

Electrical and chemical potential distribution in dye-sensitized and similar solar cells in the dark and under illumination

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Even though the first publication of a high efficiency dye sensitized solar cell (DSSC) was more than a decade ago [1], we still lack a commonly accepted theory as to how such cells work. Two basic ideas came up over the last decade, one based on the different kinetics of charge generation and recombination processes, often called the ‘kinetic model’ [2] and the other, [3] based on a built-in electric potential difference, $\delta\phi$ (in the dark), known as the ‘junction model’. It is agreed that charge separation takes place at the dye/TiO₂ interface. While the kinetic model assumes that the charge is spatially *and* energetically separated, the junction model states that there is *only* spatial charge separation while the electrons are still energetically bound to some extent to counter ions of the electrolyte solution (usually Li⁺) during diffusion through the porous TiO₂ structure. Therefore the junction model postulates an electric field at the TiO₂/TCO (transparent conducting oxide) interface, which acts to separate the electron from the counter ions of the electrolyte. A field at the interface can occur because of a difference between the TCO substrate work function and the electrolyte redox potential. Such a difference creates an electric potential drop, $\delta\phi_{bi}$, at the TCO/electrolyte interface. Because of the low intrinsic doping density and the small particle size the TiO₂ cannot screen the electric potential of the surrounding electrolyte and the TCO substrate. Thus, $\delta\phi_{bi}$ at the TiO₂/TCO interface is determined by the substrate and electrolyte potential rather than by the work function of the TiO₂. In the junction model this $\delta\phi_{bi}$ is essential for (energetic) charge separation and is the only driving force for electron collection at the TCO substrate.

Charge separation We will give a full picture of the electric (ϕ) and chemical potential (μ^e) distribution of an electron and discuss it in terms of driving forces for charge redistribution, the fundamental requirement for photovoltaic action [4]. We argue that charge separation takes place at the dye/TiO₂ interface, mainly because, after dye photoexcitation, the electron (in the LUMO) is closer in energy to the vacuum level than the TiO₂ conduction band (CB). In the absence of an electric field (straight local vacuum level across the TiO₂/dye phase boundary), a necessary condition for electron injection is that a chemical potential gradient, $\nabla\mu^e$, is present. In addition to this condition very fast electron injection is needed, too [5]. Injection may well be aided by the dipole field of the dye [6]. In this case there will be some electric potential gradient, $\nabla\phi$, contribution to the charge separation process, because of more efficient electron injection. We underline that the charge separation process is highly efficient because the rate of electron injection from dye into the TiO₂ is much faster than that of recombination with oxidized dye or electrolyte species.

Electron transport Photo-injected electrons can accumulate in TiO₂ surface states and cause a shift of the TiO₂ bands with respect to the electrolyte redox potential. This shift can be non-uniform throughout nanoparticulate films [7] and thus create some electric potential gradient $\nabla\phi$ inside the TiO₂ network. Experimentally no large band shift was observed [8] and we claim that, while a band shift might improve the V_{oc} , it is not crucial for the basic operation of a DSSC. The general driving force for electron transport is a gradient in its electrochemical potential. Because of the absence of electric fields in most of the porous TiO₂

network, electron transport is driven by $\nabla\mu^e$, i.e., an activity (\sim concentration) gradient). Diffusion models have been applied to model electron transport through the TiO_2 network, assuming ohmic contact at the TiO_2/TCO interface [9]. Because this interface is essential for the ongoing discussion we will focus on the driving forces for electron transfer from the TiO_2 into the TCO.

TiO₂/substrate interface In the simplest approach no electric field in the dark ($\delta\phi_{\text{bi}}=0$) is present at this interface (see Fig. 1b). Upon illumination the μ^e in the TiO_2 is shifted close to the CB. We assume furthermore that electron accumulation inside the TiO_2 is small enough to neglect a shift of the TiO_2 energy bands with respect to E_{redox} [8]. As pointed out earlier [10] electron drift currents occur because of a gradient in the CB level, which can originate from a gradient in the local vacuum level ($\nabla\phi$) and from a gradient in electron affinity ($\nabla\chi$). In the absence of a built in potential $\delta\phi_{\text{bi}}$ at the TiO_2/TCO interface the difference between the TiO_2 and TCO CB level is due to a difference in the electron affinities. This band offset creates a driving force for electron collection at the TCO substrate. From the energy band diagrams in Fig.1b it is intuitively clear that electrons will go from a higher energy level (TiO_2 CB) to a lower one (TCO CB). We assume that the composition of the electrolyte does not change significantly upon illumination of the DSSC so that we can use its E_{redox} as a reference potential. Upon illumination electrons from the TiO_2 CB will accumulate in the TCO substrate, which causes the TCO's electric potential to shift up with respect to the redox potential (see Fig. 1b bottom) [11]. The electrical potential drops over the width of a Helmholtz and diffusion layer where the latter is probably negligible because of the high concentration of Li^+ ions in the electrolyte (usually 0.5 M). Numerical simulations as well as analytical solutions of a simplified geometrical TiO_2/TCO interface structure [12] show that the electric potential drop occurs within the first TiO_2 particle, which is in contact with the substrate, keeping the assumption that the potential inside the TiO_2 particles is determined by its surrounding. We stress here that under our initial assumption of a $\delta\phi_{\text{bi}}=0$ at the interface, the light-induced field creates a barrier for electron collection at the substrate. However, this barrier seems to be thin enough to allow efficient electron tunneling and therefore the contact can be considered as pseudo-ohmic. This model about the interface can now be extended to substrates with work functions different from the electrolyte's E_{redox} and three extreme band structures are depicted in Figs. 1a–c, where the first one shows a built-in potential like proposed in the junction model [3], the second shows a DSSC without built-in potential as discussed above (idealized kinetic model) and the third one shows a built-in potential opposing electron collection. As long as tunneling at the $\text{TiO}_2/\text{substrate}$ interface is efficient all three-device structures will give the same V_{oc} , in agreement with experiments [2].

Conclusions In summary we claim that charge separation occurs because of a chemical potential gradient. Electron collection at the substrate electrode is also mainly driven by a chemical potential gradient and the photovoltage builds up between the substrate and the electrolyte, which subsequently determines the $\delta\phi$ at the $\text{TiO}_2/\text{substrate}$ interface. This $\delta\phi$ creates a barrier, which is thin enough for efficient tunneling and therefore the theoretical upper limit for the V_{oc} is the difference between the TiO_2 CB and E_{redox} . Nevertheless the exact shape of the barrier might be crucial for the rate constants of electron collection at the $\text{TiO}_2/\text{substrate}$ interface and recombination processes at the substrate/electrolyte interface, which might depend on the size of positive ions inside the electrolyte. These rate constants might limit the V_{oc} so that the theoretically maximal V_{oc} ($= E_{\text{CB},\text{TiO}_2} - E_{\text{redox}}$) can not be reached. This provides an alternative explanation of the experimentally observed differences in solar cell performance as a function of the positive ions of the electrolyte [13].

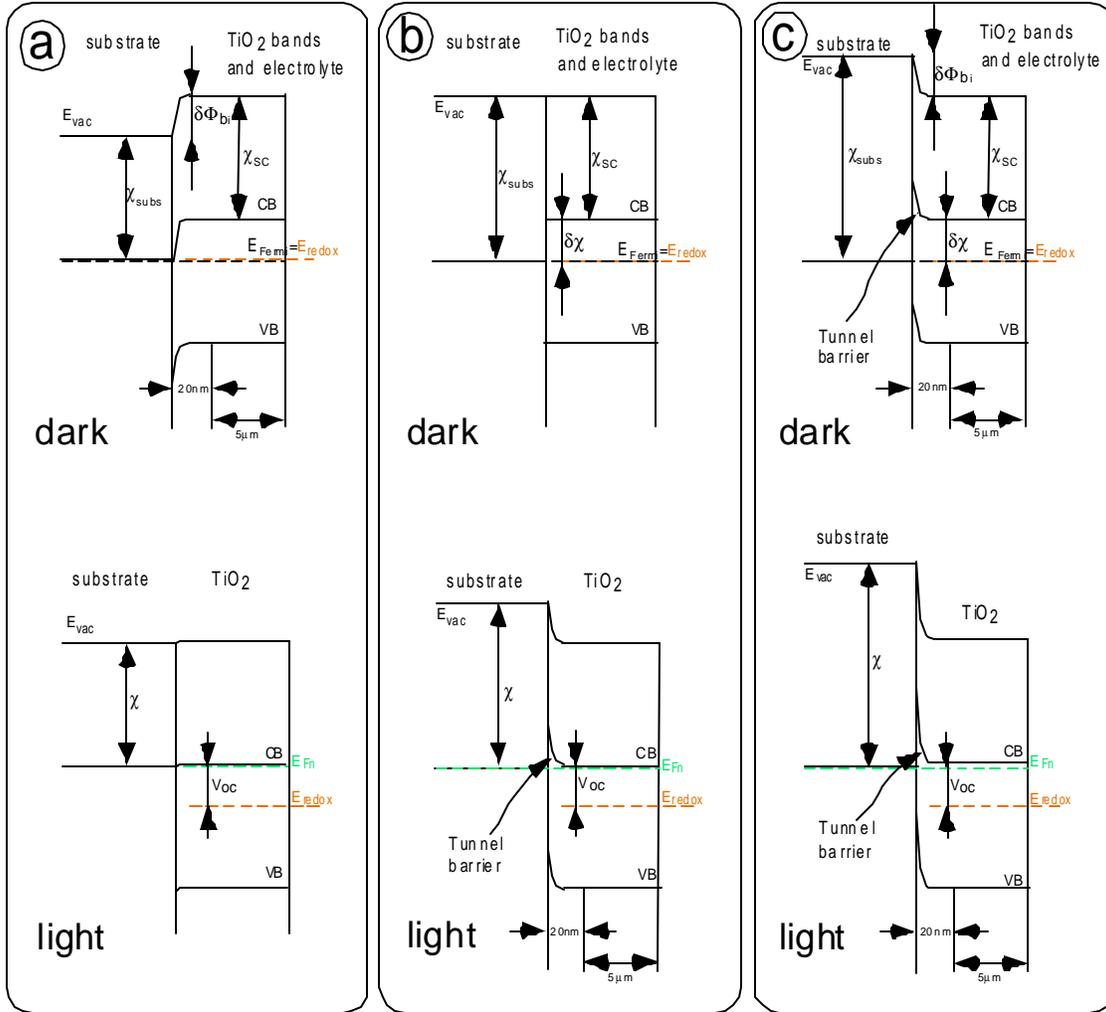


Figure 1:

Three different (schematic) situations of the electronic energy levels at the TiO_2 /substrate interface. We assume that the Fermi level (E_{Fermi}) of the dye sensitized TiO_2 equilibrates with the electrolyte's redox potential (E_{redox}) without any significant electrical potential (ϕ) drop between the two phases so that we can draw one local vacuum level for both materials. For each situation we give the potential distribution in the dark (**top**) and under dye-exciting illumination (**bottom**).

- a- The driving force for electron collection at the substrate electrode is entirely created by a dark, built-in potential, $\delta\phi_{\text{bi}}$, at the TiO_2 /substrate interface (**top**). Upon illumination the electrical potential of the substrate shifts up and the V_{oc} is limited by the initial $\delta\phi_{\text{bi}}$ (**bottom**).
- b- The driving force for electron collection at the substrate electrode is due to a CB offset created by a difference of the TiO_2 and substrate electron affinities ($\delta\chi$, see **top**). The upward shift of the substrate's electric potential upon illumination creates an electric potential barrier within the layer of TiO_2 particles immediately adjacent to the substrate. If tunneling is so efficient that the contact can be regarded as pseudo-ohmic, the maximum V_{oc} is determined by $\delta\chi$ (**bottom**).
- c- The driving force for electron collection at the substrate electrode is created because of the CB offset like in b). An initial electric potential barrier is present at the substrate/ TiO_2 interface (**top**). If this barrier has the same properties as in b), then the maximum photovoltage is given by $V_{\text{oc}} = \delta\chi - \delta\phi_{\text{bi}}$.

The width of the barrier might depend on the radii of the positive ions in the electrolyte and the contact might not be strictly pseudo ohmic so that the solar cell performance will depend on it. E_{Fermi} : Fermi level, E_{Fn} : quasi-Fermi level of the electrons in the TiO_2 ; χ_{subs} : Electron affinity of the conducting substrate; χ_{sc} : Electron affinity of the TiO_2 semiconductor; CB, VB: bottom of conduction band, top of valence band energy levels; E_{vac} : local vacuum level.

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