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Dye-Sensitized Approaches to Photovoltaics

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Sensitization of wide band-gap semiconductors to photons of energy less than the band-gap is a key step in two technically important processes - panchromatic photography and photoelectrochemical solar cells. In both cases the photosensitive species is not the semiconductor - silver halide or metal oxide - but rather an electrochemically active dye. The gap between the highest occupied molecular level (HOMO) and the lowest unoccupied molecular level (LUMO) is less than the band-gap of the semiconductor with which it is associated. It can therefore absorb light of a wavelength longer than that to which the semiconductor itself is sensitive. The electrochemical process is initiated when the dye molecule relaxes from its photoexcited level by electron injection into the semiconductor, which therefore acts as a photoanode. If the dye is in contact with a redox electrolyte, the negative charge represented by the lost electron can be recovered from the reduced state of the redox system, which in return is regenerated by charge transfer from a cathode. An external load completes the electrical circuit. The system therefore represents a conversion of the energy of absorbed photons into an electrical current by a regenerative device in every functional respect analogous to a solid-state photovoltaic cell. As in any engineering system, choice of materials, their optimization and their synergy are essential to efficient operation. While a semiconductor-electrolyte contact is analogous to a Schottky contact, in that a barrier is established between two materials of different conduction mechanism, with the possibility of optical absorption, charge carrier pair generation and separation, it should be remembered that the photogenerated valence band hole in the semiconductor represents a powerful oxidizing agent. Given that the band-gap is related to the strength and therefore the stability of chemical bonding within the semiconductor, for narrow-gap materials the most likely reaction of such a hole is the photocorrosion of the semiconductor itself. However, only relatively narrow band-gap materials have an effective optical absorption through the visible spectrum, towards and into the infra-red. Materials with an optimal band-gap match to the solar spectrum, of the order of 1.5eV, are therefore electrochemically unstable. A stable photoelectrochemical cell, without some process of optical sensitization, and necessarily using a wide-gap semiconductor is sensitive only to the ultra-violet limit of the visible spectrum. Over recent years a suitable combination of semiconductor and sensitizer has been identified and optimized, so that now a solar spectrum conversion efficiency of over 11% has been verified in a sensitized photoelectrochemical device. One key to such an efficient system is the suppression of recombination losses. When the excited dye relaxes by electron loss, the separated charge carriers find themselves on opposite sides of a phase barrier - the electron within the solid-state semiconductor, the positive charge externally, in association with the dye molecule. There is no valence-band involvement in the process, so the system represents a majority-carrier device, avoiding one of the major loss mechanisms in conventional photovoltaics. In consequence also a highly-disordered, even porous, semiconductor structure is acceptable, enabling surface adsorption of a sufficient concentration of the dye to permit total optical absorption of incident light of photon energy greater than the HOMO-LUMO gap of the dye molecule. The accepted