

Ultrafast spectroscopy of charge carrier dynamics at the interfaces of organic absorbers bound to nanostructured ZnO and TiO₂ electrodes

Jodi Szarko, Antje Neubauer, Andreas Bartelt, Klaus Schwarzburg, and Rainer Eichberger

Dynamics of Interfacial Reactions–SE 4, Hahn-Meitner-Institute Berlin, Glienicker Strasse 100, 14109 Berlin, Germany, andreas.bartelt@hmi.de

Interfacial charge transfer lies at the heart of organic-inorganic heterojunction solar cell concepts since the photo-excited electron-hole pair or exciton has to be sufficiently separated at the hetero-interface. At the same time, charge carrier recombination processes with either the oxidized dye or the hole-transporting medium (HTM) have to be suppressed. While dye sensitized solar cells (DSSC) on the basis of colloidal TiO₂ electrodes show high injection and low recombination rates, the use of volatile electrolytes containing e.g. the iodide/triiodide redox system or ionic liquids represent a conceptual problem. ZnO allows for low-temperature wet chemical generation of ordered nanostructures like nanorods [1,2], which besides exhibiting faster electron transport [3] simplify the replacement of the traditional electrolytes by organic HTMs, e.g. polymers, due to a defined and open morphology.

Metal-free organic perylene derivatives are used as absorbers, which exhibit high quantum yields, high photochemical stability and are suited for synthetic modifications to improve absorption coefficients and overlap with the sun's spectrum. Different anchor groups will allow for the optimization of electron injection rates. The injection to recombination ratio can be controlled by spatial separation of the injected electron and the hole through functionalized spacer or electron cascading donor-acceptor groups.

It is known that contrary to TiO₂ surfaces the sensitization of ZnO surfaces can lead to dye aggregation due to the formation of Zn²⁺-dye complexes, which can significantly reduce the injection efficiency [4]. The number of carboxylic acid (COOH) anchor groups plays a crucial role here. Also, exciplexes can form as intermediates during the injection, which lead to prolonged injection rates [5,6]. In this contribution, we investigate the photo-induced electron injection process of the model perylene chromophore 2,5-Di-*tert*-butyl-perylene into ZnO and compare two different anchor/bridge groups (a) propionic acid, and (b) acrylic acid, which have both single carboxylic anchors. Perylene allows for monitoring the charge transfer dynamics by detection of the spectrally separated neutral, excited and cationic state transient absorption [7]. The pump-probe experiment employs a visible pump pulse of sub-15 fs fwhm duration supplied by a low power non-collinear optical parametric amplifier (NOPA) operating at 150 kHz repetition rate, and a white light continuum probe pulse. During the experiments, the sensitized metal-oxide films are kept under UHV conditions.

We find strong evidences of an electron injection into ZnO without the formation of exciplexes or other intermediates: (a) The cationic state absorption increases monoexponentially after excitation of the dye by the pump pulse, which indicates a single injection process between only two species. (b) The cationic rise time corresponds well with the decay time of the excited state absorption, rendering it unlikely to have additional states involved in going from the excited state to the cationic state. (c) An isosbestic point is observed in the transient probe spectra, further indicating the mere presence of only two states during the electron transfer reaction [8].

In all cases, electron injection is fast and takes place within 200 – 300 femtoseconds into colloidal ZnO and 10 – 60 femtoseconds into colloidal TiO₂. The unsaturated bond of the acrylic acid leads to faster injection than in the case of the propionic acid anchor/bridge group due to the delocalization and direct coupling to the ZnO surface. The recombination rate however stays mostly constant for all dye/electrode combinations. Starting with one double bond in the acrylic acid anchor/bridge group (chromophore b), a set of perylene derivative sensitizers with increasing spacer length up to five double bonds was investigated in respect to injection and recombination rates into TiO₂. While the electron injection is equally fast for all chromophores, the recombination times of the injected electron back into the oxidized chromophore tend to increase with spacer length of the side group. This demonstrates the possibility to retard geminate recombination while keeping with a fast injection by spatially separating electron and hole after charge separation. In regard to prolonging the recombination between injected electron and hole transporting medium (HTM) this result is also very promising, especially since in the case of solid state HTMs this recombination can be very fast [9].

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