

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 be **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**. Understanding the role of individual materials is key to optimising device design.

1. Water splitting

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

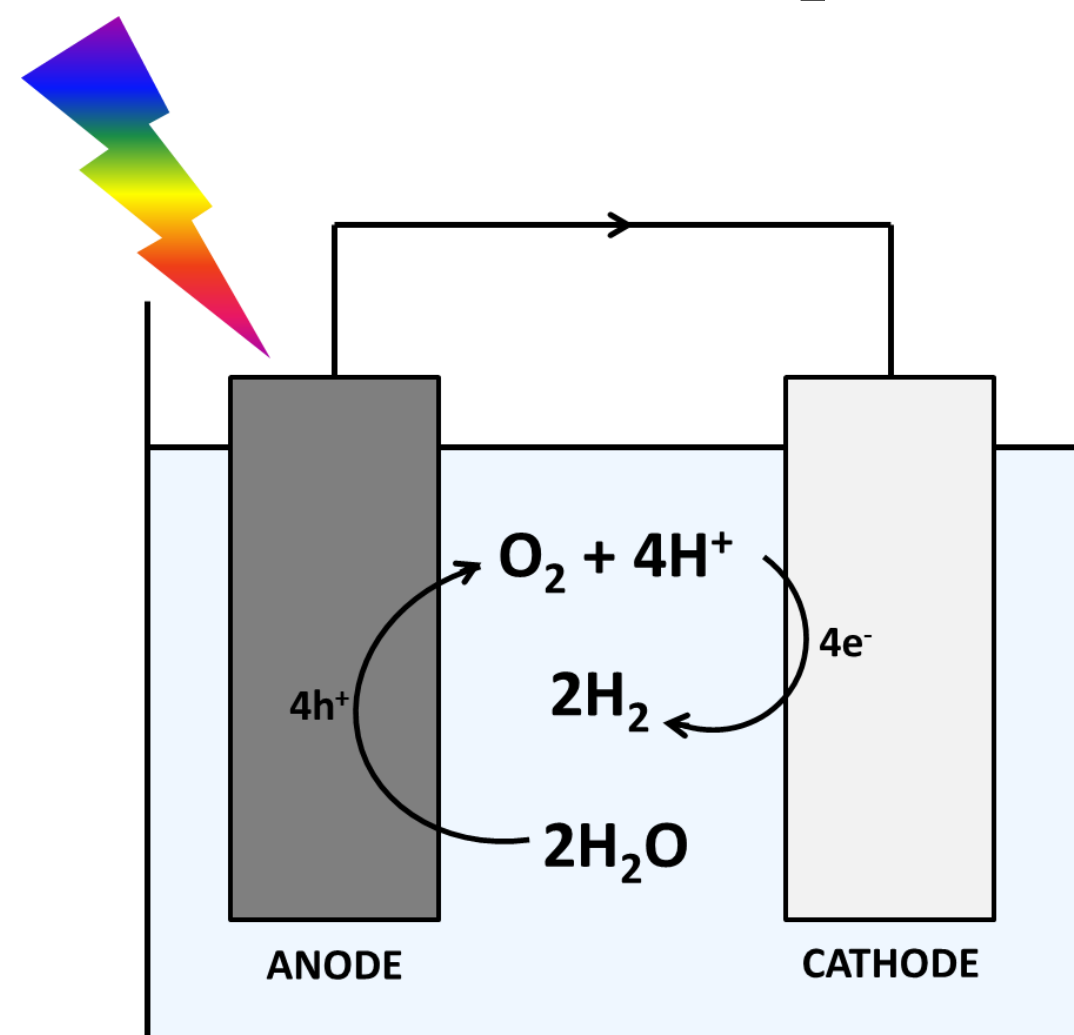
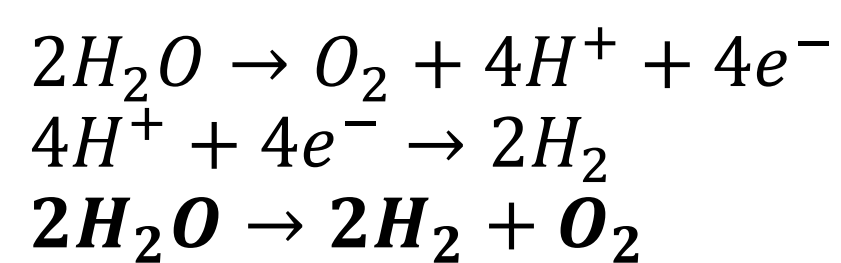


Fig. 1. Overview of a PEC cell.

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).

2. Metal oxides as photoanodes

Metal oxides have been widely studied as photoanode materials due to their **stability** in aqueous environments and **low cost**.¹

Key examples include: **TiO₂**, **WO₃**, **α-Fe₂O₃** & **BiVO₄**

Different materials are limited by different factors. In some cases, the bandgap is too wide to absorb light in the visible portion of the solar spectrum. In other cases, the photogenerated charges recombine too quickly, before they have been able to participate in the water splitting half reactions.¹

Forming **heterojunctions** of two or more different materials means a photoanode can benefit from the complementary properties of each of the materials.

For example, the **BiVO₄/WO₃** heterojunction benefits from the visible light absorption of BiVO₄ and the high conductivity of WO₃, achieving photocurrents close to the theoretical maximum.²

Future Work

This PhD project will broadly investigate the fabrication and kinetic characterisation of metal oxide heterojunctions for PEC water splitting. By using another co-catalyst with an absorption peak significantly different to that of BiVO₄, TAS should be able to further understand the role of the interlayer in films from the Eslava Group. Further work on BiVO₄ will take place through collaborations with Sixto Giménez and Camilo Mesa through the EU-funded SUN2CHEM project.

3. Pump-probe spectroscopy

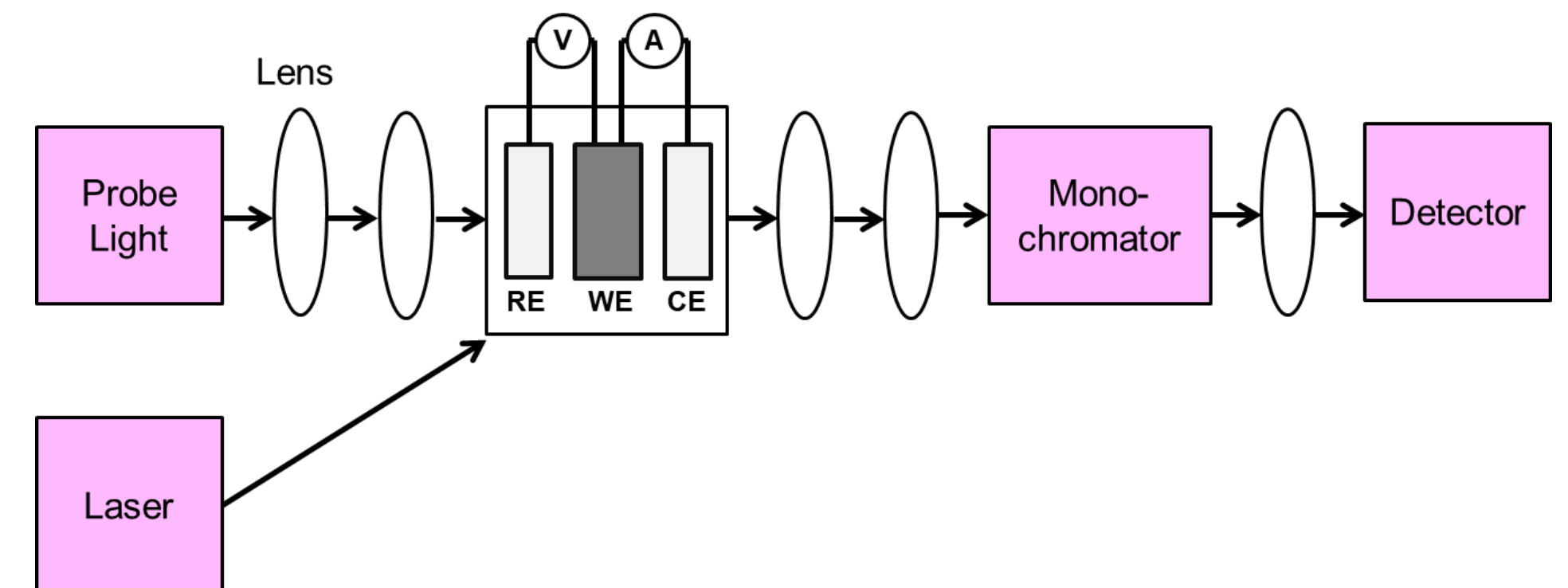


Fig. 2. Schematic diagram of a Transient Absorption Spectroscopy (TAS) setup. RE = reference electrode, WE = working electrode, CE = counter electrode

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**.

4. Investigating BiVO₄-based photoanodes

BiVO₄ has a relatively **narrow bandgap**² and has been widely studied as a photoanode material, including in the Durrant Group^{3,4}.

Co-catalysts can be used to enhance BiVO₄ performance.⁵

In this work, some initial TAS measurements were carried out to investigate the effect of an **interlayer** in some BiVO₄-based heterojunction films synthesised by Junyi Cui in the Eslava Group.

The co-catalyst used absorbed in a similar region to BiVO₄, making it difficult to distinguish the individual components. The kinetics seem slightly more favourable with both the interlayer and co-catalyst.

These data give an example of how pump-probe techniques will be used to investigate heterojunctions in this PhD.

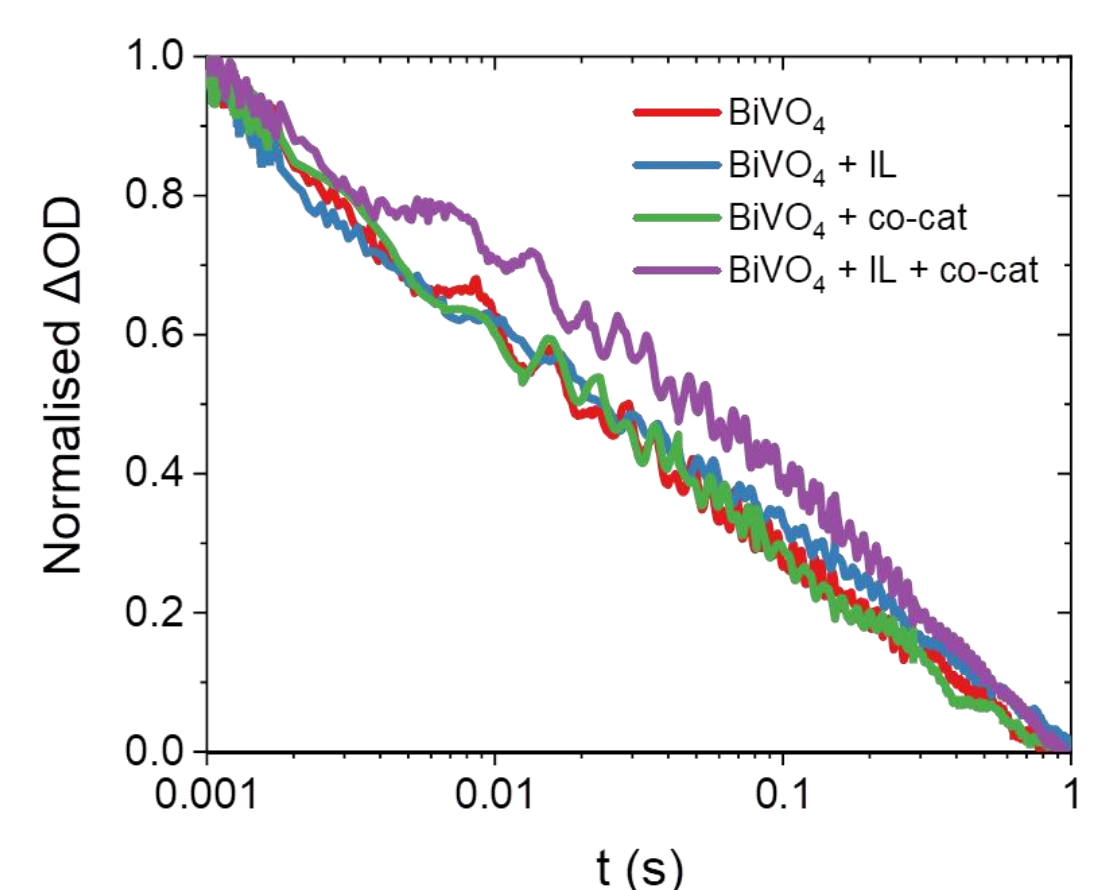


Fig. 3. Normalised TAS kinetics at 550 nm. IL = interlayer, co-cat = co-catalyst