

Solar fuels, such as green hydrogen, store the sun's energy in chemical bonds. These solar fuels can be stored and transported, two key challenges in the global transition to **zero-carbon energy**. Photoelectrochemical (PEC) water splitting utilises semiconductors to harness solar energy and generate charged species, which directly participate in the water splitting half reactions to produce hydrogen. The semiconductor materials used must be **efficient**, **stable** and **cost-competitive** with traditional fossil fuel-based methods of hydrogen production. In the Durrant Group, pump-probe spectroscopic techniques are used to study materials and investigate their **charge carrier dynamics and kinetics**. **BiVO₄**, a promising semiconductor for this process, faces **stability challenges** during these pump-probe measurements.

1. Water splitting

Water can be split into hydrogen and oxygen *via* two half reactions.

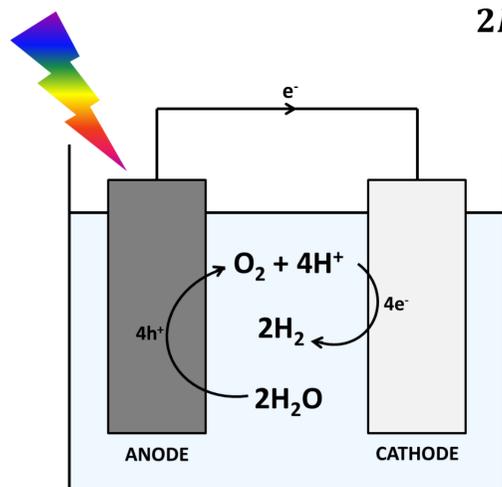
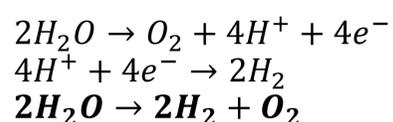


Fig. 1. Overview of a PEC cell.

In PEC water splitting, incident light with energy greater than that of the semiconductor's bandgap can **excite charge carriers**.

Water oxidation at the photoanode is the more kinetically challenging reaction, as four holes are required per molecular oxygen formed (compared to two electrons per molecular hydrogen).

BiVO₄ is a popular material for use as the photoanode. Its bandgap is narrow enough to utilise **photons in the visible** portion of the solar spectrum, it is **non-toxic** and it has been used in some of the **highest performing devices** in the literature.¹



Fig. 2. BiVO₄ film synthesised *via* modified metal-organic deposition and spin-coated on to FTO-substrate glass.

3. Stability issues for BiVO₄

BiVO₄ films show significant **performance degradation** with successive PIA measurements.

This is a particular challenge when trying to measure rate law. The optical signal (hole population) at a given light intensity and applied potential is the same at the start and end of a day of measurements. However, the photocurrent (electron population) is significantly reduced. This results in **high error** in rate law measurements.

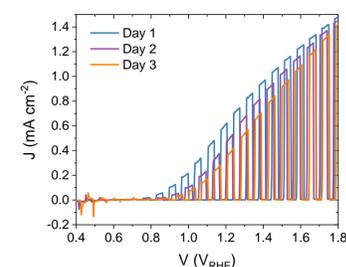


Fig. 4. Current-voltage response under chopped light (~1 sun) of a BiVO₄ film at the start of three successive days of PIA measurement. Electrolyte = 1 M KP buffer, pH 7.

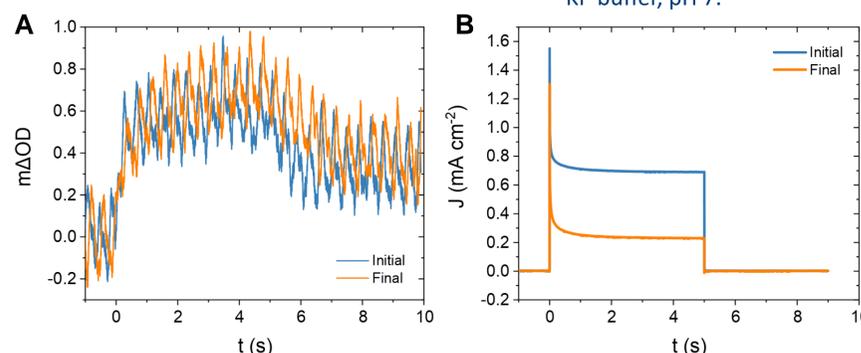


Fig. 5. PIA measurements of BiVO₄ at 1.4 V_{RHE} and 1 sun illumination in 1 M KP buffer (pH 7). (a) Initial & final optical measurements. (b) Initial and final photocurrent measurements.

4. Improving BiVO₄ stability through electrolyte choice

Choi & Lee have previously reported that the use of a V⁵⁺ saturated electrolyte can minimise photodegradation of BiVO₄ by limiting dissolution of surface V ions.² However, the yellow colour of this electrolyte may limit its suitability for pump-probe spectroscopy.

Borate buffer is being increasingly used in the literature to improve BiVO₄ stability.^{3,4} The reduced photodegradation in borate buffer **decreases the error** in rate law measurements.

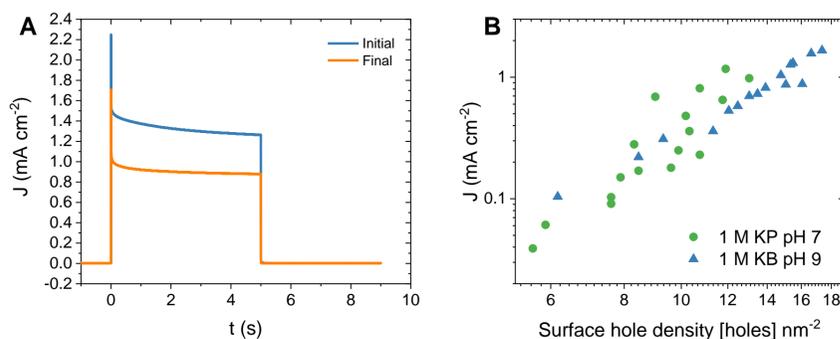


Fig. 6. (a) Initial & final photocurrent measurements of BiVO₄ measured at 1.4 V_{RHE} in 1 M KB buffer (pH 9) under 1 sun illumination. (b) Rate law plot of BiVO₄ films measured at 1.4 V_{RHE} in 1 M KP buffer (pH 7) and 1 M KB buffer (pH 9).

2. Pump-probe spectroscopy

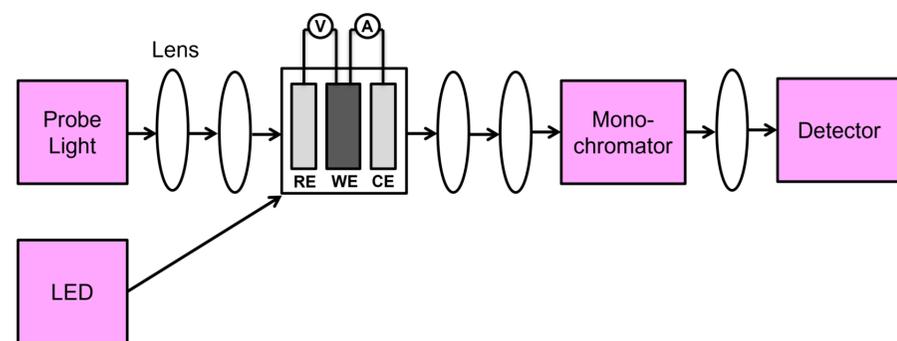


Fig. 3. Schematic diagram of a Photoinduced Absorption (PIA) spectroscopy setup. RE = reference electrode, WE = working electrode, CE = counter electrode.

The charge carriers generated in photoanodes have characteristic absorptions at specific wavelengths. By using pump-probe spectroscopy, it is possible to excite charge carriers using a laser or an LED and measure the absorption at certain wavelengths.

These techniques can give important information about the **population** of charged species and their **lifetimes**.

Conclusion

The instability of BiVO₄ photoanodes made by metal organic deposition under PEC conditions poses a significant challenge in studying this material. The use of co-catalysts⁵ or a protective layer⁶ can be used to improve stability in heterojunctions, but other strategies are required to limit photodegradation sufficiently to study the charge carrier dynamics of BiVO₄ individually. Improved stability with **pH 9 borate buffer** (compared to pH 7 phosphate buffer) allows for the **more precise measurement of BiVO₄ rate law**.