On the kinetics and mechanism of light-induced electron transfer at the semiconductor/electrolyte interface

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Kinetics of photoinduced electron transfer at the solid–liquid interface is receiving a lot of attention which is particularly directed to the charge injection process occurring in the dye-sensitization of large bandgap semiconductors. The back electron transfer from the conduction band of the solid to the oxidized state S^+ of the sensitizer is as well quite important for photochemical conversion, since it competes kinetically with charge separation. The detailed mechanism of these reactions and the rationalization of their rates with respect to current electron transfer theories are still subjects of discussion. Yet, results obtained with model systems constituted of dye-sensitized nanocrystalline TiO_2 can be used to assess some important points.

The kinetics of charge injection from the excited state of the redox sensitizer coumarin-343 to the conduction band of aqueous colloidal titanium dioxide has been measured by fluorescence up-conversion. The rate constant was found in this case to be as high as 5.6×10^{12} s^{-1} [1]. Such an electron transfer process taking place within 180 fs appeared hardly compatible with nuclear reorganization of the medium, and indeed the general applicability of the Marcus theory to charge injection processes was questioned in the workshop. Recently, however, experimental measurements using the same coumarin dye have demonstrated in conjunction with computer simulations that an inertial solvent response on a time scale faster than 50 fs can dominate aqueous solvation dynamics [2]. The existence of this ultrafast librational reorganization component implies that solvent friction still plays an important role in the sensitization of semiconductors, like in many electron transfer processes [3].

In comparison to the forward reaction, recombination of conduction band electrons with oxidized dye species adsorbed on the surface of the semiconductor is found to be extremely slow. Whereas charge injection from efficient sensitizers is typically observed in the ps time scale, back electron transfer generally occurs in microseconds. In the model case of coumarin-343, the recombination rate constant was found to be 2×10^6 s^{-1} [4], which is more than 6 orders of magnitude lower than that of the corresponding forward process. This slow event can in most cases

be intercepted by the reaction of the oxidized dye with a suitable electrolyte, leading to the very efficient charge separation obtained in particular in dye-sensitized regenerative photoelectrochemical cells [5]. Whether electron transfer occurring through the solid–liquid interface proceeds directly from free electrons in the conduction band or is mediated by surface states is an important clue in the understanding of the mechanism and kinetics of the reaction.

The role of trapping sites in TiO_2 nanocrystalline porous electrodes could be clearly identified by examining the bias potential dependence of the recombination rate [5]. In the case of a carboxylated $Ru(bipy)_3$ sensitizer, the decay of about two-thirds of the initial concentration of S^+ formed in a laser pulse has been found to be potential dependent. The last third of the signal follows a first order kinetics with a rate constant $k = 3 \times 10^6$ s^{-1}, essentially independent of the applied bias and identical to that observed with colloidal dispersions of the oxide. This peculiarity of sintered mesoscopic membranes can be rationalized in terms of trapping of injected electrons at grain-boundaries and at sites that are absent in dispersed particles, where the reaction in presence of surface-complexing dyes is believed to involve free conduction-band electrons or carriers that are poorly localized in shallow traps [6].

In nanodispersed materials where there is hardly any space charge layer in the solid, the return electron transfer reaction is a thermodynamically well defined process and does not involve medium-dependent surface states. For an optimized sensitizer, the free energy associated to the reaction is close to the value of the dye's excitation energy and ranges between 1 and 2 eV. Such a large driving force should make the kinetic of the process fall deep in the inverted region. Experimental evidence for this behaviour in heterogeneous systems has been brought recently [4,7].

The dynamics of the back electron transfer from the conduction band of TiO_2 nanoparticles to various sensitizer cations was investigated and was shown to be essentially insensitive to temperature [4], as well as to medium changes [8]. A pseudo-activationless behaviour is indeed predicted in the inverted region by the semi-classical theory of non-adiabatic electron transfer, provided that part of the reorganization takes place through vibrational modes that are treated quantum mechanically. Fitting of experimental data yields values of the coupling matrix element $|V|$ of the order of only a few cm^{-1}. This electronic coupling is obviously much weaker than in the case of charge injection where the electronic interaction between the sensitizer's LUMO and the Ti^{IV}-3d orbital manifold of the semiconductor is nearly optimized. Besides, the lack of an effect of the medium suggest that the Franck–Condon barrier to electron transfer is dominated by high frequency modes which make its rate of crossing mainly controlled by nuclear tunnelling.

References

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