Time-Resolved Photoacoustic Calorimetry as a tool for assessing electron injection and charge recombination dynamics and energetics in DSSC.

Purpose of the visit

This short visit had the main purpose of starting a collaboration between the groups of Prof. Luis Arnaut (University of Coimbra, Portugal) and Prof. James Durrant (Imperial College London, UK). Both groups have been working in the field of solar energy conversion, giving special attention to the dynamics of charge separation and recombination in semiconductor materials, in the context of dye-sensitised solar cells (DSSC) and photoelectrochemical cells (PEC) for water splitting.

In DSSC, optical excitation of adsorbed dye molecules results in the injection of electrons into the semiconductor. In our group, at the University of Coimbra, we have recently described an approach based on the detection of the pressure wave generated during the conversion of excitation energy into heat as the electronically excited dye evolves to a charge-separated state (CS), with the electron located in the conduction band of the semiconductor.[1] This is the principle of operation of time-resolved photoacoustic calorimetry (TR-PAC). Using this method we have observed higher energy release when the environment of the dye is made less polar, and attributed this effect to a more pronounced raise of the dye oxidised state than that of the edge of the conduction band of TiO_2. To confirm this interpretation and demonstrate the applicability of TR-PAC for the determination of conduction band energy and assessment of electron injection and recombination efficiencies it is important to apply this methodology to systems that are well characterised.

Transient absorption spectroscopy (TAS) has recently been employed to study photocatalytic water splitting on TiO_2 films, and allowed the determination of transient lifetimes. [2,3]

In solution photochemistry, TAS and TR-PAC are frequently used as complementary techniques, allowing the assessment of kinetics and energetics of radiative and non-radiative deactivation processes, even in systems with relatively complex mechanisms. [4,5] Our purpose is to use a similar approach and combine TAS and TR-PAC to study the dynamics of charge carriers in nanocrystalline semiconductor films for solar energy conversion, namely TiO_2 and Fe_2O_3.

Description of the work carried out during the visit

One of the purposes of this visit was to discuss the application of TR-PAC to the study of the kinetics of recombination in dye-sensitised solar cells. The design of the most suitable experimental setup and PAC cell (mostly to avoid problems related to electrolyte absorption, and the filter effect resulting from the presence of the counter electrode), and definition of the best experimental conditions to separate and isolate the different radiationless processes that follow laser excitation of the dye, are mandatory in order to obtain meaningful results from the

analysis of experimental acoustic waves. In the first TR-PAC experiments on dye-sensitised TiO$_2$ performed in our group, we used a setup with vertical front-face irradiation.[1,6] For studies on fully functioning DSSC, the presence of an electrolyte requires a setup with horizontal front face irradiation, and the application of a bias potential requires the use of a counter electrode. The new setup designed, shown in Figure 1, will be used in future studies on DSSC.
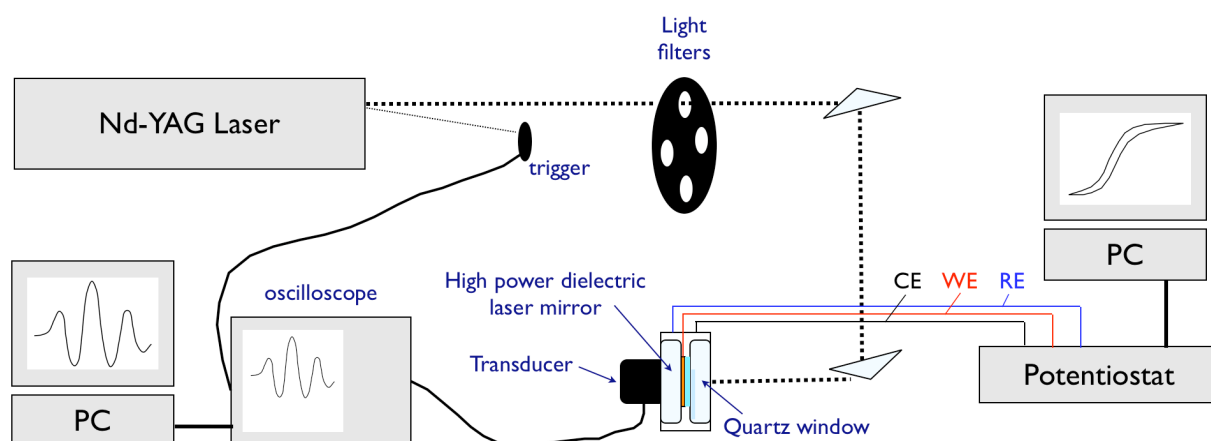

Figure 1. Experimental setup projected for TR-PAC studies on a DSSC model system.

The effect of electrolyte composition in electron injection and charge recombination reactions at the TiO2/dye/redox electrolyte interface has been studied by the group of Prof. James Durrant, using techniques such as transient absorption and emission studies.[7] One important conclusion of that study was that the electrolyte influences the energetics of the conduction band of the TiO$_2$ electrode. The design of the next TR-PAC experiments now includes the application of a bias voltage to the DSSC in order to relate the generated acoustic wave to the position of the conduction band in the film.

Recently we have performed TR-PAC studies on Fe$_2$O$_3$ photoanodes with the purpose of studying recombination dynamics in these films, when used as photoelectrodes for water splitting. Examples of photoacoustic waves obtained for undoped and Nb-doped films are shown in Figure 2. The determination of transient lifetimes from TR-PAC results, in this particular case, is not possible, due to the lack of suitable acoustic references. Presently, we are in the process of testing materials that could be used as references for this system, and to do so, reliable kinetic information is necessary for comparison with PAC results. Such data can, in principle, be obtained by transient absorption spectroscopy. We have used the same experimental setup as Tang *et al.* for TiO$_2$ films,[3] and studied the dynamics of transients in undoped Fe$_2$O$_3$ films.
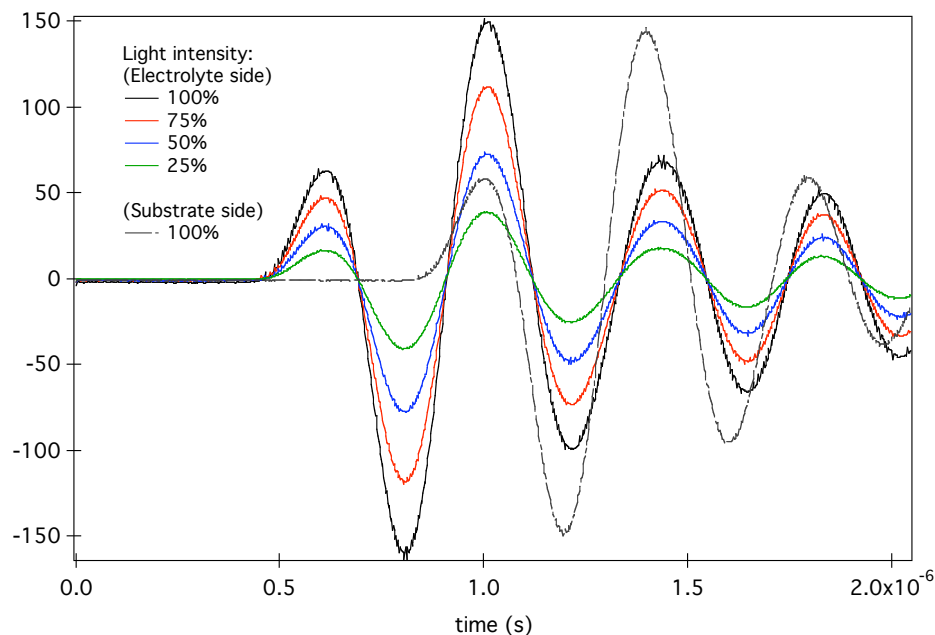
Figure 2. Acoustic waves obtained with a nanostructured Fe_2O_3 film, upon laser irradiation (532 nm) and using a 2.25 MHz transducer. Laser intensity effect (colours) and comparison of waves obtained with irradiation from film side (full lines) and substrate side (dashed line) are shown.

Main results obtained

Fast electron-hole recombination is one of the factors responsible for the low efficiency of photocatalytic water splitting using Fe_2O_3 photoanodes. This aspect is usually associated to short hole diffusion length, low absorption coefficient and slow water oxidation at the semiconductor surface, which decrease the efficiency of charge separation. Nevertheless, despite the profusion of studies concerning the performance of Fe_2O_3 as photoanodes for water splitting, very little is known about the dynamics of charge carriers in these films, as well as the mechanism of water oxidation at the surface of the electrode.

Following the works of Katoh *et al.* [2] and Tang *et al.* [3] we have explored the transient absorption of undoped Fe_2O_3 films prepared previously by ultrasonic spray pyrolysis.[9] Prior to use, films were heated to 250 ºC for 15 minutes, cooled in air and placed in a sealed quartz cuvette. Experiments were performed in argon atmosphere, argon saturated acetonitrile and an argon saturated mixture of acetonitrile and methanol (50:50 v/v).

Transient absorption spectra of charge carriers in nanostructured Fe_2O_3 were measured by a laser system with resolution in the microsecond-millisecond time window. The setup has been described elsewhere.[3] Excitation source was a PTI GL-3300 nitrogen laser (337 nm, 1.0 Hz, 1ns pulse duration) and a 100W tungsten lamp provided the probe light. A liquid guide was used to direct the laser pulse to the sample and neutral density filters were employed for light excitation dependence studies.

Figure 3 shows the wavelength dependence of photogenerated charge carriers in nanostructured hematite films in Ar saturated acetonitrile. The spectra are characterised by an absorption peak at 550 nm and a small band at 800 nm. The decay kinetics for the two maxima appears to differ slightly, suggesting the presence of different transient species, but this observation needs confirmation. These features are common to the three environments considered in these experiments.
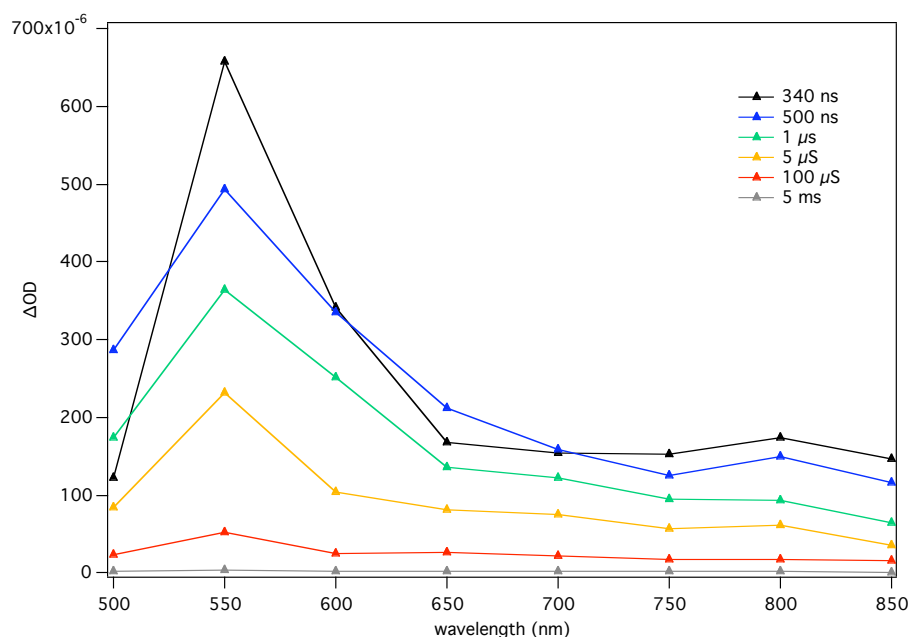

Figure 3. Transient absorption spectra of photogenerated charge carriers in Fe_2O_3 films in Ar saturated acetonitrile, following laser excitation with wavelength of 337 nm and intensity of 470 μJ. Time delays for spectra collection are indicated in the figure.

Unlike for TiO_2 films, the transient absorption profile is unaffected by the presence of methanol (Figure 4) suggesting that this is not an effective hole scavenger for Fe_2O_3. In the three sets of experiments, we failed to discriminate the transient absorption profiles of photogenerated holes and electrons, which indicates that, in order to identify the dynamics of charge carriers, more effective scavengers need to be used.

Illumination direction has no effect on the decay kinetics. The lower transient absorption observed when the film is illuminated through the substrate is attributed to a filter effect due to the FTO layer on the glass.

The results presented here are preliminary but, to the best of our knowledge, show for the first time the transient absorption spectra for a film of nanocrystalline Fe_2O_3, and open new possibilities towards the understanding of charge carrier dynamics and the mechanism of water oxidation in these systems. Currently we are studying the transient absorption of undoped iron oxide films prepared by different methods (namely APCVD[9]) in order to understand the effect of structure and morphology on the dynamics of photogenerated charges.
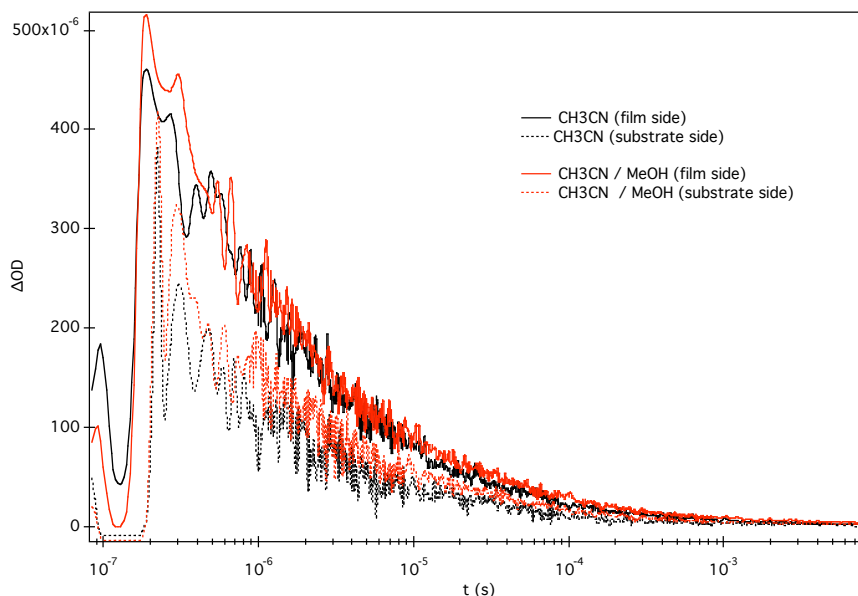
Figure 4. Temporal profile of transient absorption spectra of photogenerated charge carriers in Fe_2O_3 films, in Ar saturated acetonitrile (black) and acetonitrile/methanol (50:50 v/v) (red), at the absorption maxima (550 nm). Illumination from the film side (full lines) and substrate side (dashed lines) is compared.

Future collaboration with the host institution/Projected publications

The initial work plan for this short visit focused on the discussion of the application of TR-PAC to the study of recombination processes in DSSC, and optimisation of experimental setup and conditions in order to separate different non-radiative processes occurring in the cells upon laser excitation. This objective was fully achieved and a new setup for TR-PAC experiments on DSSC is already in use.

Future visits to both groups are planned in order to continue the collaboration in the work related to dye sensitised solar cells and water splitting. In particular, transient absorption spectroscopy studies on Fe_2O_3 films will be continued, where different hole and electron scavengers will be used. The effect on recombination dynamics of different film dopants and surface catalysts (like cobalt) will also be addressed. These results will be compared with the ones obtained in TR-PAC experiments. The publication of these studies is projected.

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