

Influence of chemical environment on electron transfer dynamics of organic absorbers bound to nanostructured TiO₂ electrodes

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The performance of hybrid organic-inorganic and dye sensitized solar cells can be influenced by controlling the heterojunction interface energetics resulting in a beneficial change in the open-circuit voltage [1]. Also, the charge transfer dynamics across the interface will be affected and can have an impact on the net yield. Engineering the interface energetics can improve the charge separation and decrease the back recombination of split carriers. For example, changing the pH [2, 3] or introducing surface dipoles and interface modifiers [4] can lead to a better electronic level alignment and decrease the cross section for interfacial charge recombination. Still, fundamentally little is known about the charge transfer dynamics induced by interface modification because the designated experimental signals are mostly unavailable from electrical measurements using setups that require completely assembled cells. Here, we will focus on the investigation of dynamical phenomena in model dye-sensitized systems immersed in different model chemical environments that can be easily interchanged using a special measuring chamber. The rate constants for charge injection from a photo-excited molecular donor into the wide band gap semiconductor of a dye sensitized solar cell are governed by the electronic coupling and the energetic position of the injection level with respect to the conduction band minimum reflecting the density of available acceptor states. It is known that a reduction of the latter can considerably slow down the charge injection process [5]. The recombination dynamics is further influenced by trap states of different nature lying below the conduction band edge of nanocrystalline TiO₂. Coadsorbates on the semiconductor surface can shift the conduction band due to their electrostatic interaction with the surface, affecting the interfacial charge transfer. They can also modify the surface trap density leading to a change in the recombination rates [6].

We have investigated the effect of the presence of selected chemical species on the ultrafast electron injection and charge recombination dynamics of model organic absorber dyes bound to colloidal TiO₂ using time-resolved pump-probe spectroscopy with 20-fs time resolution. The ultrafast injection and recombination processes were recorded by transient absorption of the photo-excited and cationic dye states using a super-continuum probe spectrum. Two identical perylene derivatives bound to the TiO₂ surface either via propionic or acrylic acid anchor/bridge groups exhibit completely different charge transfer dynamics in ultrahigh vacuum (UHV) due to their respective weak and strong couplings to the TiO₂ surface [5]. We find that the injection dynamics for these molecules is very sensitive to the variation of the chemical environment. Starting with a dye-sensitized TiO₂ film under vacuum conditions, the electron injection is slowed down as a chemical environment is introduced. Going from different inert atomic and molecular gases to different polar solvents, the ultrafast sub-50 femtosecond injection process originally found under UHV conditions is subsequently retarded up to two orders of magnitude. Thereby, the injection dynamics correlates with the degree of polarity and the density of the chemical species: The more polar and the denser the adsorbing species, the slower the injection process. In Fig. 1a, this behaviour is shown for the propionic acid coupled system. The electron injection slow-down is consistent with an electronic shift of the oxide conduction band to more negative values, decreasing the gap between conduction band minimum and injecting molecular level (Fig. 1b).

The injection dynamics controlled by the different anchor/bridge groups of the examined perylene derivatives are differently affected by the coadsorbates. Under vacuum conditions an injection rate ratio, $R_{\text{inject}} = \tau_{\text{Acryl}}/\tau_{\text{Prop}} \sim 0.18$ was previously determined in high temporal resolution experiments [7] and explained by the presence of an ultrafast partial direct optical charge transfer specifically for the acrylic acid system. For Ar and N₂, we find an injection rate ratio $R_{\text{inject}} = \tau_{\text{Acryl}}/\tau_{\text{Prop}} \sim 0.6$ suggesting a decrease of the direct optical electron injection pathway due to even a very weak chemical environment. As the surface dipole interactions increase with the polarity of the environment, the injection rates of the two examined

molecular absorbers become closer and the effect of the electronic coupling difference washed out. In the case of liquid Tetrahydrofuran, the most polar compound, we find $R_{\text{inject}} \sim 0.85$.

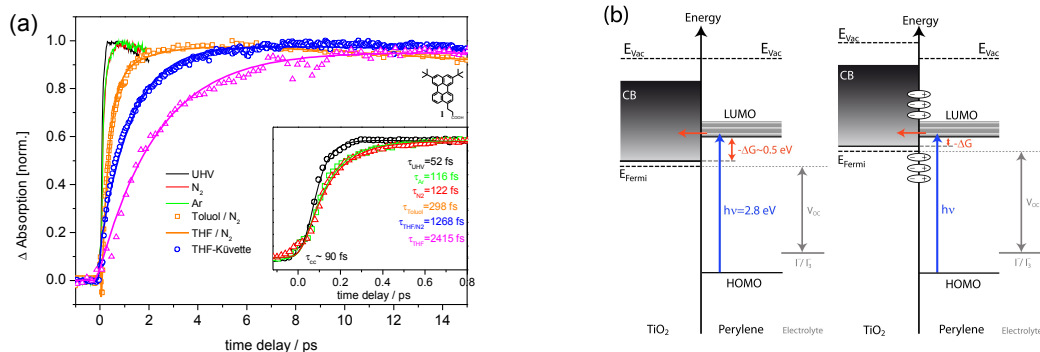


Fig. 1: (a) Electron injection dynamics from 2,5-Di-tert-butyl-perylene-propionic acid into TiO₂ under the presence of various chemical environments. Plotted is the dye cation transient absorption at $\lambda_{\text{probe}} = 570$ nm after excitation with $\lambda_{\text{pump}} = 440$ nm. The introduction of inert Ar and N₂ gases slows down the injection by about a factor 2, with N₂ interacting slightly stronger (insert). Toluene and Tetrahydrofuran (THF) vapour (orange and blue) and THF liquid (pink) reduces the injection speed further. The dipole moment of Tetrahydrofuran is about four times that of Toluene. All transients can be fitted by mono-exponential rise functions. (b) Left: Energy diagram of the inorganic-organic heterojunction. The density of states in the TiO₂ conduction band increases with energy. Right: Band edge shift due to dipolar surface coadsorbates increases V_{oc} and reduces the driving force for electron injection ($-\Delta G$) associated with a decreased TiO₂ density of states.

In comparison to the injection, the recombination effect of the coadsorbates is less pronounced, but it also leads to a retardation of the back transfer of injected electrons with increased coadsorbate polarity (Fig. 2). This is most pronounced for the early time window where recombination under vacuum conditions is very fast and leads to a 50% loss of injected electrons within 100 ps. The recombination in this case shows multiphasic and non-exponential dynamics with characteristic time constants from a few picoseconds to a few nanoseconds, which can be attributed to an energetic and spatial distribution of trap states. As the coadsorbate polarity is increased, the recombination dynamics becomes more mono-exponential and, as in the case of the injection, the influence of the electronic coupling on the recombination dynamics is reduced.

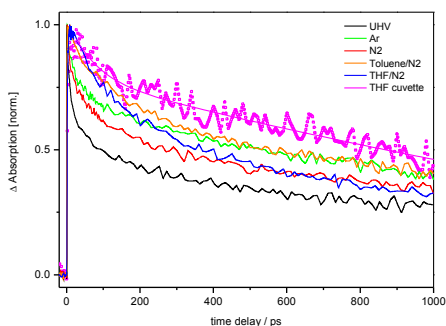


Fig. 2: Back transfer dynamics of injected electrons into the cationic 2,5-Di-tert-butyl-perylene-acrylic acid absorber. The cationic transient absorption recorded at $\lambda_{\text{probe}} = 590$ nm depicts a highly non-exponential recombination dynamics in the vacuum case. The recombination rate decreases as the coadsorbate dipole moment is increased, and the dynamics approaches a mono-exponential behaviour.

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