

Molecular and nanostructured catalysts for the photochemical reduction of CO₂

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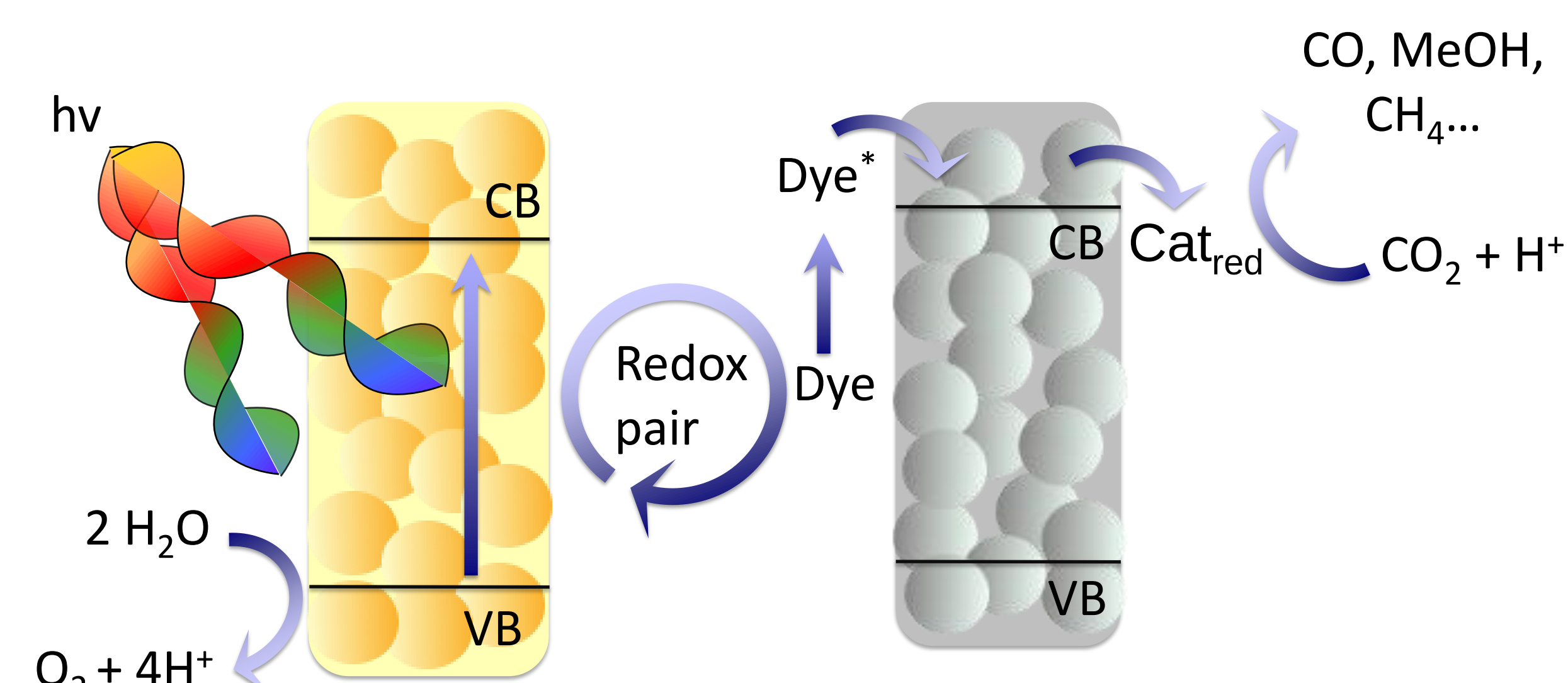
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PHOTOCATALYTIC SYSTEMS FOR CO₂ REDUCTION:

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 CO₂ to fuels is a promising alternative to capture and storage solar energy.

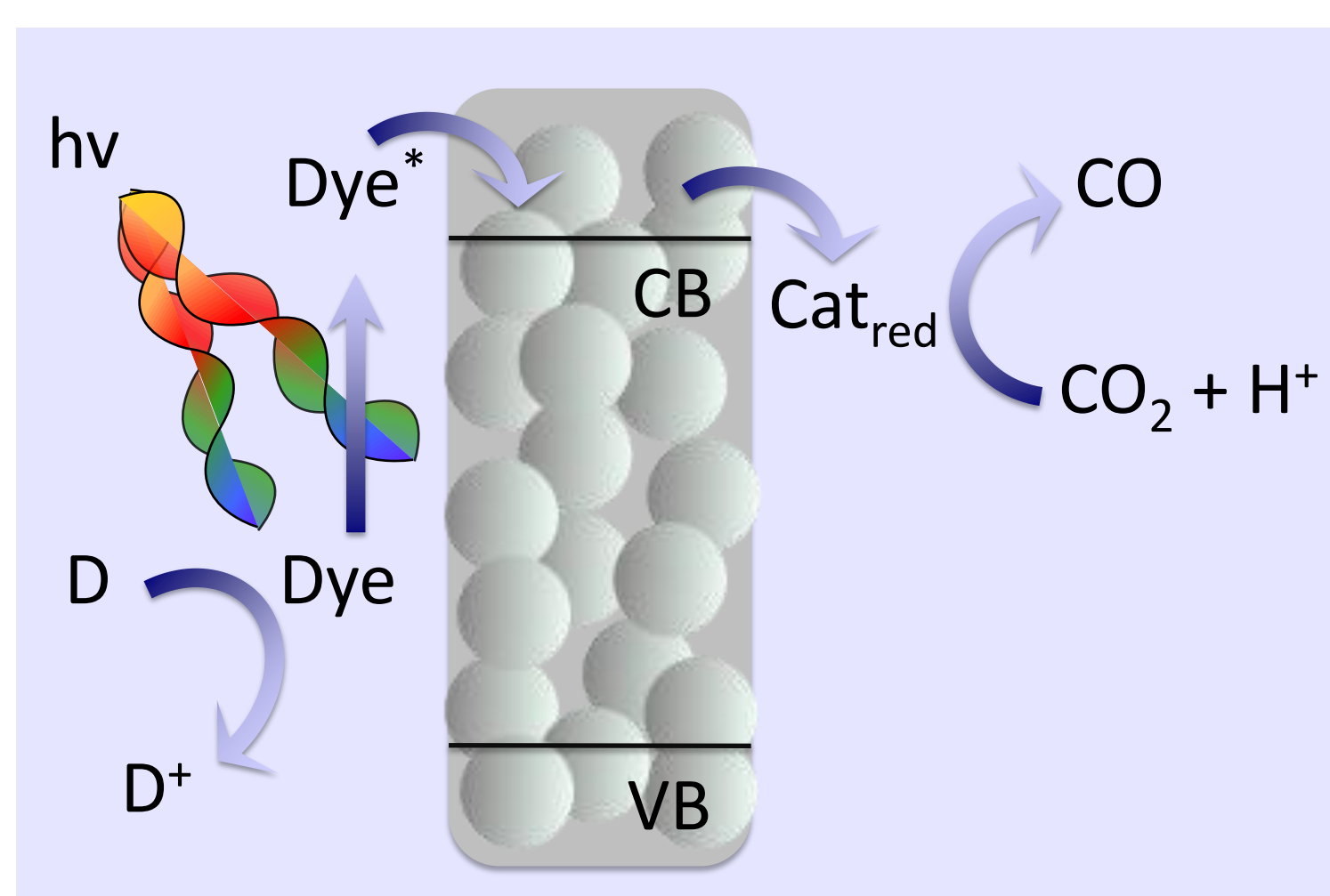
Our group is mainly focused on the study of a wide range of nanostructured and molecular catalysts as photocathodes for the reduction of CO₂ into valuable chemicals. From a practical point of view, heterogeneous systems seem more appropriate for the CO₂ reduction. For this reason, two main approaches are used in the CO₂ 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 CO₂.

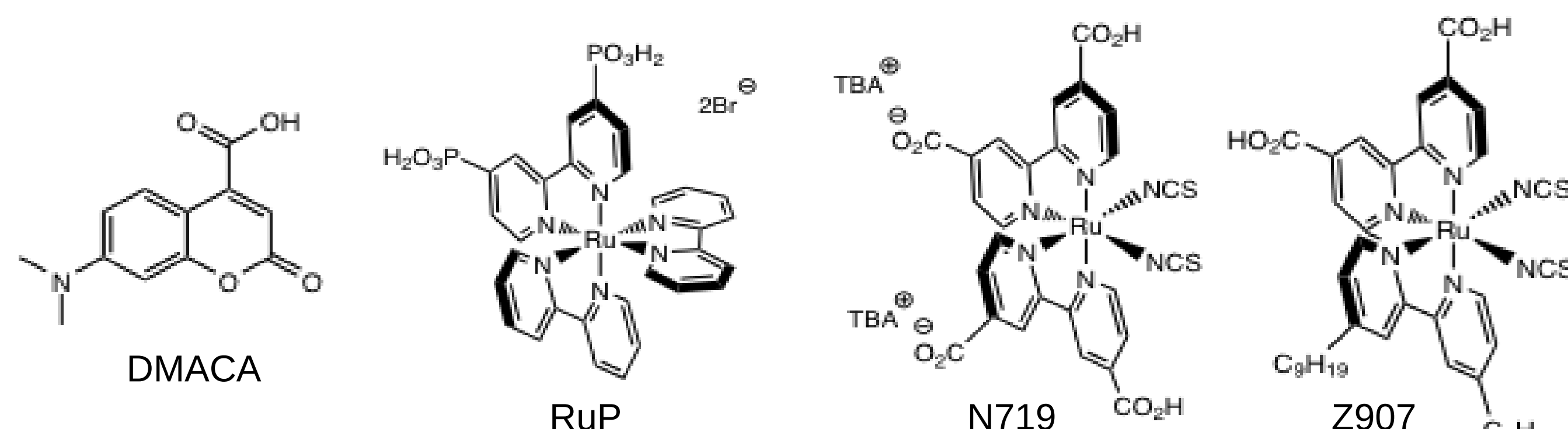
n-TYPE POTOCATHODES FOR CO₂ REDUCTION



The preparation of functional devices at a molecular level for the photochemical CO₂ 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. These electrons are then transferred to the CO₂ 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

TiO₂, TiO₂/ZnO, Cd₂SnO₄, Ti_xZr_yO₂, NaTaO₃, SrTaO₃, Ag-BiWO₃

Catalysts: Able to accelerate the CO₂ reduction reaction

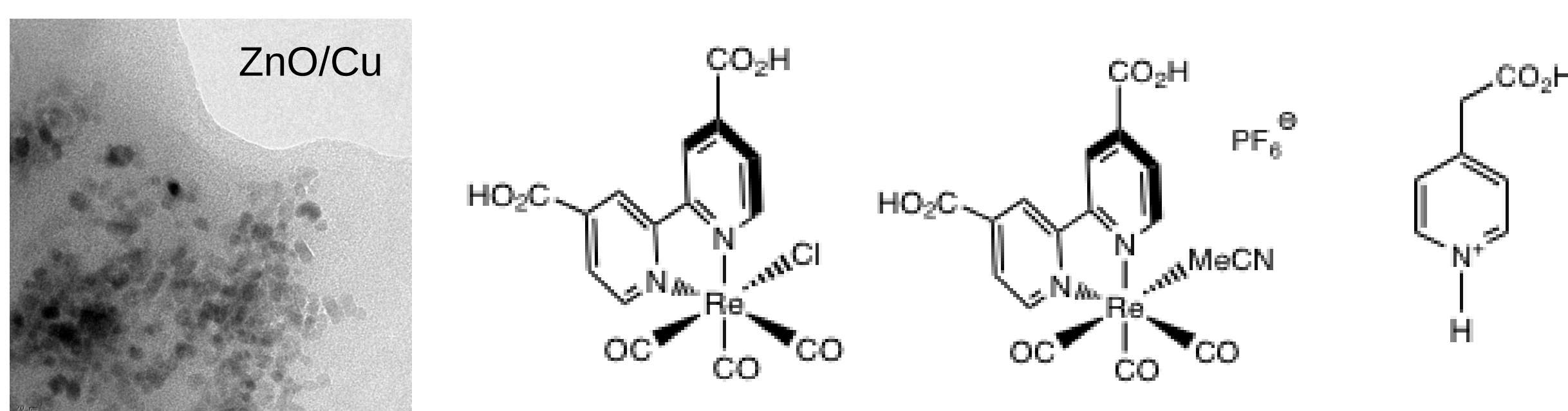
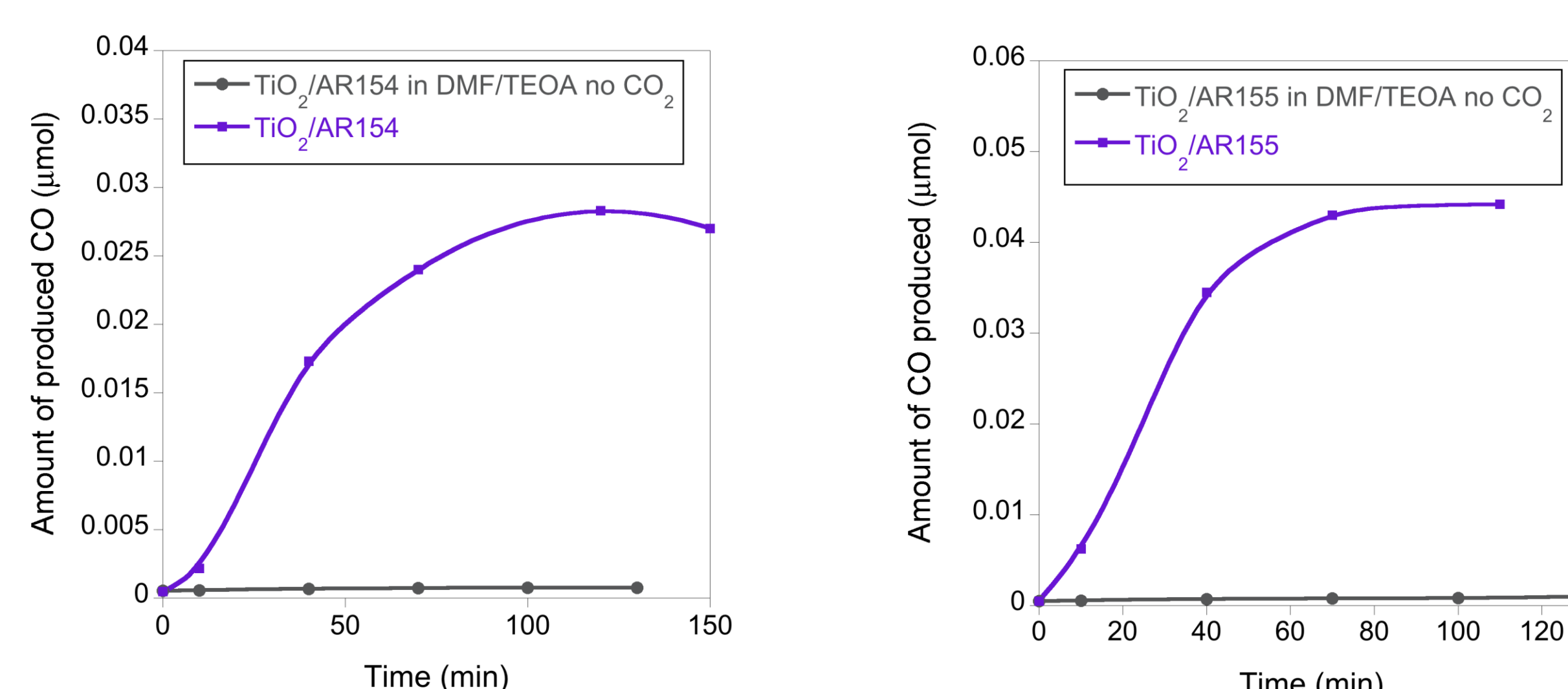
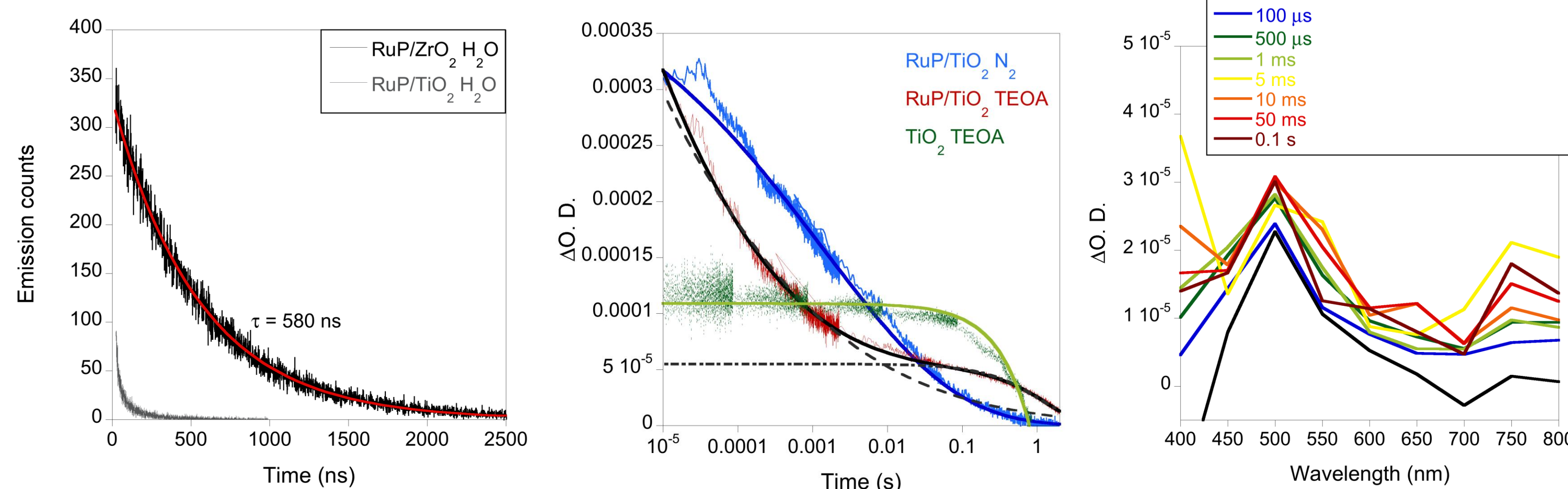


Photo-catalytic studies

The photocatalytic activity of the molecular and nanostructured CO₂ reduction catalysts is measured by GC both in solution and in films under visible and UV light irradiation. A sacrificial electron donor (Triethanolamine, Na₂SO₃) is used to regenerate the system.



Kinetic studies

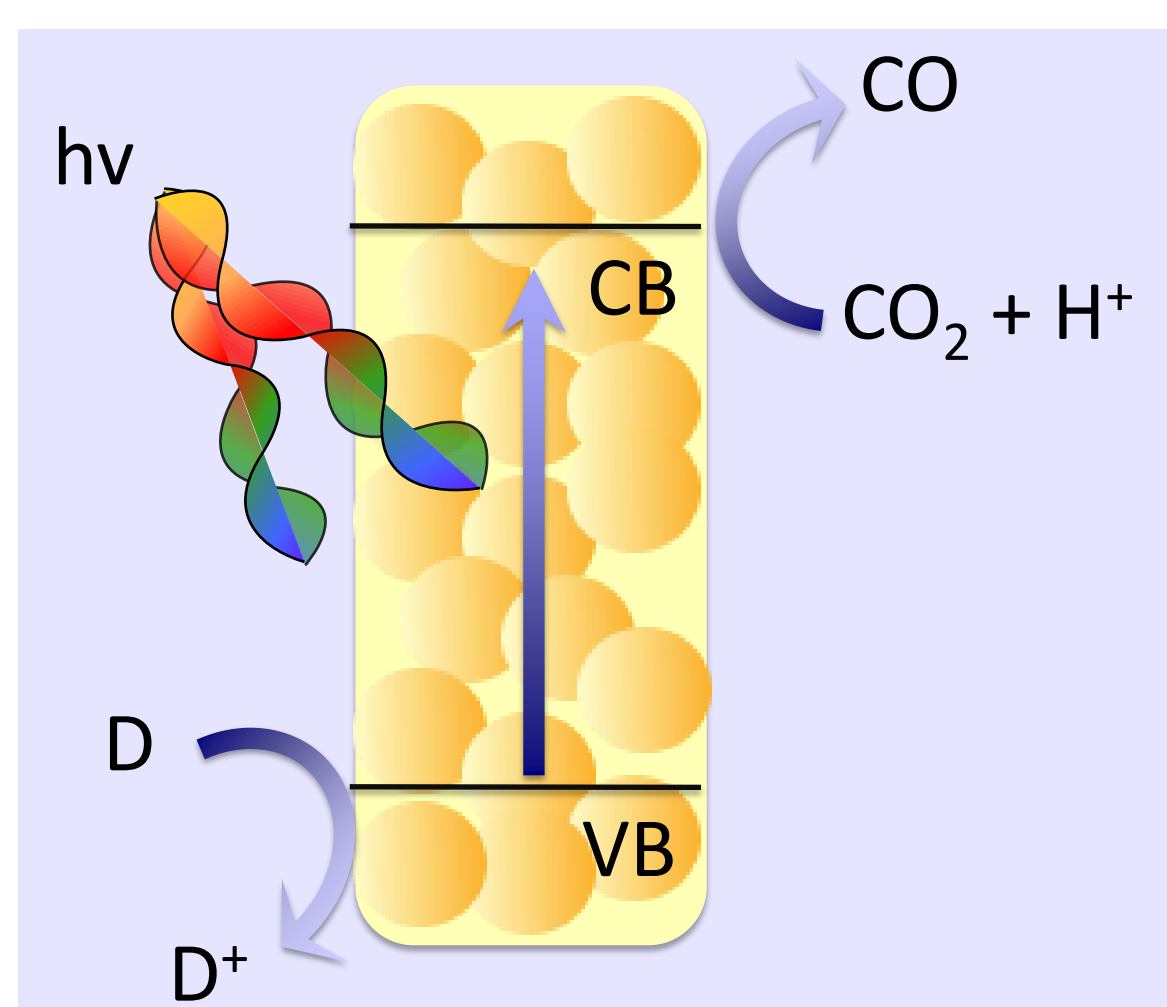


The photo-induced electron injection of dyes into the TiO₂ CB can be qualitatively determined by comparing the quenching of the luminescence of the dye when anchored onto TiO₂ with that of a material with a CB above the dye excited state.

L-TAS is used to determine the kinetics of the dye⁺/e⁻-TiO₂ 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 TiO₂.

The different intermediates in the CO₂ reduction reaction, as well as the electron transfer from the TiO₂ to the molecular catalyst can be monitored by L-TAS.

p-TYPE POTOCATHODES FOR CO₂ REDUCTION



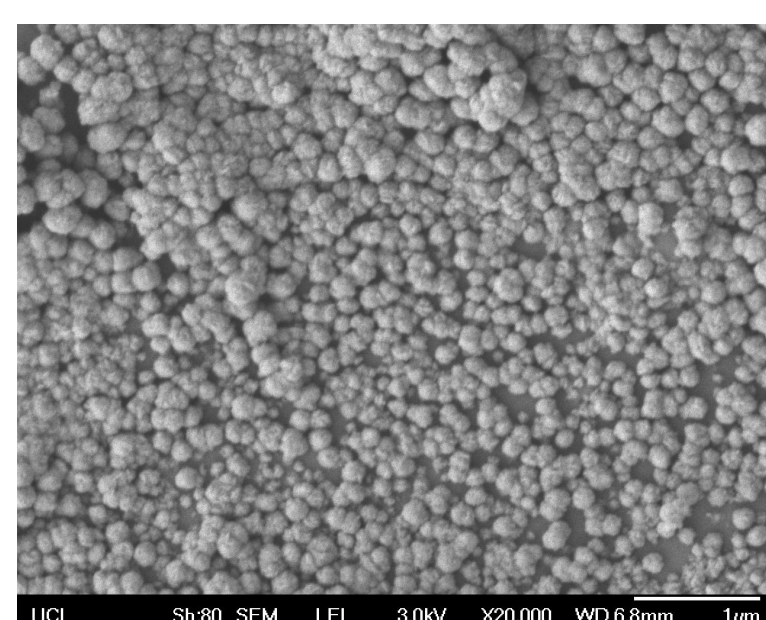
p-type semiconductors with an appropriate position of the conduction and valence bands can be used for the photochemical CO₂ reduction under visible or UV light irradiation.

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 CO₂ reduction, while the photo-generated holes are transferred to a sacrificial electron donor molecule.

In order to enhance the CO₂ reduction, different molecular catalysts or nanostructured materials can be attached onto the surface of the p-type semiconductor.

Semiconductors:

p-type Cu₂O



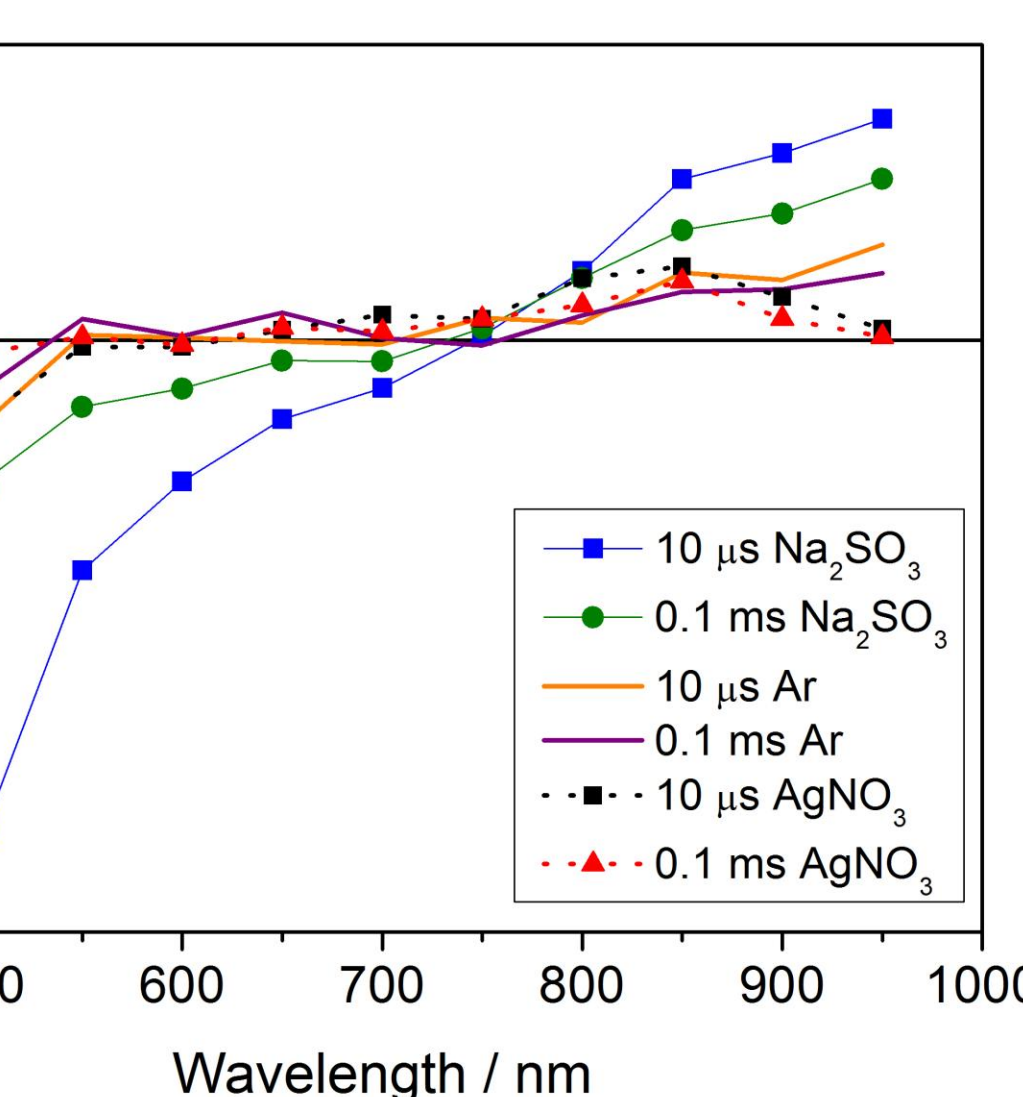
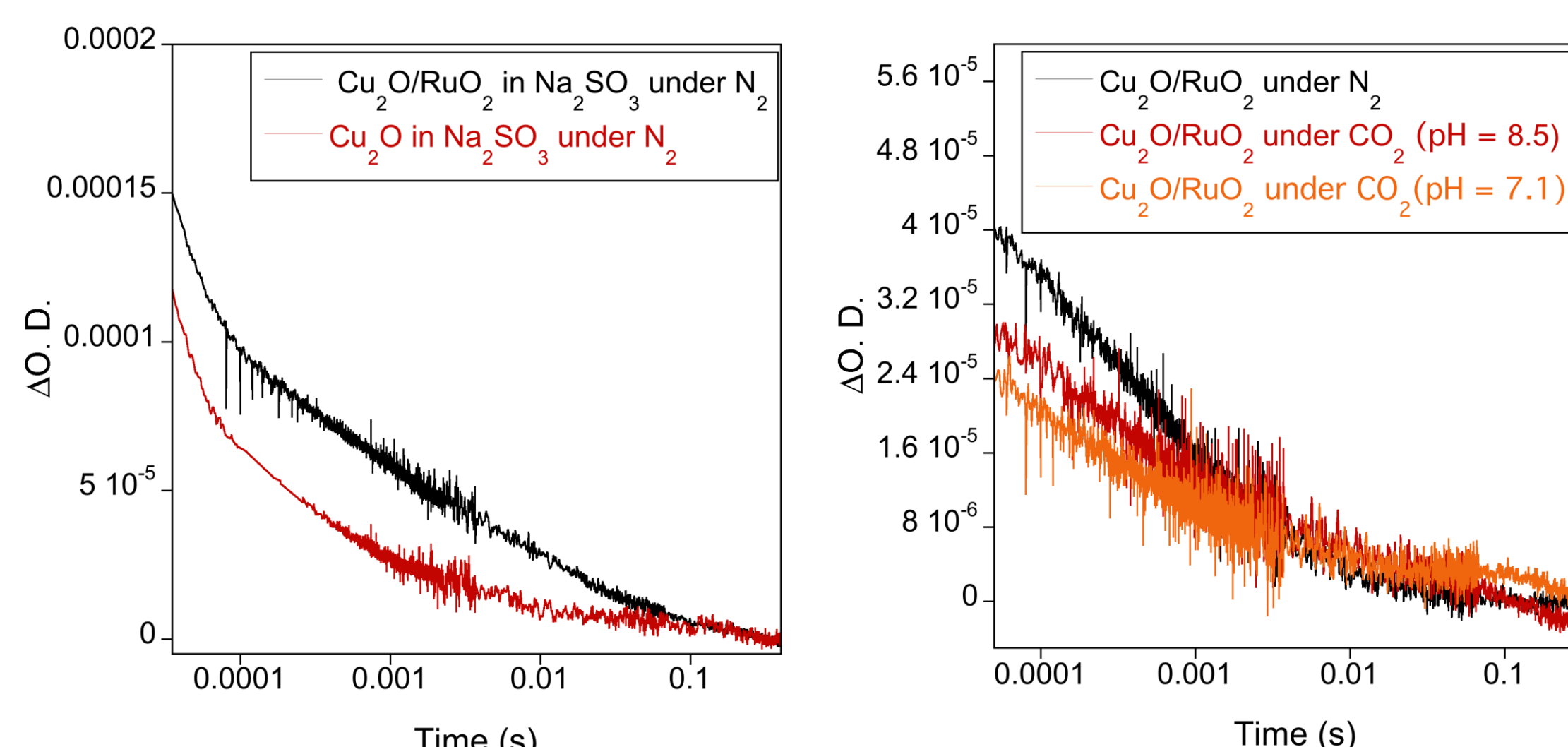
Molecular catalysts and nanostructured materials:

- [Re(bpy)(CO)₃X] catalysts, pyridinium cations
- RuO₂, TiO₂, ZnO

Kinetic studies

The transient absorption spectrum of the p-type semiconductors can be obtained by L-TAS measurements using hole and electron scavengers (Na₂SO₃ and AgNO₃, respectively).

The transient absorption spectrum of photo-excited electrons of Cu₂O 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 Cu₂O/RuO_x films, indicating an effective decrease of the e⁻/h⁺ recombination reaction.

When CO₂ 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 CO₂ reduction into CO.

ACKNOWLEDGEMENTS

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