Excited State Dynamics of Electron Injection and Hole Shift in a Dye-Sensitized Photocatalytic System

C. Govind[1], D. Romito[2], V. Nikolaou[2], G. Charalambidis[3], S. Diring[2], A. Coutsolelos[3], F. Odobel[2], E. Vauthey[1]*

[1]Department of Physical Chemistry, University of Geneva, Switzerland, [2]Nantes Université, CNRS, CEISAM, France, [3]Laboratory of Bioinorganic Chemistry, Department of Chemistry, University of Crete, Greece

Abstract : The development of renewable and environmentally friendly energy sources is of key importance for a sustainable society[1]. In this context, dye-sensitized photo electrocatalytic cells (DSPECs) comprising an organic photosensitizer (PS) co-adsorbed with a hydrogen evolution catalyst (HEC) onto an n-type semiconducting (n-SC) nanoparticles (NPs) is a promising strategy. However, a better understanding of the photoinduced charge transfer process is necessary to improve the photocatalytic efficiency of DSPECs. Ultrafast spectroscopy is a highly powerful technique to assess the dynamics of photogenerated carriers in the photocatalytic systems. Here, the electron injection, hole shift and charge recombination dynamics of a DSPEC system with a dye chemisorbed on TiO_2 NPs and associated with a TEMPO (2,2,6,6-tetramethyl-1-piperidine N-oxyl) catalyst for the selective oxidation of alcohol into aldehyde have been studied using steady-state and time-resolved spectroscopies. Upon visible excitation of the PS, the electron is injected from the excited state of the dye to the conduction band (CB) of the n-SC on the fs-ps time scale. Femtosecond transient absorption measurements allow to identify the generation of the radical cation of the dye after the fast electron injection. Further, the hole shift from the dye cation to TEMPO catalyst and the regeneration of the dye are probed by nanosecond transient absorption spectra. Transient absorption in the mid-infrared region is used to probe the absorption of the injected electrons in the conduction band of the n-SC. To understand the hole diffusion within the dye molecules, transient absorption anisotropy measurements are also performed for the dyad on TiO_2 on the fs-ps and ns-ms time scales. This study reveals that the functionalization of the dye with TEMPO catalyst could lead to a more efficient photocatalytic system.

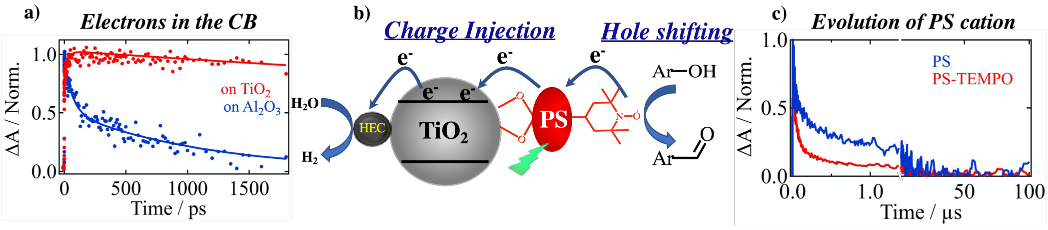

Fig. 1 a) The IR TA dynamics of electrons in the CB of TiO_2 and Al_2O_3 after electron injection from the dye , b) schematic representation of the working processes occurring in the DSP system and c) TA dynamics of the radical cation of the dye after photoexcitation.

References

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