Interfacial Charge- Transfer from Organic Dye Molecules: Role in Thin Films, Organic Heterojunctions and Composite Materials

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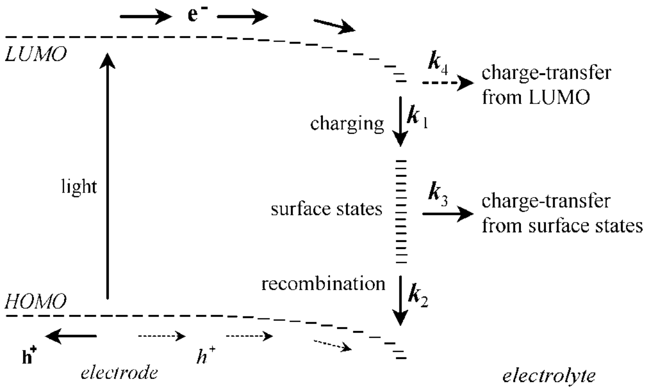
Interfacial states that were established in contacts of molecular semiconductors with liquid electrolytes or in contacts with another organic semiconductor as a solid film were analyzed by photoelectrochemical experiments and by photoelectron spectroscopy. A crucial role of such states was indicated in the interfacial charge transfer and recombination kinetics of light-induced charge carriers and also in the energetic alignment in the solid contacts. The role of chemical interactions in the establishment of these interfacial states was investigated by use of different reaction partners, i.e., different redox couples in the electrolyte contacts and molecular semiconductors of different ionization potential in the solid contacts. Implications of these results for the use of organic semiconductor thin films in organic heterojunctions and of dye molecules in dye- sensitized solar cells are discussed [1].

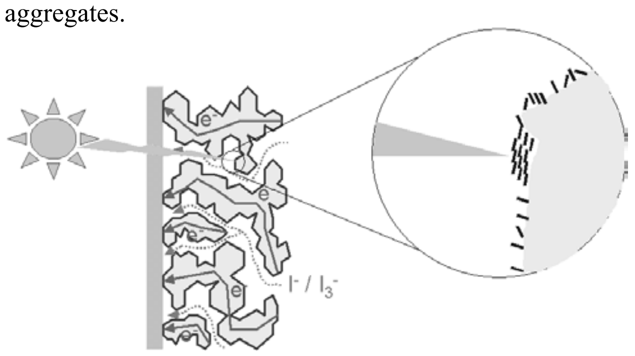
Vapour- deposited thin films were studied in photoelectrochemical reactions [2]. The films were characterized as molecular semiconductors. Time-resolved photocurrent measurements in the ms- regime and intensity- modulated photocurrent spectroscopy (IMPS) in the range 0.2 Hz - 100 kHz showed charging and discharging of trap states at the electrode surface. The kinetics of charge- transfer and recombination of charge-carriers produced by light- absorption in the organic semiconductors were investigated.



Charging of the interfacial states at these films either represented an intermediate step of charge transfer or solely a recombination pathway. Implications of the results for the use of molecular semiconductors as active materials in photoelectrochemical or solid photovoltaic junctions are discussed.

The photoelectron spectroscopy analysis served to determine the alignment of electron energy levels in organic heterojunctions. Ionization by ultraviolet light (UPS) was used for this purpose. Interfacial trap states were directly detected by appearance of an interface dipole among different organic semiconductors in a heterojunction. A redox gradient across the junction as well as chemical interactions of the molecules could be detected as origin for these states [3].

In composite electrodes of dyes and ZnO deposited by electrochemical self- assembly a strong difference was seen in the photoelectrochemical efficiency when either monomeric or aggregated forms of dyes were present [4,5]. Monomers generally showed a superior quantum efficiency of light- induced electron transfer to ZnO whereas aggregates seemed to have a better coupling to the electrolyte at the price, however, of a clearly increased recombination probability within the aggregates.



Efficient electrodes could therefore be obtained in particular from those dye molecules for which a high surface concentration could be obtained without intense intermolecular electronic coupling. Molecules that carry bulky substituents hindering electronic coupling have therefore been most successful as sensitizers [6].

The photoelectrochemical work on dye films was performed together with T. Oekermann, now at Gifu University, Japan and N. I. Jaeger at the University of Bremen, Germany. Photoelectron spectroscopy at the organic heterojunctions was performed during research stays in the group of N. R. Armstrong at The University of Arizona, USA. Electrochemical self- assembly and dye-sensitized electrodes are studied jointly with the groups of T. Yoshida and H. Minoura, Gifu University, Japan and of D. Wöhrle, University of Bremen, Germany. Financial support by Deutsche Forschungsgemeinschaft, Volkswagen- foundation, Hanse Science Center and Fonds der Chemischen Industrie is gratefully acknowledged.

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