Imperial College London

Photochemistry Group

Molecular and nanostructured catalysts for the photochemical reduction of CO_2

Anna Reynal, Ernest Pastor, James Durrant

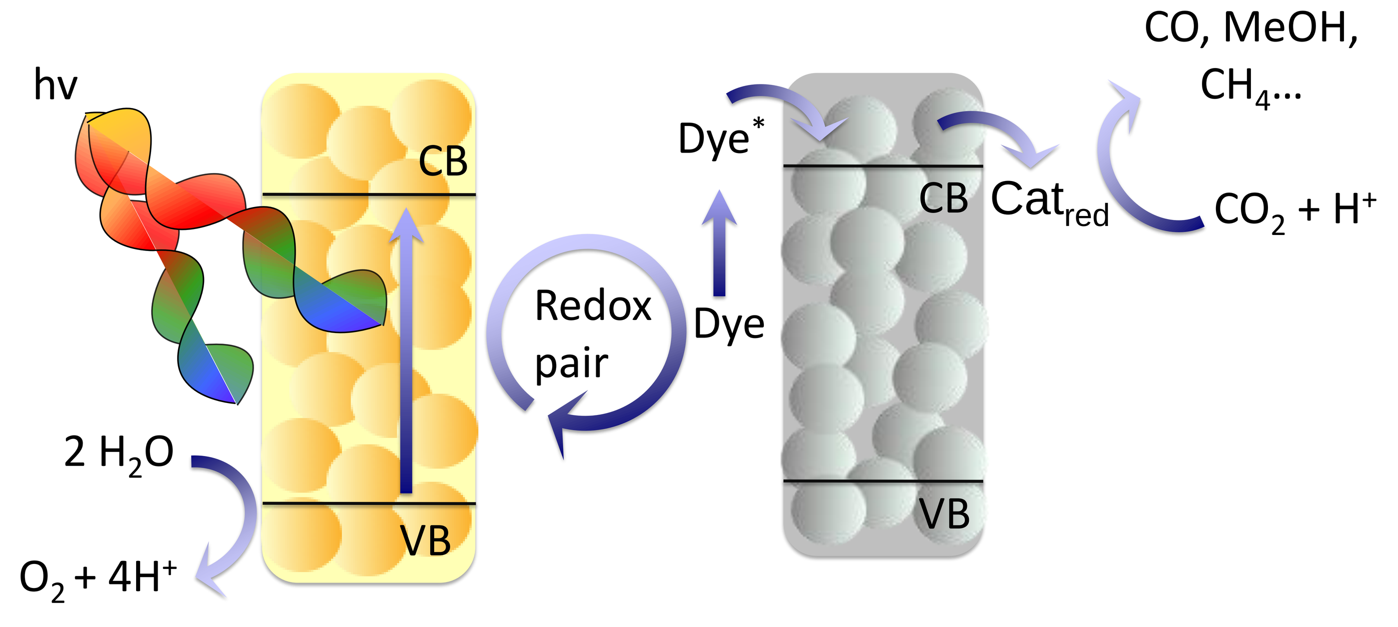
Department of Chemistry, South Kensington Campus, Imperial College London (a.reynal-verdu08@imperial.ac.uk)

PHOTOCATALYTIC SYSTEMS FOR CO_2 REDUCTION:

The growing energy demand from our society requires the development of a sustainable, environmentally clean and secure energy source and storage system. In this context, the light-induced catalytic reduction of CO_2 to fuels is a promising alternative to capture and storage solar energy.

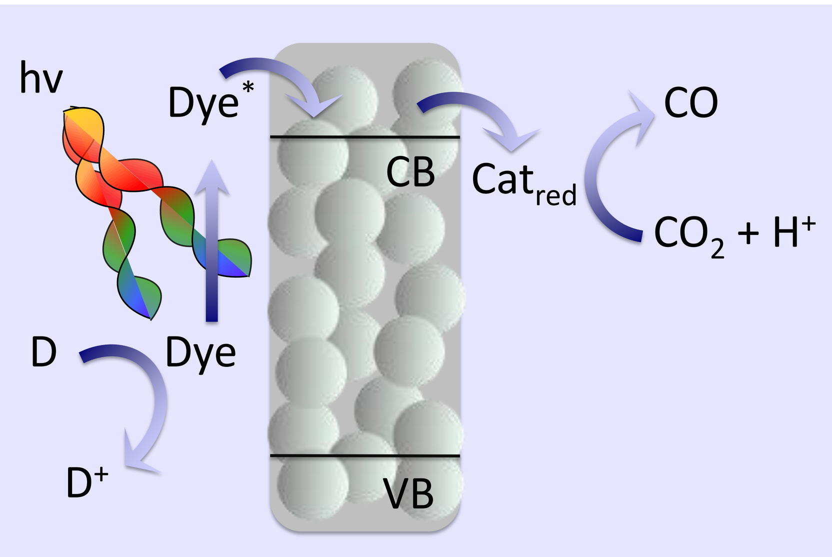
Our group is mainly focused on the study of a wide range of nanostructured and molecular catalysts as photocathodes for the reduction of CO_2 into valuable chemicals. From a practical point of view, heterogeneous systems seem more appropriate for the CO_2 reduction. For this reason, two main approaches are used in the CO_2 reduction systems: (1) Using an n-type semiconductor with a photosensitiser and a catalyst co-attached onto the surface, and (2) Using a p-type semiconductor

The photocatalytic activity of the catalysts is measured by GC and the electron transfer processes that take place at the interface of those materials is characterised by time-resolved luminescence spectroscopy, laser-transient absorption spectroscopy (L-TAS) and photo-electrochemical measurements.



Principles of operation of a molecular-based device for the production of fuels from water and CO_2.

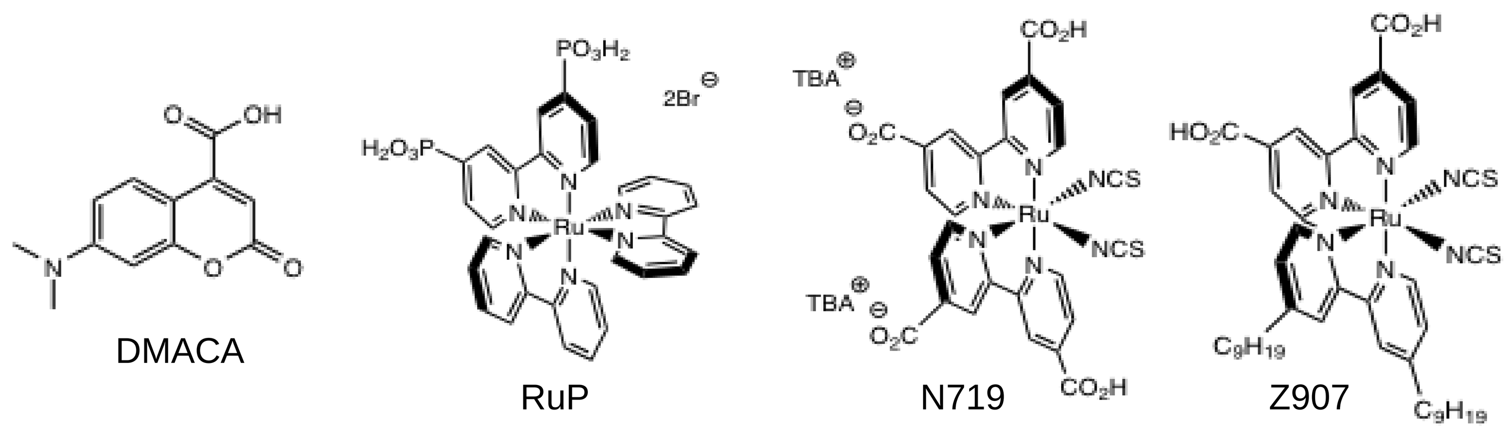
n-TYPE POTOCATHODES FOR CO_2 REDUCTION



The preparation of functional devices at a molecular level for the photochemical CO_2 reduction under visible light involves the integration of a photosensitiser, a semiconductor and a photocatalyst.

Upon irradiation, the sensitiser injects an electron into the conduction band of the semiconductor. This electrons are then transferred to the CO_2 reduction catalyst. Finally, a sacrificial electron donor is used to regenerate the dye.

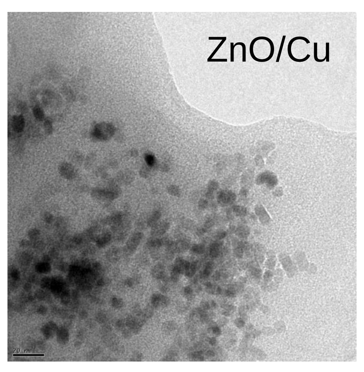
Photosensitisers: Able to absorb light in the visible region of the solar spectrum



Semiconductors: To transfer electrons from the photosensitiser to the catalyst

TiO_2, TiO_2/ZnO, Cd_2SnO_4, $Ti_xZr_yO_2$, $NaTaO_3$, $SrTaO_3$, Ag-$BiWO_3$

Catalysts: Able to accelerate the CO_2 reduction reaction



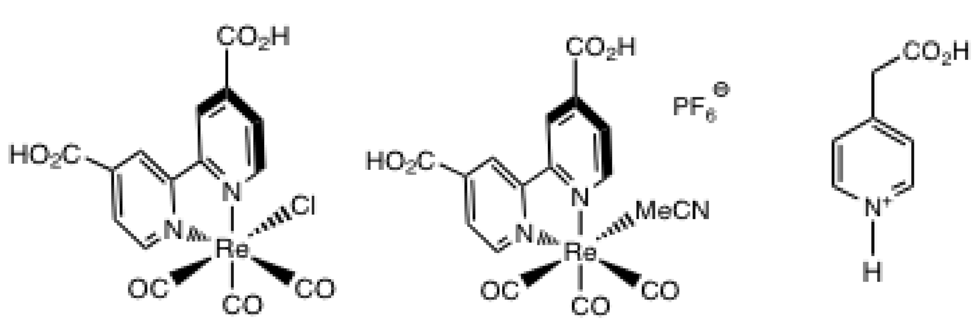
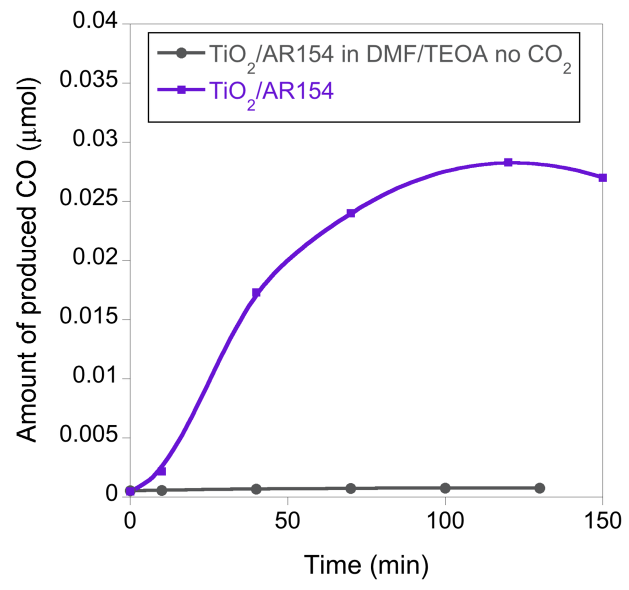
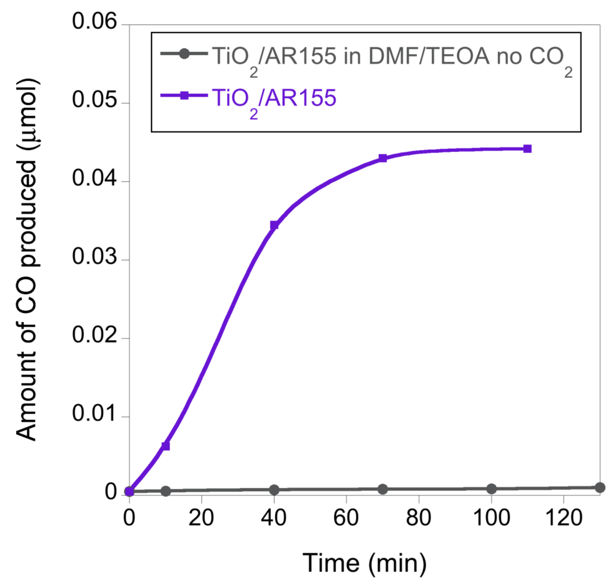


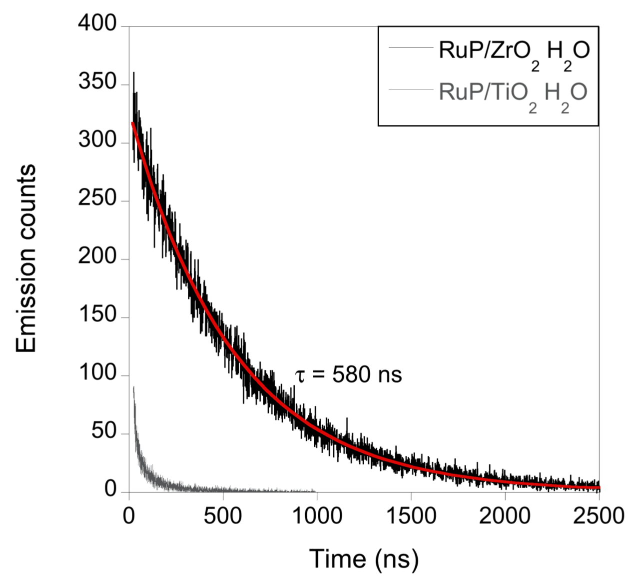
Photo-catalytic studies

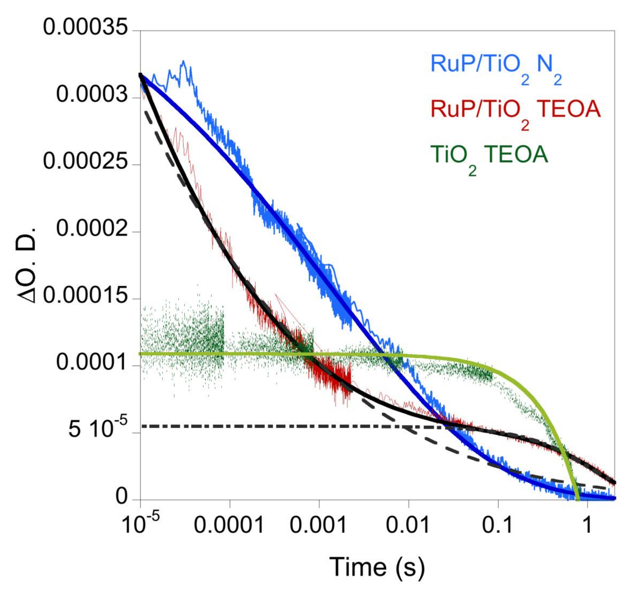
The photocatalytic activity of the molecular and nanostructured CO_2 reduction catalysts is measured by GC both in solution and in films under visible and UV light irradiation. A sacrificial electron donor (Triethanolamine, Na_2SO_3) is used to regenerate the system.

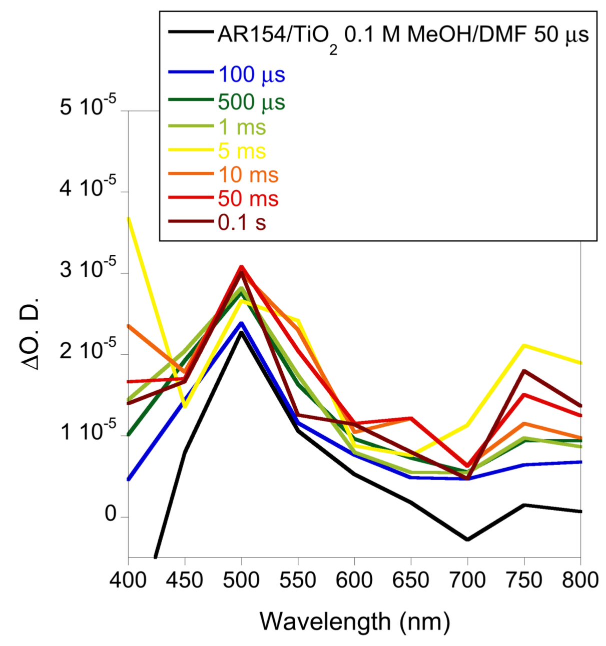




Kinetic studies





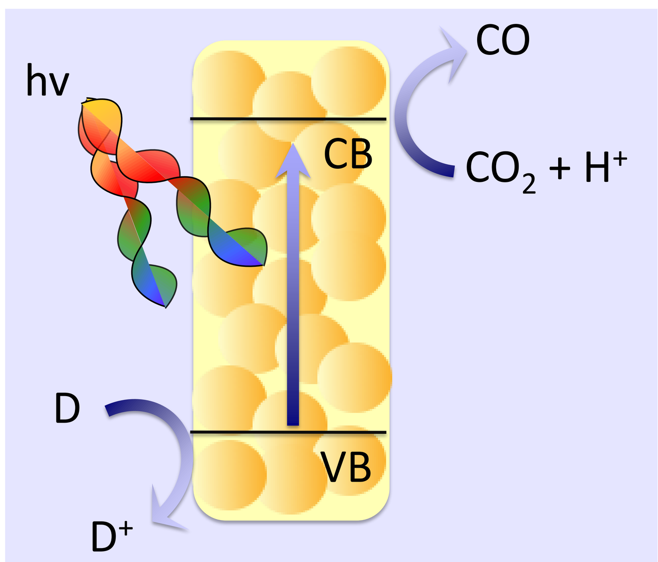


The photo-induced electron injection of dyes into the TiO_2 CB can be qualitatively determined by comparing the quenching of the luminescence of the dye when anchored onto TiO_2 with to that of a material with a CB above the dye excited state.

L-TAS is used to determine the kinetics of the dye⁺/e⁻-TiO_2 recombination reaction. The decay of the dye⁺ is monitored when a sacrificial electron donor is added to the system, showing a biphasic behaviour due to the faster regeneration of the dye, and the presence of longer-lived e⁻ in the TiO_2.

The different intermediates in the CO_2 reduction reaction, as well as the electron transfer from the TiO_2 to the molecular catalyst can be monitored by L-TAS.

p-TYPE POTOCATHODES FOR CO_2 REDUCTION



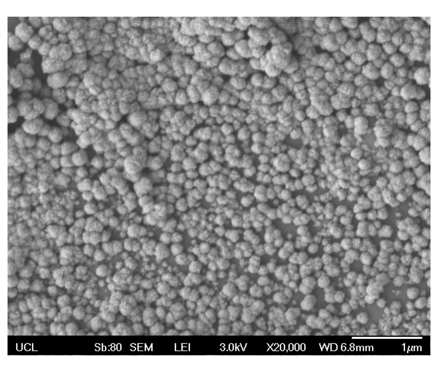
p-type semiconductors with an appropriate position of the conduction and valence bands can be used for the photochemical CO_2 reduction under visible or UV light irradiation.

The absorption of light by a semiconductor promotes the transition of an electron from the valence band to the conduction band. These photo-excited electrons can be used for CO_2 reduction, while the photo-generated holes are transferred to a sacrificial electron donor molecule.

In order to enhance the CO_2 reduction, different molecular catalysts or nanostructured materials can be attached onto the surface of the p-type semiconductor.

Semiconductors:

p-type Cu_2O



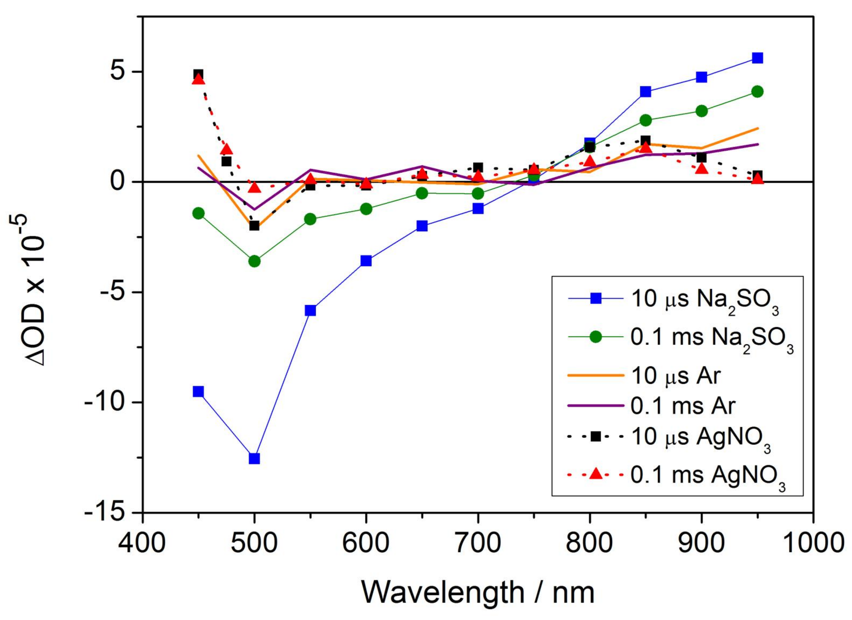
Molecular catalysts and nanostructured materials:

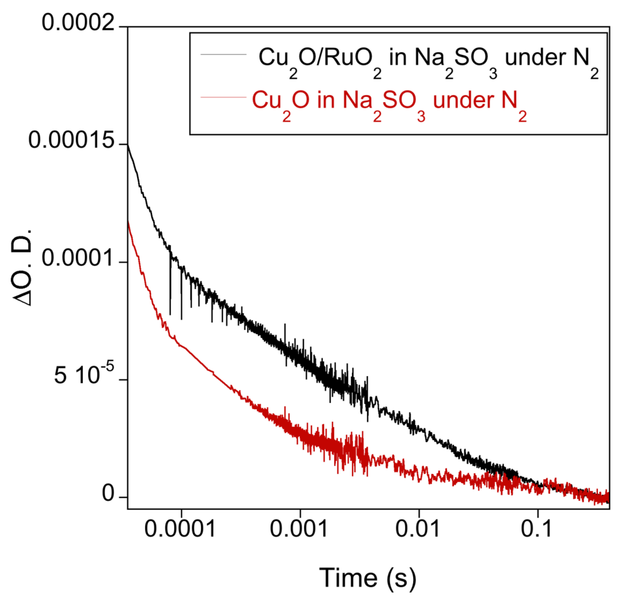
- [Re(bpy)(CO)$_3$X] catalysts, pyridinium cations
- RuO_2, TiO_2, ZnO

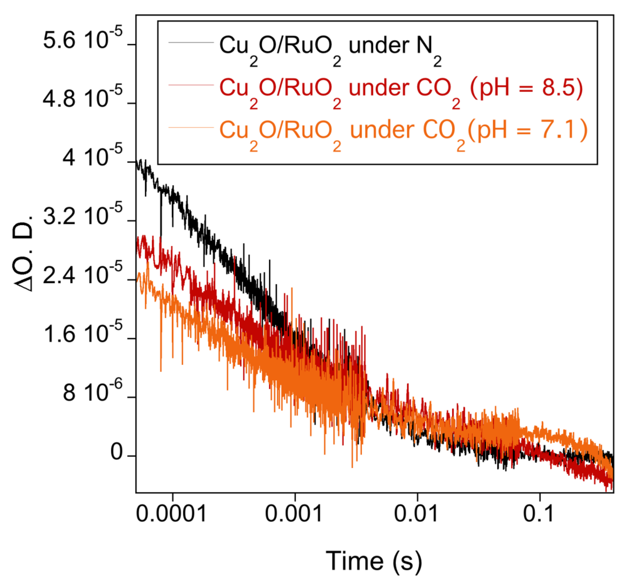
Kinetic studies

The transient absorption spectrum of the p-type semiconductors can be obtained by L-TAS measurements using hole and electron scavengers (Na_2SO_3 and $AgNO_3$, respectively).

The transient absorption spectrum of photo-excited electrons of Cu_2O shows a maximum peak at 950 nm. By comparing the life-time of the photo-generated charge carriers, the electron transfer that takes place in this kind of materials can be studied.







The lifetime of photo-excited electrons is significantly longer-lived for the Cu_2O/RuO_x films, indicating an effective decrease of the e⁻/h⁺ recombination reaction.

When CO_2 is added to the system, the lifetime of these photo-generated electrons decreases dramatically. This is a clear indication of the electron transfer that causes the CO_2 reduction into CO.

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