

Electron Transfer in a Donor/Acceptor System Coupled to the Surface of Semiconductor Nanoparticles: Direct Electron Transfer vs. Electron Transfer Through Surface

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Introduction

Interfacial electron transfer (ET) between molecular adsorbates and semiconductor nanomaterials has attracted much interest during the past years. In many applications, such as water purification [1], solar energy conversion [2], and molecular electronics [3], interfacial ET plays a key role. A detailed description of this process is complicated by the presence of surface states and structural inhomogeneities of systems [4-6].

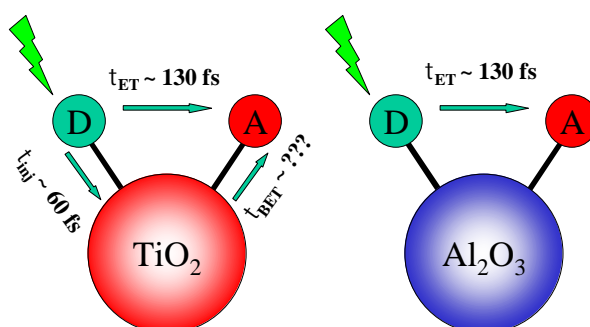


Fig. 1. Schematic representation and dynamics of the photophysical processes for a molecular donor/acceptor pair coupled to the surface of semiconductor nanoparticles.

A composite model system which consists of a molecular donor/acceptor pair coupled to the surface of semiconductor nanoparticles (Fig. 1) has been proposed to study the contribution of the surface trap states and their influence on the ET processes in the dye/semiconductor system. A similar system has been previously used for the construction of a new type of photochromic device, which is based on ET process involving a donor/acceptor pair coadsorbed onto the surface of nanocrystalline TiO_2 [7]. The alizarin molecule has already been established as suitable electron donor [4-6] and different derivatives of N,N' -dimethyl-4,4'-bipyridinium (methylviologen) [8] can serve as electron acceptor.

Results and Discussion

TiO_2 , and Al_2O_3 nano-structured films were prepared from colloidal nanoparticles in acidic solution (5-10 nm in diameter). As an electron donor we used alizarin (purity 97%, Aldrich). An electron acceptor (phosphonated derivative of viologen (PV^{2+})) has been synthesized in the laboratory of Dr. J. E. Moser. The experimental setup used for the transient absorbance measurements was previously described [6]. The desired excitation pulses (480 nm, 20 fs) were obtained from a home built nonlinear optical parametric amplifier. The samples were probed in the visible (347–675 nm) and mid-IR (5.1–5.5 μm) spectral regions.

In order to study the intrinsic ET in the donor/acceptor couple, the Al_2O_3 film was used as a bearing substrate. The coupling of the dyes should be similar in Al_2O_3 and TiO_2 , but in Al_2O_3 any electron injection into the semiconductor is prevented due to its much higher band gap ($\sim 8 - 9$ eV). A complete set of the transient absorbance data obtained for the alizarin sensitized Al_2O_3 film in the visible spectral range is shown in Fig. 2a. Here, mainly the relaxation of the alizarin excited state via radiative processes was observed. The three dimensional plot of the alizarin/ Al_2O_3 system (Fig. 2a) consists of three dominant characteristics: the excited state absorption (ESA) in the spectral range from 350 to 580 nm, the stimulated emission (SE) for the probe wavelengths longer than 580 nm and the ground state bleach (GSB) with a maximum at $\lambda_{\text{probe}} \approx 480$ nm, that is seen as a gap in the ESA band. Finally, the alizarin/ Al_2O_3 system reflects the simple relaxation of the excited state of coupled alizarin.

Additional coupling of the electron acceptor PV^{2+} to the alizarin sensitized Al_2O_3 film leads to significant changes in the photoinduced dynamics, which become evident from the comparison of the respective 3D plots in Figures 2a and 2b. First of all, the negative absorbance difference in the red spectral region, which was assigned as the SE of alizarin, disappears completely. Instead of SE a positive difference signal is developed in the first 200 fs. The absence of the stimulated emission is in agreement with a complete quenching of the alizarin

fluorescence observed upon addition of PV^{2+} . Moreover, at the same time two absorption bands with maxima at 400 and 600 nm (maxima of the absorption bands of monoreduced $PV^{\bullet+}$ radical) were formed.

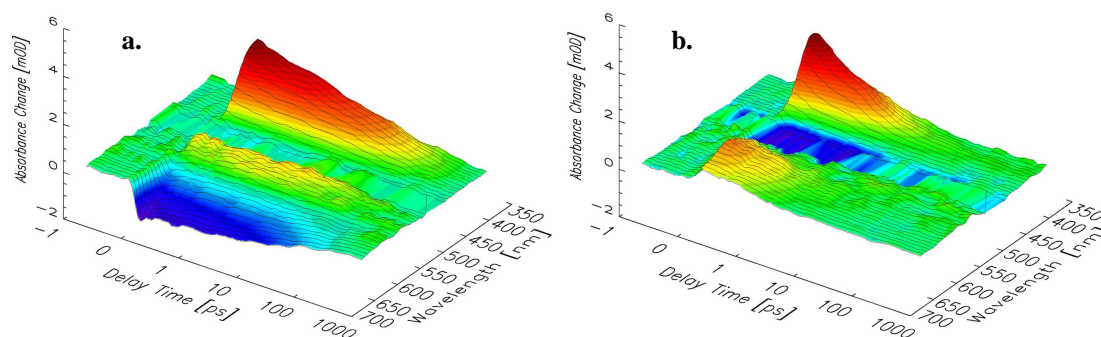


Fig. 2. Transient absorption data of alizarin sensitized Al_2O_3 film a.) without electron acceptor PV^{2+} and b.) with PV^{2+} . The time scale is plotted linear from -1 to 1 ps and logarithmic thereafter.

The effects of the fluorescence quenching observed by steady state spectroscopy and absence of SE in time-resolved experiments as well as appearance of the new absorption bands unambiguously indicate that intrinsic ET ($S^* + PV^{2+} \rightarrow S^+ + PV^{\bullet+}$) in the donor/acceptor couple proceeds on the ultrafast time scale. A global fit analysis of the experimental data results in the intrinsic ET time of ~ 130 fs.

In the case of TiO_2 semiconductor as the bearing substrate, the electron injection from photoexcited alizarin to the TiO_2 conduction band ($S^* \rightarrow S^+ + e_{CB}^-$) has to be taken into account. A careful analysis of the time resolved experimental data of alizarin/ PV^{2+} pair adsorbed onto a TiO_2 film shows that initially generated photoexcited state of alizarin relaxes during the first 50 fs. During this time formation of the monoreduced $PV^{\bullet+}$ radical and injection of the electron to the conduction band of TiO_2 were observed. Moreover, additional transient absorbance experiments in the mid-IR spectral region were done in order to unambiguously observe the possible reduction of the electron acceptor PV^{2+} by the electron in the conduction band ($PV^{2+} + e_{CB}^- \rightarrow PV^{\bullet+}$). These measurements show no hints of ET from the conduction band of TiO_2 to PV^{2+} for $t_{delay} > 300$ fs, where 300 fs is the resolution of our experimental setup in the mid-IR spectral range. These results are in some disagreement with the experimental results for PV^{2+}/TiO_2 , where efficient and ultrafast ET of the photoexcited electron from the conduction band of TiO_2 to PV^{2+} was observed.

Conclusions

A detailed analysis of the photophysical processes in the photoexcited donor/acceptor pair coupled to the surface of different metal oxide mesoporous films was performed. From a comparison of the time resolved data for alizarin/ TiO_2 and alizarin/ TiO_2/PV^{2+} coupled systems we can conclude that ET between the molecular donor and acceptor coadsorbed onto a TiO_2 surface proceeds rather directly through “space” than through surface of the bearing semiconductor.

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4. References

- [1] T.X. Wu, G.M. Liu, J.C. Zhao, H. Hidaka, N. Serpone, *J. Phys. Chem. B* 103, 4862 (1999).
- [2] B. O'Regan, M. Grätzel, *Nature* 353, 737 (1991).
- [3] A. Nitzan, M.A. Ratner, *Science* 300, 1384 (2003).
- [4] R. Huber, S. Sporlein, J.E. Moser, M. Grätzel, J. Wachtveitl, *J. Phys. Chem. B* 104, 8995 (2000).
- [5] R. Huber, J.E. Moser, M. Grätzel, J. Wachtveitl, *J. Phys. Chem. B* 106, 6494 (2002).
- [6] V.V. Matylitsky, M.O. Lenz, J. Wachtveitl, *J. Phys. Chem. B* 110, 8372 (2006).
- [7] M. Biancardo, R. Argazzi, C.A. Bignozzi, *Inorg. Chem.* 44, 9619 (2005).
- [8] T. Watanabe, K. Honda, *J. Phys. Chem.* 86, 2617 (1982).