

Dye-sensitized photoelectrochemical cells for solar driven water splitting and CO₂ reduction

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Efficient dye-sensitized photocathodes offer new opportunities for converting sunlight into storable energy cheaply and sustainably.¹ We are developing dye-sensitized NiO cathodes for the photo-reduction of carbon dioxide or water to high energy products (solar fuels) using the lessons we have learnt from solar cells.² The potential advantage of this strategy is it exploits the selectivity of a molecular catalyst in a robust device. Assembling two photoelectrodes in a tandem configuration (see figure) enables water oxidation at the photoanode to supply electrons to the photocathode to be consumed in the reduction of e.g. H⁺ to H₂. Generating hydrogen on one electrode and oxygen on another enables the two gasses to be collected separately. Additionally, by separating the functions of light absorption, charge transport and catalysis between the colloidal semiconductor and molecular components, the activity of each can be optimised, rather than relying on one material to have all the necessary credentials. However, the complexity of the system requires advanced experimental techniques to evaluate the performance.

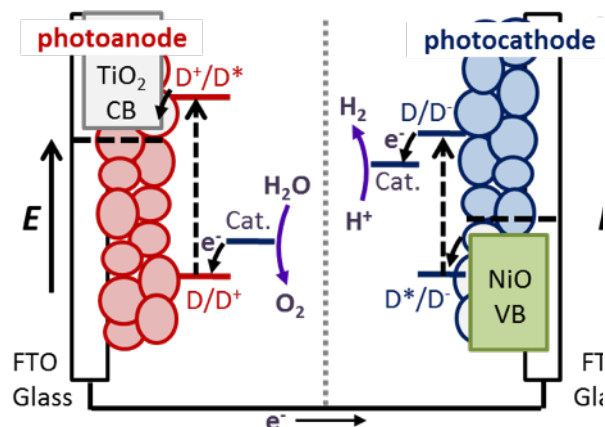
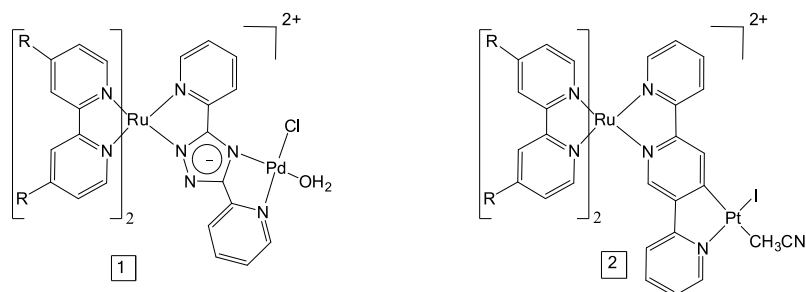


Figure 1. Schematic illustration of a dye-sensitized photoelectrochemical cell for solar driven water splitting.

A number of simple approaches are possible, such as co-adsorbing dyes and catalysts on electrode surfaces or replacing the reversible redox shuttle in a dye-sensitized solar cell with a molecular catalyst in solution. Our strategy is to take supramolecular photocatalysts, which have been developed and studied over several decades, typically as half-reactions in solution using sacrificial electron acceptors or donors, and immobilising them on mesoporous metal oxide electrodes. For the last twenty five years, most of the work on photoelectrochemical devices using dyes to absorb light and transparent semiconductors to transport charge has been based on TiO₂. Our main focus has been the photocathode, based on p-type materials such as NiO, and high Faradaic efficiencies and

promising stabilities have been reached.³ However, the photocurrents generated are 10-100 times lower than we typically attain with our photocathodes in dye-sensitized solar cells. We are tackling the main limitations to photocurrent, by improving the quality of the NiO electrodes⁴ and engineering new photocatalysts specifically for the photoelectrochemical system, to increase the quantum efficiency.

The electron-transfer dynamics are key to the performance. In efficient molecular solar cells, long term stability above 20 years is feasible because the regeneration of the components is fast. Unlike many homogeneous photocatalytic systems which rely on long-lived excited states, the dye injects charge to the semiconductor rapidly upon excitation and is subsequently returns to the ground state by transferring charge to the catalyst. Providing both these processes are efficient, the fast kinetics means dye degradation is less likely to occur. A major challenge in NiO photocathodes is slowing down charge recombination between the photoreduced dye and the oxidised NiO so that chemistry can take place. Here, a supramolecular approach where a built-in electron transfer cascade away from the electrode surface, towards the catalyst has led to promising improvements. Highlights from recent work examining charge-transfer at the interface between NiO and new supramolecular photocatalysts⁵ using transient absorption spectroscopy and time-resolved infrared spectroscopy will be presented. The advantage of our supramolecular catalysts is that they have distinct signals for the reduced dyes in both the optical and infrared regions. The behaviour at the Pt or Pd catalyst



centre, however, has been more challenging to monitor. Our current understanding of the factors governing electron transfer across the interface between the semiconductor, dye and catalyst will be described in this talk and future directions and challenges for this field will be outlined.

Figure 2. The structures of the dye-catalyst assemblies **1** and **2** (R = CO₂Et).

The performance of dye-sensitized photocathodes based on NiO, whether for solar cells or solar fuels, lags behind that of TiO₂. Our research has led us to the conclusion that the fundamental limitation of these devices arises from the NiO material itself and we have re-focused our efforts on finding a replacement transparent p-type semiconductor. n-Type transparent conducting oxides are present in many devices but their p-type counterparts are not largely commercialized as they exhibit much lower conductivities. The core part of our current project focuses on making libraries of mixed metal oxides and selecting those which are promising p-type semiconductors. Preliminary results will be discussed together with the challenges faced in optimising the device as a whole.

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