditions. Varying the light intensity at a single wavelength is also prevalent in PEEC studies. A linear relationship between photocurrent and light intensity demonstrates that the mechanism is photonic, as a thermal process would result in an exponential relationship (Kale et al., 2014). Probing behavior at different wavelengths can lead to a fundamental understanding of the mechanism of plasmon-enhanced charge transfer (Boerigter et al., 2016). To accurately compare different PEEC electrodes it is important that researchers measure and report the light spectrum and intensity at the electrode surface for any illuminated experiments.

Additionally, researchers should confirm that the cell components intended to define the illumination and active area of a plasmonic cathode (e.g., epoxy or o-rings) are opaque for all of the light spectrum (not just the visible) that will be used for illumination. A UV-transmissive epoxy or o-ring could result in the photoactive area of an electrode being much larger than the electrochemically active area (Döscher et al., 2014). For example, in a cell with an electrochemically active area of 1.0 cm^2 and an o-ring outer diameter (OD) of 1.4 cm , a UV-transmissive o-ring would result in an actual illumination area of 1.6 cm^2 , an increase of 60%.

Surface Changes Under Reaction Conditions

The activity and performance of all photoelectrocatalysts depends on the specific surface morphologies and structural features (e.g., high index planes, step edges). Both PEC and PEEC photoelectrode behavior can be extremely sensitive to nanoscale morphology. In PEC, nanofeatures can influence charge separation and transport, scattering rate, and the size of the band gap (Shen et al., 2018). For PEEC, the size, shape, and proximity of nanostructures can change the peak plasmon resonance wavelength, energy distribution and number of hot carriers, and intensity of the local electric field (Linic et al., 2011; Manjavacas et al., 2014). Active catalysts can delaminate from the electrode surface or undergo dramatic

morphological, composition, phase, and activity changes under reaction conditions (Hodnik et al., 2016; Tao and Salmeron, 2011) or when exposed to voltage (Creel et al., 2019). All of these changes can impact not only the catalytic performance but also the optical properties of the photoelectrode. Thus, it is critical to characterize microscopic catalyst evolution and any differences in optical properties in order to understand and control or prevent morphological changes induced by reaction conditions.

Researchers often use the stability of the current over time in long-term constant voltage experiments as a measure of electrode stability, but this method gives no insight into the mechanism for activity degradation. It is well known that successive oxidation and reduction cycles can degrade catalysts, but constant-voltage experiments also induce catalyst dissolution, corrosion, and restructuring. Our recent study of a silver thin film cathode showed decreased electrochemical surface area (ECSA), increased broad-spectrum absorption, and a broader grain size distribution after performing CO₂ electrolysis without illumination (Figure 3). We found that the changes in optical properties and electrochemical surface area changed quickly in the first few minutes of applied potential but reached a steady state between 30 and 60 minutes of electrolysis. In this case, we were able to “electrochemically condition” the plasmonic silver cathode for 45 minutes to achieve stable performance over hours. After 45 minutes the absorption at the plasmon resonance was 37% higher and the relative surface area was 50% lower than the as-prepared electrode (Creel et al., 2019).

Measuring the changes in morphology during any electrochemical reaction is critical when attempting to understand the structure-function relationships of an electrode. It is especially important for PEEC researchers to check for reaction-induced morphology changes because the optical properties of the plasmonic electrode may change significantly (Figure 3). Changes to the absorption of the electrode will alter the IQE as well as the photoactivity. Just as in PEC, PEEC researchers should, at a minimum, compare the morphology and optical changes before and after PEEC using scanning electron microscopy (SEM), transmission

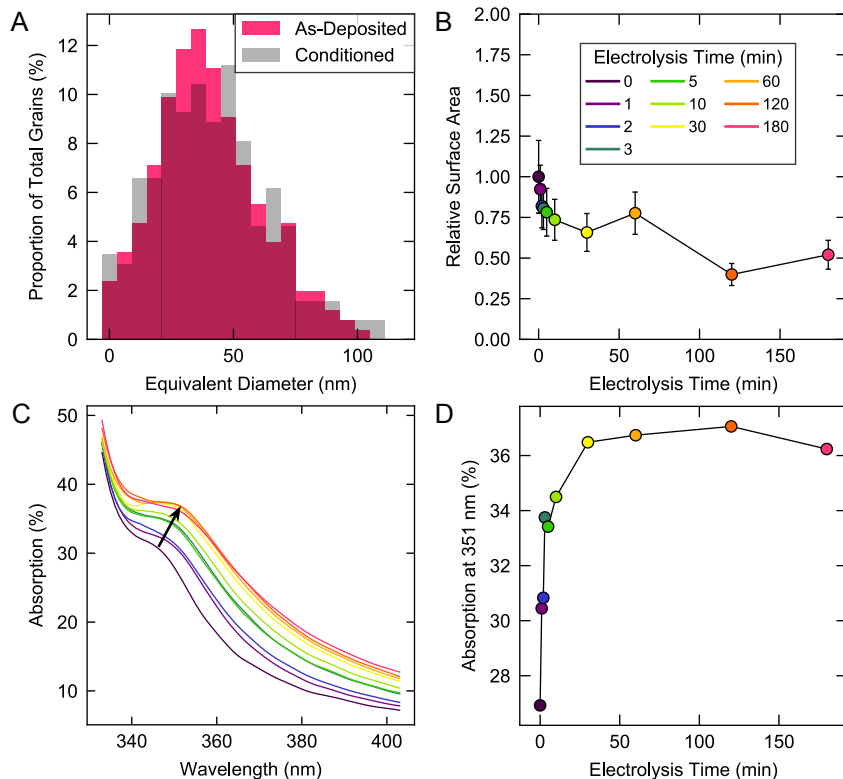


Figure 3: Changes in morphology and optical properties of a silver thin film cathode after CO₂ electrolysis without illumination in 0.5 M K₂CO₃ at -1.1 V_{RHE}. The electrode was made by electron-beam (e-beam) depositing 200 nm of silver over a glass slide with 5 nm of titanium used as an adhesion layer. (A) Comparison of the silver grain size distribution on the cathode in terms of equivalent diameter—the diameter of a circle with the same projected area as the projected area of the grain—as measured by AFM. “As-Deposited” indicates a silver film that has not been used as an electrode, and “Conditioned” indicates that the silver thin film has undergone 45 minutes of CO₂ electrolysis. (B) Evolution of the ECSA of the cathode relative to the as-deposited silver film after various CO₂ electrolysis times. Legend for parts B-D where electrolysis time is the time that the silver electrode was used as a CO₂ electrolysis cathode. (C) Evolution of the UV-visible absorption spectra of the cathode after various CO₂ electrolysis times. (D) Evolution of the absorption of the electrode at 351 nm after various CO₂ electrolysis times. Absorption is calculated as 100% - %R where %R is the total reflection measured by an integrating sphere. Figures adapted from Creel et al. (2019).

electron microscopy (TEM), atomic force microscopy (AFM), UV-visible spectroscopy, or other readily available techniques (Chen et al., 2013).

Conclusion

We have shown that standards developed in the established field of PEC can be used to build best practices for PEEC. Cell temperature control is still critical for PEEC, especially when comparing light and dark performance. While not all efficiency measures from PEC are relevant to PEEC, EQE and IQE are valid and useful for characterizing plasmonic electrodes. However, it is important to recognize that fundamental differences between semiconductors and plasmonic metals result in EQE and IQE values for PEEC systems that are often two orders of magnitude lower than PEC systems. Surface morphology can affect the catalytic and optical properties of semiconductors and plasmonic metals. Changes to the surface induced by reaction conditions should be monitored and controlled for repeatable results. By learning from the 50-year history of PEC water splitting we can ensure that PEEC research is comparable and reproducible.

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Declaration of Interests

The authors declare no competing interests.

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