

# Nanocomposite solar cells: the requirement and challenge of kinetic charge separation

Helmut Tributsch

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**Abstract** Nanocrystalline solar cells promise significant advantages with respect to cost-efficient mass production, since they do not require imprinted chemical potential gradients for charge separation (e.g., electrical fields generated by p, n doping, which should last for one to three decades). They, however, require kinetic charge separation and chemical electronic mechanisms, which rectify photocurrents for energy conversion. Such mechanisms are presently not well understood, since the existing nanosolar cells (dye and polymer solar cells) have evolved largely empirically. It is shown in this paper that function and properties of kinetically determined solar cells can be derived from irreversible thermodynamic principles considering minimum entropy production (or the principle of least action) and involve solid-state electrochemical processes. Based on this model, presently studied nanosolar cells and also the primary photosynthetic mechanism are analyzed to identify the most significant physical–chemical factors involved.

**Keywords** Nanocomposite solar cells · Dye solar cells · Photosynthetic membrane · Kinetic charge separation · Irreversible thermodynamics

## Introduction

During the past one to two decades, nanocomposite solar cells such as dye solar cells (reaching 11–12% solar cell efficiency as small laboratory cells and 6–8% in prototypes) and polymer fullerene solar cells (reaching up to 5.5% efficiency) have received significant attention [1–5]. Major efforts are made on the way of commercializing them, but they still suffer from significant difficulties. They, before all, do not have sufficient long-term stability [5, 6]. They also contain quite expensive components (ruthenium complexes as sensitizers in dye solar cells and fullerenes in polymer solar cells), which can presently not be replaced. And they lack, as this contribution will elaborate, a theory, which explains how they actually work and what properties need to be considered in order to make them more efficient and stable. An understanding of the basic principles involved, however, appears to be necessary for accelerating the presently quite slow learning curve [3, 7].

In order to better understand the problems involved with the development of present nanocomposite solar cells, it is helpful to shortly retrace their experimental history.

Sensitization of photographic emulsions containing semiconductor particles with the help of organic dyes has been known for a long time [8]. The electrochemistry involved in these processes was studied in the 1960s and was based on the emerging knowledge of the electronic structure of semiconductor materials available during that period [9, 10]. The first demonstration that electrical energy could be gained from the phenomenon of spectral sensitizations was made shortly later, both with electrodes sintered from zinc oxide powder and with zinc oxide single crystals [11]. The latter were basically applied as a tool for basic research, since sintered specimens are more difficult to understand due to large grain boundary surfaces. Efforts to

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Dedicated to the 85th birthday of John O'M. Bockris.

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H. Tributsch (✉)  
Department of Solare Energetik, Hahn-Meitner-Institut,  
14109 Berlin, Germany  
e-mail: tributsch@hmi.de

find out how the green chlorophyll molecules in plants are able to convert solar light into electricity played a major role during the early history of the dye solar cell [12]. Its function was demonstrated by operating an electricity-generating dye solar cell with chlorophyll extracted from spinach and with other dyes derived from chlorophyll species. The principles involved were explained on the basis of photoelectrochemical theory [13]. These cells and cells operated with dyes from other classes of compounds turned out to be quite unstable and deteriorated within hours, days, or weeks. During the following two decades, dye solar cells based on sintered oxide powder material were repeatedly studied [14, 15], and an energy conversion efficiency (for illumination within the energy band of the sensitizer) of up to 2.5% was obtained [16]. In order to make ZnO more porous to obtain higher surface areas for dye adsorption, Al was, for example, added in the latter case. However, in all these cases, the instability of the dye solar cells remained obvious, and there was no mayor incentive for developing them for even higher efficiency. In 1991, Grätzel and coworker proposed a significantly more efficient dye sensitization solar cell based on a ruthenium complex-sensitizing  $\text{TiO}_2$ , which he expected to last for 20 years and to become very cost efficient [17]. This attracted a lot of scientific interest and various industrial efforts. However, in spite of a drastic acceleration of research efforts, this type of solar cell is still not being commercialized 17 years later, and it is obvious that the main reason for this is insufficient long-term stability. It is also remarkable that in this so-called Grätzel cell, neither the quite expensive ruthenium complex nor the chemically problematic redox couple  $\Gamma/I_3^-$  could be replaced in spite of extensive efforts. When this was attempted, a significant efficiency and stability loss was typically the observed consequence. Replacement of the  $\Gamma/I_3^-$  system, by hydroquinone/quinone or  $\text{Fe}(\text{CN})_6^{3+/4+}$ , for example, leads to a break down of the solar cell performance. The same happens after addition of catalysts (e.g. Au, Pt,  $\text{RuO}_2$ ) to the front contact, which facilitates the electron transfer to the iodine, which is otherwise quite sluggish. This special property of the preferred redox couple, to easily donate electrons via the iodide but not to accept them easily back to iodine, is apparently a very crucial factor for dye solar cell performance. It was essentially trial and error, which has conducted to reasonably efficient solar cell behavior. However, there is obviously not enough basic scientific understanding to replace the critical redox system by a more stable and convenient alternative.

A similar empirical development can be observed with the nanocomposite polymer fullerene solar cell. The 1970s have already seen significant efforts to develop polymer solar cells. They were, however, not efficient. In the early 1990s, during an effort to dilute polymer with carbon,

fullerenes were casually mixed with polymer to dilute them and a much better solar cell performance was observed [18, 19]. Since then, practically all organic solar cells studied contain fullerene molecules because they make the solar cell more efficient. The same molecular system, however, contributes also to the high instability of this type of solar cell. Most theoretical models consider the fullerene just to be the electron acceptor during exciton splitting. They therefore just take into account the position of electronic states, which are involved in this process. However, also in the case of the polymer–fullerene solar cell, it is a kinetically induced rectification of electron transfer, which is a key factor. Fullerene molecules relax electronically after accepting an electron, and the reverse reaction of the electron with the donor species is thus significantly inhibited.

These kinetically determined processes of electron current rectification, such as generated by the  $\Gamma/I_3^-$  redox system and the fullerene, which play a key role in nanostructured solar cells, where in-built electrical fields cannot easily be sustained, are not sufficiently understood. The aim of this contribution is an effort to derive this solar cell principle from more fundamental considerations of irreversible thermodynamics and to analyze what we can learn from our present knowledge about nanosolar cells and what we should especially consider when aiming at innovative research toward improved and more cost-competitive photovoltaic energy technology based on them. This article is intended to honor J. O'M. Bockris, who has pioneered energy research with many innovative ideas (e.g. [20]) and has given an example on how science, by focusing on relevant problems, may contribute to overcome mankind's ongoing energy crisis.

### Solar cell function derived from irreversible thermodynamic principles

During the development of photovoltaics, considerable efforts were developed, which aimed at understanding the principles involved based on reversible thermodynamics [21]. There was significant success since, for example, the diode equation could be derived from the Planck radiation formula. In addition, the complementarity of photovoltaic cells and light-emitting diodes could well be explained. There were also efforts to study and to select photovoltaic materials based on their luminescence properties [22]. These results are to some extent astonishing, since we know that solar cells are not reversible systems. They are open systems turning over energy and generating heat. If kinetic parameters are involved, as expected for current rectification in nanocomposite solar cells, we cannot count at all on their derivability from reversible thermodynamics,

since reversible thermodynamics cannot give answers on kinetics. It is therefore to be expected that efforts to apply principles of irreversible thermodynamics (linear range) to solar cells may yield a more reliable and more general framework of photovoltaic concepts. It is especially expected to contribute to the understanding of nanosolar cells, which really seem to be governed by irreversible mechanisms and kinetic factors.

Both reversible and irreversible thermodynamics make statements on entropy. While reversible thermodynamics states the experimental fact that, in a closed system, entropy tends to increase to a maximum, irreversible thermodynamics (linear range) states that the system concerned will approach a minimum of entropy production. What does this intuitively mean? In fact, it is nothing else than the principle of least action applied to thermodynamics and chemistry.

The principle of least action is a very fundamental empirical concept, which is known to govern an entire family of important laws in different branches of physics. It has conducted to the Hamilton principle of mechanics, to the Fermat principle of optics, and it has also been used by Einstein to derive the general theory of relativity with the additional condition that the light velocity is constant. To take a simple example: The principle of least action also controls the turn over of electrical energy within electrical circuits. Ohm’s law directly results from the principle of least action. It may consequently be concluded that applying this principle of least action, or equivalent, the minimum entropy production principle, to photovoltaic systems should be a reliable strategy and worthwhile being explored.

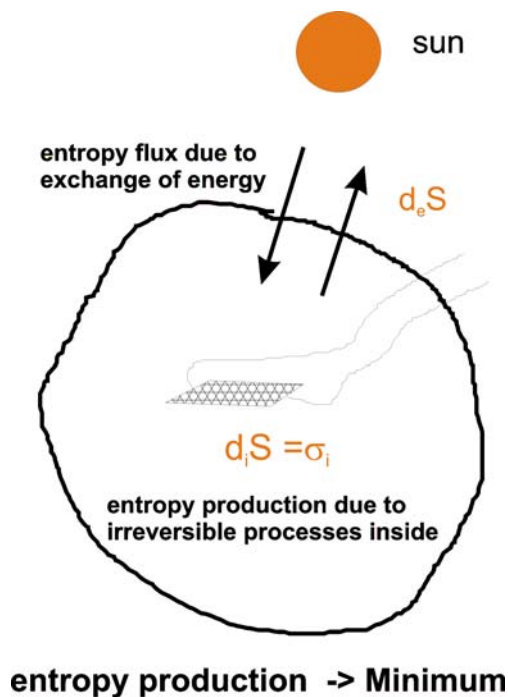
Some efforts have already been made in the literature to understand entropy fluxes with respect to solar cells [23]. The balance of entropy fluxes of a solar cell exposed to solar radiation is shown in Fig. 1.

There are entropy fluxes due to the exchange of energy between the sun and the photovoltaic cell, and there is irreversible entropy production due to heat generation within the photovoltaic cell. There is also electrical power generation, which is exported as an entropy flux when this power is divided by the ambient temperature. Equation 1 explains these entropy fluxes as incoming entropy flux equivalent to outgoing entropy flux plus electric power turn over at ambient temperature, plus irreversible entropy production ( $\dot{E}_s$  and  $\dot{E}_r$  are the energy fluxes of incoming and escaping photon fluxes respectively.  $W$  is the production of useful electrical power,  $T_a$  is the ambient temperature and  $\dot{S}_{irr}$  is the irreversible entropy production that is always observed, when solar cells are operated):

$$\left(\frac{\dot{E}_s}{T_a} - \dot{S}_s\right) = \left(\frac{\dot{E}_r}{T_a} - \dot{S}_r\right) + \frac{W}{T_a} + \dot{S}_{irr} \tag{1}$$

In the literature, the above formula was used to verify that solar cells never engage in negative entropy production [23] (such a property is obvious for photovoltaic cells, since this would mean that they would be able to build up order at the expense of the overall entropy production. This would be restricted to the realm of the non-linear range of irreversible thermodynamics, where self-organization may occur). Our aim will be different. We will investigate what a solar cell is capable to do and how it can perform while minimizing its entropy production (approaching a situation of least action).

The most basic function of a solar cell is simply that of a membrane, which, during solar illumination, generates a directional electronic current. In this study, it is not important how this current rectification occurs. In classical silicon and related solar cells, a thermodynamic force, an electrochemical potential gradient, is built into the photovoltaic membrane in the form of a p/n junction. It is generating an electron exchange, which leads to the build up of an electrical field. When photons are absorbed within this field to generate electron-hole pairs, or when charge carriers diffuse into this region, a directional photocurrent is generated, while the acting electrical voltage will be adjusted. This is the way the classical photovoltaic cell is exporting electrical power  $W$  from the system.



**Fig. 1** Scheme explaining how a solar cell can be considered as an open, irreversible system, described via its entropy turnover balance. The solar cell operation itself is characterized by its tendency to approach a minimum of entropy production (principle of least action). Solar cell optimization consists in extracting entropy turnover in form of electrical power ( $W/T_a$ ) at the expense of irreversible entropy production ( $d_e S$ )

When such a device (Fig. 1) is considered to be subject to linear irreversible thermodynamic laws, it will, in a stationary state, adjust to minimal entropy production within the given system parameters. When an electrical voltage is applied to an ordinary electrical circuit, the system parameters, which govern potential distribution and energy turnover, will be the size and the position (within the circuit) of resistances and the energy will be distributed according to Ohm's law. Being an open system, a solar cell maintains, due to the absorption of solar energy and the generation of electric power and waste heat, entropy fluxes with the outside environment. An inefficient solar cell will generate extensive irreversible entropy fluxes  $S_{\text{irr}}$  and low-entropy fluxes  $W/T_a$  related to electric power extraction. In contrast, a highly efficient cell will be characterized by low  $S_{\text{irr}}$  and high  $W/T_a$ . In both cases, the photovoltaic system will aim at minimizing entropy production within the constraints of the respective system. The task of nanosolar cell development should consequently be to optimize the constraints of a system in such a way as to make irreversible entropy production as small as possible by maximizing the output of electrical power  $W$ .

A mathematical formula describing entropy turnover, and thus applicable to minimum entropy production (the principle of least action), should therefore provide essential clues for the optimization of the power output of solar cells from a basic point of view. Quite generally the entropy production,  $\sigma$ , is known to be the sum of the products of thermodynamic forces and thermodynamic currents involved, both from transport ( $\sigma_d$ ) and from chemical reactions ( $\sigma_{\text{ch}}$ ) [24]. In our case, we are dealing with thermodynamic forces and fluxes generated by light:

$$\sigma = \sum_i I_i F_i = \sigma_d + \sigma_{\text{ch}} = - \sum_i j_i \nabla \frac{\mu_i}{T} + \sum_i w_i \frac{A_i}{T} \quad (2)$$

( $I_i$ =thermodynamic flux,  $F_i$ =thermodynamic force) and the entropy production terms:

$$\sigma_d = - \sum_i j_i \nabla \frac{\mu_i}{T} \quad (3)$$

[ $j_i$ =current flux,  $\nabla \mu_i$  = thermodynamic potential gradient [e.g., voltage, concentration gradient)] and

$$\sigma_{\text{ch}} = \sum_i w_i \frac{A_i}{T} \quad (4)$$

( $w_i$ =chemical reaction rate,  $A_i$ =chemical affinity, equivalent to the deviation from equilibrium and proportional to the Gibbs free energy turnover). The chemical affinity here is approaching zero when a system reaches equilibrium, that is, when illumination stops.

In order to modify minimum entropy losses so that a gain in useful energy output is achievable, thermodynamic forces or fluxes acting within the solar cell device have to be activated for the generation of electric power so that it can be extracted from the system in the form of  $W/T_a$ . From Eqs. 2, 3, and 4, it is obvious that there are two qualitatively different routes to extract electrical power from a solar cell. One occurs via chemical or electrical potential gradients ( $\nabla \mu_i$ ) and additionally by favorable transport conditions leading to a macroscopic current density,  $j_i$ . This is apparently the condition generated in classical solar cells (via Eq. 3), where a thermodynamic potential gradient ( $\nabla \mu_i$ ) is produced in the form of a p/n or similar gradient for electronic charge separation and electronic currents result from drift and diffusion processes.

For cases where inbuilt thermodynamic forces ( $\nabla \mu_i$ ) cannot be sustained, such as in nanostructures, the first term in Eq. 2 disappears. However, the last term in Eq. 2, the chemical entropy production term (Eq. 4), offers an additional opportunity for generating mechanisms, which can obviously be used to optimize the cell for electric power production. It works via the chemical affinity  $A_i$ , which is describing the distance of a photo-induced chemical reaction from equilibrium and is proportional to its Gibbs free energy change. In fact, today's IUPAC definition of chemical affinity is that it expresses the negative partial derivative of the Gibbs free energy with respect to the extent of the reaction (at constant pressure and temperature).

$$A = -\Delta G_i \quad (5)$$

It is positive for spontaneous (photo-induced reactions) and, via Eq. 5, related to the solid-state concept of a light-intensity-dependent quasi-Fermi level splitting.

An additional multiplying factor in Eq. 4 is however the reaction rate  $w_i$  of the chemical reaction involved. Since  $\sigma_{\text{ch}} = \sum_i w_i \frac{A_i}{T}$  in a nanosolar cell should be transformed into  $W/T_a$  of useful power, it follows that

$$\begin{aligned} W &\sim \sum_p w_p A_p \\ &= - \sum_p w_p v \left( \sum_j \mu_j \nu_{jp} + k_B T \log \prod_j \rho_j^{\nu_{jp}} \right) \end{aligned} \quad (6)$$

In this formula,  $w_p$  describes the reaction rate of the process involved,  $\mu_p$  the chemical potential of the components  $p$  involved, and  $\rho_j$  the corresponding concentrations. The quantity  $\nu$  describes the number of molecules involved in the specific reactions.

In a nanosolar cell, appropriate mechanisms have to be implemented, which allow the excited electron to run predominantly into one preferred direction. Up to now, nanosolar cells have mainly been developed by trial and error and rely on a kinetically determined directional

separation of photo-induced electronic charges (a role played by the  $\Gamma/I_3^-$  redox system in the dye solar cell and by the fullerene in the polymer cell).

In order to understand the meaning of relation 6, a simple model calculation should be made. For a basic charge separation reaction within a nanosolar cell, as it occurs in the polymer fullerene solar cell ( $R$ =polymer,  $P^-$ =reduced fullerene), with a forward and a reverse reaction:



the chemical activity  $A$  in Eq. 5 yields

$$A = k_B T \log \frac{k_1 [R]}{k_2 [P^-]} \tag{8}$$

and the reaction rate  $w$  is

$$w = k_1 [R] - k_2 [P^-] \tag{9}$$

By providing a reaction mechanism, in which  $k_1$  of the photoreaction is much larger than  $k_2$  of the reverse reaction (such as is the case with the fullerene in polymer solar cells), one allows both  $w$  and  $A$  in Eq. 9 and 8, and thus the chemical entropy production term  $\sigma_{ch}$ , (relation 4) to maximize. By properly organizing molecules, so that electrons have a preference to percolate into one direction (as observed in polymer/fulleren solar cells), one can create directed currents. Within the total equation of chemical entropy production for a solar cell,  $\sum_i I_i F_i = \sigma_d + \sigma_{ch}$ , one can thus, even in absence of a thermodynamic potential gradient ( $\sigma_d=0$ ), manipulate the molecular and structural cell properties to obtain a significant contribution of useful extractable electrical power. In a polymer/fullerene solar cell, the very low reverse reaction rate of the electron captured by the fullerene generates a high chemical affinity (relation 8). An appropriate morphology of mixing polymer and fullerene, which allows percolation, will generate a unidirectional electron flow mediated by a large rate constant  $w$  (relation 9), which equally takes advantage of a very low reverse reaction constant  $k_2$ .

The technical quality of such a nanosolar cell will of course depend on the degree of light absorption (solar harvesting efficiency,  $\eta_{SH}$ ) in the solar cell and on its molecular nature and on the morphology (efficiency factor,  $\eta_M$ ), which will be relevant for unidirectional current generation. Equation 6 for the power output of a nanosolar cell consequently changes to

$$W = \eta_{SH} \eta_M w A = \eta_{SH} \eta_M w(I_L) A(I_L) \tag{10}$$

when the dependence of  $w$  and  $A$  on the light intensity  $I_L$  is additionally considered. This formula describes the factors that determine the efficiency of nanosolar cells. It indicates that the main aim in nanosolar cell research should be the optimization of photo-induced reaction rate

$w(I_L)$  and of the photo-induced chemical affinity  $A(I_L)$ . The highest impact is to be expected from minimizing the reverse reaction ( $k_2$ ). This will maximize both  $A(I_L)$  and  $w(I_L)$ . An additional relevant factor is the photochemically induced side reactions. All processes that will deviate photo-activated electrons from the power generating key reaction by facilitating side reactions or recombination mechanisms will decrease the photochemical affinity and the reaction rate. Expressed in photo-physical terms these will be undesired recombination and trapping processes. Among these, photochemical side reactions that generate undesired chemical products will significantly interfere with both efficiency and stability of the nanosolar cell.

A basic theoretical understanding and knowledge for identifying suitable mechanisms for kinetic charge separation ( $k_1 \gg k_2$  in Eq. 9) is obviously critical for the development of efficient and stable nanosolar cells. It is also necessary to optimize the molecular–morphological factor  $\eta_M$ . It accounts for the need for polymer donor and fullerene acceptor molecules to organize in such a way that charge separation and transport can occur via efficient percolation mechanisms. The additional factor  $\eta_{SH}$  considers the trivial fact that, according to their spectral properties, different polymers will have different solar-energy-harvesting abilities.

In present nanosolar cells, the current rectifying elements are also partially responsible for insufficient stability. The  $\Gamma/I_3^-$  redox system is both chemically aggressive and photoactive. Fullerenes react with oxygen and under illumination. New and better performing molecular current rectifying elements have to be identified and the mechanism of their function understood. This is a challenging task and unfortunately not easily achievable based on the established Marcus theory of electron transfer. It requires new approaches [7]. Marcus theory is only applicable to weak interactions and completely neglects the effect of polarization of the molecular environment during electron transfer. But polarization and feedback on electron transfer within a non-linear electron transfer theory is a necessary precondition for generating directional electron transfer [25, 26–28] as will be discussed in more detail later.

### What can be learned from existing nanosolar cells?

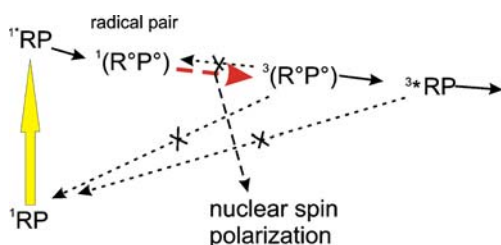
#### Photosynthetic process

The most impressive example of a working nanosolar cell principle is the photosynthetic membrane. It evolved 2–3 billion years ago and apparently conserved the same principle of charge transfer rectification in all later biological applications among more advanced photosyn-

thetic species. The reason is obviously the high efficiency of this process. It should therefore serve as a model system for the functioning of the nanosolar cell principle. Excitation energy is activated within a radical pair for electron transfer. A nuclear spin polarization is occurring, and under spin conservation, the electron spin is inverted simultaneously (Fig. 2). While this is occurring, some energy is lost so that the entire process is a combined quantum-classical one. The consequence is that, for a back reaction into the ground or excited state, the electron would have to overcome first a 0.2 eV high activation barrier while simultaneously inverting its spin.

Such a process has, of course, a very low probability. The reverse reaction rate constant that enters into chemical affinity  $A$  and into the reaction rate  $w$  is correspondingly low (compare Eqs. 8 and 9 for the simple reaction 7, leading to a correspondingly high output in photovoltaic energy  $W$  (relation 10).

The fact that all biological photosynthetic systems, primitive and advanced, have conserved the mechanism of photo-dynamically induced nuclear polarization [29] (which is described in a simplified way in Fig. 2) during evolution, speaks for its high mechanistic quality. It also points attention to the sophistication [30], which was required to obtain rectification of electron transfer. Obviously, the strategy adopted by nature could act as a model system toward solid-state photocurrent rectification mechanisms for innovative nanosolar cells. Inorganic complexes working based on similar photocurrent rectification mechanisms should definitively be taken into consideration for nanosolar cells. However, major research will have to be concentrated on mechanisms that amplify the inhibition for spin reversal during the reverse reaction, since the inhibition for ordinary intersystem crossing will not be sufficient. In primary photosynthesis (Fig. 2), it is an additional energy barrier, which adds a significant multiplication factor to the inhibition of the reverse reaction.



**Fig. 2** During the primary photosynthetic process, photo-induced radical pair formation is involved. Electron transfer is rectified via a photo-dynamically induced nuclear spin polarization, a combined quantum-classical process. It blocks reverse reaction via a 0.2 eV activation barrier, which would have to be surpassed, while the spin orientation is changed back (dotted lines)

## Polymer–fulleren solar cell

Figure 3 is used to discuss the derived nanosolar cell concept in relation to the polymer–fulleren solar cell. A scanned photocurrent image is shown together with a scanned reflected light image [31] (left) and an energy scheme, showing the photoreaction responsible for the solar energy conversion process (right). It is seen that the distribution of photocurrent efficiency is inhomogeneous. Considering our formula (Eq. 10), and taking into account that the reflection image is quite homogeneous, the reason will be that the factors  $A$  (photochemical affinity),  $w$  (photochemical reaction rate), and  $\eta_M$  (morphological efficiency factor) will locally vary. This means that one or more of these factors will be locally different due to slightly changing chemical conditions. It is known from the literature that even different solvents for polymer crystallization may influence cell efficiency [32].

The scheme on the right side of Fig. 3 explains the energy generation process in a poly(phenylene vinylene) (PPV)–polymer–fulleren solar cell. The excited state (exciton) in the PPV is split and an electron transferred to the fullerene, which relaxes to a lower state (Jahn–Teller effect). The chemical affinity of a photochemical reaction is related to the Gibbs free energy change via relation 5. The latter is related to the electromotive force (the expected solar cell photovoltage  $V_{ph}$ ) via  $\Delta G = -nFV_{ph}$  (with  $n$  = number of electrical charges involved in the photoreaction,  $F$  = Faraday constant). It follows for the photovoltage, with Eq. 5, when  $n$  is assumed to be  $n=1$ :

$$V_{ph} = \frac{A}{F} \quad (11)$$

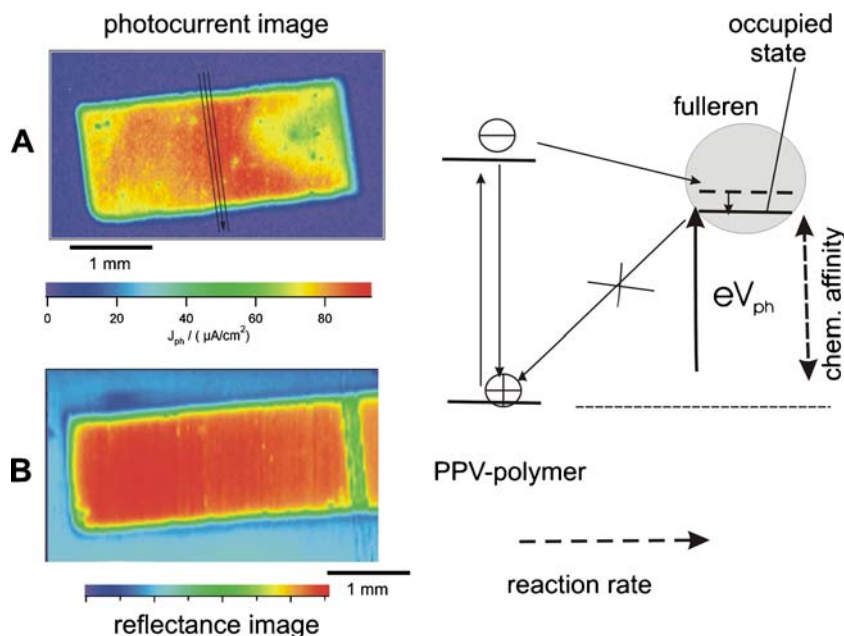
This means that the nanosolar cell basically works as a solid-state electrochemical cell, which converts photo-generated Gibbs free energy (photo-chemical affinity) into an electromotive force generating the cell voltage. Since the Gibbs free energy change (the photochemical affinity) is generated by the energy-rich product (the reduced fullerene) as referred to the original PPV ground state, the free energy (chemical affinity) activated by light will be a light-intensity-dependent fraction of the distance between the PPV ground state  $E_{PPV}$  and reduced fullerene excited state  $E_{F-}$ . The energetic difference between these two states is equal to the light intensity dependent affinity plus an entropy loss ( $T\Delta S$ ), which will decrease with increasing light intensity.

$$E_{F-} - E_{PPV} = FV_{ph} + T\Delta S \quad (12)$$

When the dependence of  $T\Delta S$  on light intensity  $I_L$  is considered, the following relation can be obtained for the photovoltage of the nanosolar cell:

$$V_{ph}(I_L) = \frac{1}{F} (E_{F-} - E_{PPV} - T\Delta S(I_L)) \quad (13)$$

**Fig. 3** Space resolved photocurrent and light reflection images of a PPV–fulleren solar cell (2.6% efficiency) showing inhomogeneous photocurrent distribution (*left*). On the right side, an energy scheme is depicted to explain the charge separation mechanism involved



The photovoltage of the organic cell should consequently change proportional with the electron affinity of the fullerene species used. Furthermore, with increasing light intensity, entropy losses will decrease. The power output  $W$  will, following relation 10, also depend on the directional reaction rate  $w$ . According to relation 9, there will be a largely reduced power output if the fullerene would be replaced by a polymer with exactly the same electronic levels but a faster reverse reaction. This is the reason why the expensive and poorly stable fullerene is so intensively used in plastic solar cell development. This finding indicates in what direction mayor research should be aimed, namely in direction of understanding kinetic current rectification via more stable molecular systems. Other critical factors are, of course, charge recombination and trapping losses in polymer solar cells. Such processes will affect concentration and lifetime of photo-reduced acceptor states and will lead to a reduction of photo-induced affinity  $A$  and reaction rate  $w$ . The consequence will be a decrease of solar cell efficiency (relations 6 and 10). The effect of undesired side reactions of this type on these quantities can, in principle, be calculated via chemical kinetic theory, provided the nature and rates of the solid state and polymer-based or liquid-state mechanisms (in case of humidity) involved are known. This may help to understand the conditions, which control solar cell efficiency. In practice, however, an experimental, empirical optimization may be more promising because of the complexity of the systems involved.

The nanocomposite dye solar cell

Figure 4 helps to analyze nanostructured dye solar cells with respect to the proposed kinetic model. Figure 4a shows

an energy scheme explaining how injected electrons activate a directional photocurrent without an inbuilt thermodynamic gradient (electrical field). No thermodynamic potential gradient, generating an electrical field, separates the photo-injected charges, but kinetic factors. Electrons injected into  $\text{TiO}_2$  nanoparticles can easily be re-supplied by iodide and simultaneously have a low probability to engage in a reverse reaction with iodine. The same is true for electrons at the fluorinated  $\text{SnO}_2$  front contact, up to which the  $\Gamma^-/3^-$  electrolyte may equally penetrate. The low reverse reaction constants give rise to a high chemical affinity  $A$  of the photo-conversion process and a high rate constant  $w$  for current generation.

In order to analyze the expected behavior of the nanodye solar cell further, Eq. 10 for the solar cell power output  $W$  can be rewritten using relation 11 to ( $f_F$ =fill factor,  $F$ =Faraday constant,  $I_{ph}$ =photocurrent,  $V_{ph}$ =photovoltage):

$$W = f_F I_{ph} V_{ph} = \eta_{SH} \eta_M w A = \eta_{SH} \eta_M F w V_{ph} \tag{14}$$

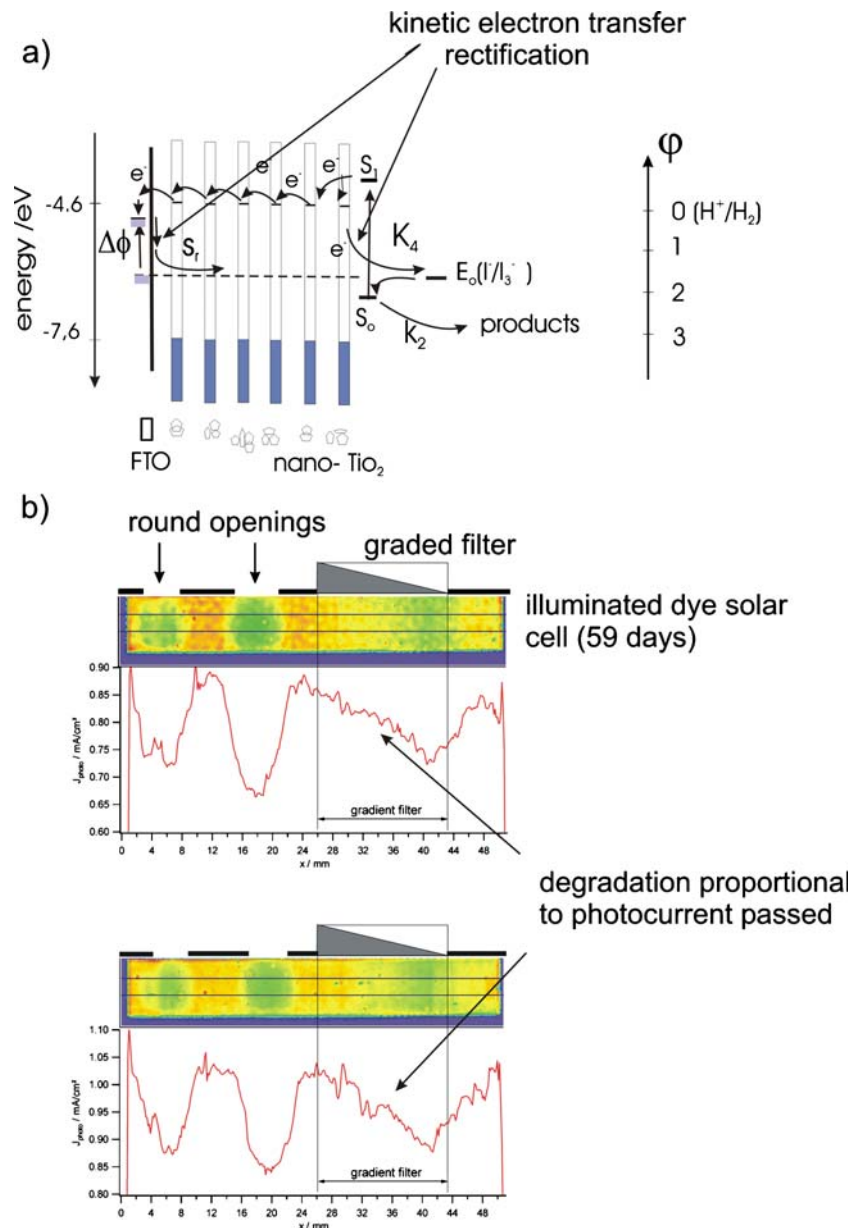
From this relation, it follows that the reaction rate  $w$  is proportional to the photocurrent generated:

$$w \sim I_{ph} \tag{15}$$

This actually shows that optimization of the photocurrent in a nanosolar cell actually means optimization of a reaction rate (like seen in Eq. 9 for a very simple reaction, which can only become large when the reverse reaction constant  $k_2$  becomes very low). A low reverse reaction constant is thus the most critical factor for a nanosolar cell. In order to strongly increase the photocurrent output, the reverse reaction has to be drastically reduced.

It should now be investigated what is to be expected when part of the photoreaction in a nanosolar cell,

**Fig. 4 a** Energy scheme explaining electron transport, charge separation, and suppression of reverse reaction in a TiO<sub>2</sub>-based nanodye solar cell, sensitized with a N3 Ru-complex. **b** Photocurrent images obtained after illumination during 59 days through round openings and a graded optical filter, respectively



equivalent to part of its photocurrent, simultaneously leads to its degradation with the reaction rate  $w_2 = w - w_1$ .

It follows from Eq. 15 ( $a = \text{constant}$ ,  $k' = \text{rate constant for sustainable photocurrent generation}$ ,  $k'' = \text{rate constant for photocurrent fraction leading to sensitizer degradation}$ ,  $S = \text{sensitizer concentration}$ ):

$$aI_{ph} + (1 - a)I_{ph} = w = w_1 + w_2 = k'I_L S + k''I_L S \quad (16)$$

From this relation, it is seen that the reaction rate  $w_2 = k''I_L S$  for photo-degradation is not only proportional to the light intensity  $I_L$  but also proportional to the photocurrent  $I_{ph}$  and thus to the power generated.

$$w_2 = k''I_L S \sim I_{ph} \sim W \quad (17)$$

Such an expected behavior was tested in the experiment shown in Fig. 4b and confirmed. Illumination of two dye solar cells through a graded filter showed indeed that photo-degradation is proportional to the light intensity and to the photocurrent passed. It could also be demonstrated that, as a consequence, inhomogeneous photocurrent distribution within a dye solar cell tends to level off the differences in photocurrent density during prolonged operation [6]. Faster degradation occurs where higher photocurrent densities are active.

The consequences from such a behavior are quite significant and disturbing. A solar cell of 8% efficiency containing a well-defined quantity of sensitizer  $S$  will degrade four times faster than the one that was tested for



stability at 2% efficiency (e.g., [33]). This shows how carefully photoreactions have to be selected, tailored, and optimized for nanosolar cell applications to avoid degradation processes.

Experience from the early days of dye solar cell research may help us to understand another relevant factor: the dependence of kinetic charge separation on oxide material morphology. The first dye solar cells were either prepared with sintered oxide powder (then typical electrodes because they were easy to produce) [11, 14–16] or with single oxide crystals (to clarify fundamental mechanisms [13], which are otherwise affected by large grain boundary surfaces). Later, emphasis was put on nanostructured materials, produced by sintering of the same kind of powders or of sol/gel material [1]. But typically, the electrodes were fabricated as much thinner layers, which also allowed penetration of the electrolyte toward the front contact. The  $\Gamma/I_3^-$  electrolyte proved to be unavoidable for a high efficiency of the latter cells. Different electrolytes however appeared to be practical for the earlier less-efficient dye solar cells besides the  $\Gamma/I_3^-$  system [9–16]. An explanation is offered in Fig. 5. Depending on the quality of the oxide material, either a significant electrical field in the oxide interface was present, as in the single crystal experiments (Fig. 5a), or only a weak field was present, as in strongly sintered oxide powders (Fig. 5b). Alternatively electrical fields were essentially absent, such as in poorly sintered thin nanolayers (Fig. 5c). When looking at formula 1 and 2, it is immediately seen that the irreversible thermodynamic solar cell model describes both cases, solar energy conversion via an inbuilt thermodynamic potential gradient  $\nabla\mu_i$  (e.g., generating an electrical field; Fig. 5a) and via a kinetic mechanism of charge separation (Fig. 5c; relations 3 and 4 respectively), which is typically controlled by molecular processes.

The general relation for the obtained power output will be ( $a$  and  $b$  are different constants):

$$W = awA + bj\nabla\mu \quad (18)$$

It means that there is a contribution from a kinetically determined cell and from a potential gradient (electrical field) determined cell adding to the performance of a combined solar device (Fig. 5b). In the first case of a kinetically determined mechanism (Fig. 5a), any redox system, which can supply electrons to the oxidized sensitizer, can apparently support solar cell operation. In the case of the nanomaterials (Fig. 5c), only an irreversibly behaving redox system such as  $\Gamma/I_3^-$  can sustain solar cell function in a sufficient way because current rectification is needed. Highly reversible redox systems, on the other hand, such as hydroquinone/quinone or  $\text{Fe}(\text{CN})_6^{3+/4+}$ , which energetically would match, cause a breakdown of solar energy conversion. This may explain why modern dye solar

cells only use  $\Gamma/I_3^-$  as electrolyte. In this case, it may additionally be that the known irreversible electrochemical character of the  $\Gamma/I_3^-$  redox system is enhanced in a  $\text{TiO}_2$  nanoenvironment to which iodine is known to adsorb.

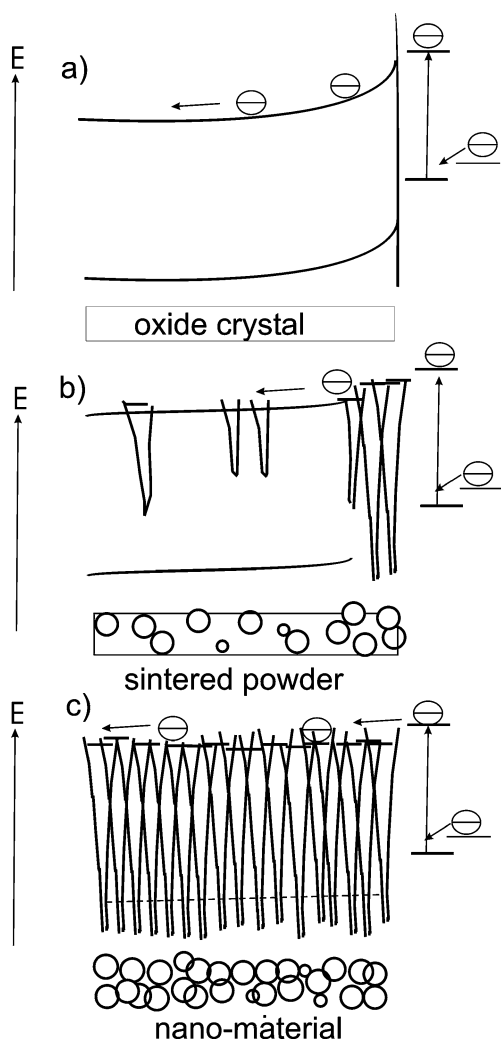
#### Molecular bridges for electron transfer rectification in $WS_2$ sensitized nano- $\text{TiO}_2$

Sensitization of  $\text{TiO}_2$  nanoparticles with inorganic sensitizers is an attractive research strategy toward an increase of optical absorption and a reduction of chemical degradation.  $WS_2$  offers the advantage of a valence band derived from d-states, which is able to engage in photo-induced coordination chemical reactions. This guarantees a high degree of electrochemical stability [34, 35]. In very small dimensions,  $WS_2$  can chemically be generated in the form of two-dimensional sheets, which, after light absorption, can sensitize  $\text{TiO}_2$  nanolayers [36] (Fig. 6). The observed photocurrent densities were quite small (a few tenths of a  $\text{mA}/\text{cm}^2$ ), apparently due to a too strong reverse reaction of electrons injected into  $\text{TiO}_2$ . The question arose as to how a more pronounced current rectification could be generated. Based on various considerations, outlined in [7], cysteine was selected. It is an amino acid with a thiol group and was shown to attach to the very similar  $\text{MoS}_2$  [36]. When electrons are taken from the thiol sulfur, which attaches to the metal, the remaining molecule will adjust by lowering and redistributing the electron density. If, however, an electron would be donated to the sulfur, this would not work. Electron transfer through the cysteine molecule is thus essentially rectified. Treatment of the nanocomposite with cysteine actually led to a threefold increase of photocurrent density into the milliamperere range ([37], Thomalla and Tributsch, to be published). In addition, thioglycolic acid showed a significant improvement (compare later, Fig. 9), not however molecules like 3-mercaptopropionic acid. Cysteine is apparently able to rectify electron transfer (it may also improve  $WS_2$  nanosheet attachment to  $\text{TiO}_2$  by binding to it via the carboxyl group).

In terms of our theoretical considerations, introducing a rectifying molecule into the electronic pathways of a photoreaction would mean that both the affinity  $A$  and the reaction rate  $w$  would be increased by reducing the reverse reaction rate. This would lead to an improvement of the power output conditions of the nanosolar cell (relation 10), which is also experimentally observed.

#### Surface conductivity nanosolar cell

In order to identify electron transfer rectifying chemicals for efficiently operating nanostructured solar cells, liquid chemical environments are needed to provide the necessary flexibility for research or combinatorial studies. Pure solid-



**Fig. 5** Energy schemes showing space charge layer with high electrical field in oxide crystal interface (a), a low electrical field in sintered oxide powders (b), and practically no field in thin oxide nanolayers, which are permeable for the electrolyte (c)

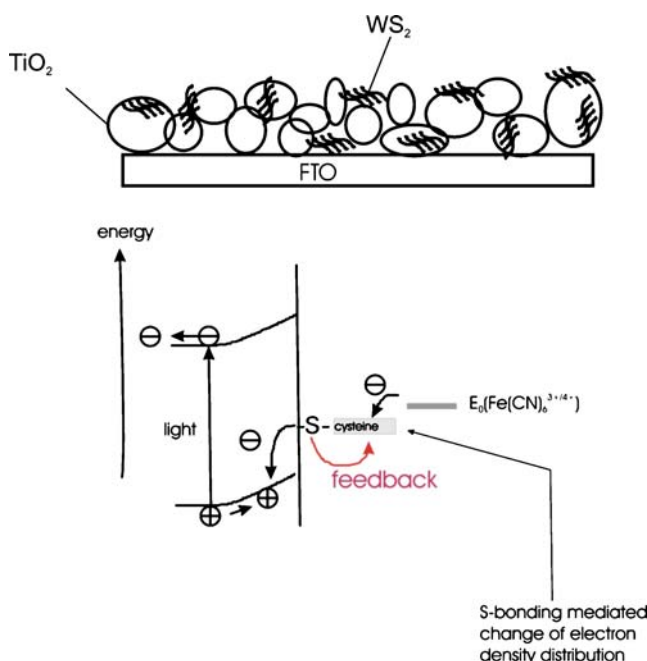
state dye solar cell systems are difficult to access with chemical modifications and also involve significant photochemical instabilities [38]. Since confinement and stabilization of electrolytes in wet dye solar cells poses a mayor problem, it was attempted to operate such cells by just allowing a thin surface electrolyte film to form on the nanoparticle surfaces in equilibrium with the atmosphere (Junghaenel and Tributsch, manuscript in preparation). This was achieved by dipping the nanoparticle-sensitizer composite into a  $10^{-3}/10^{-4} \Gamma/I_3^-$  organic electrolyte, containing additional chemicals, and subsequently evacuating to  $10^{-4}$  bar. The obtained quasi-dry dye solar cell still worked, showing a solar energy conversion efficiency of up to 2% [(Fig. 7). However, the scientific understanding of surface conduction and of heterogeneous photochemical processes in electrolyte films on nanoparticles is still to be elaborated. A vapor transport system was designed to transfer tiny

quantities of chemicals into the dye solar cell to test the effect of additions. Because of the given chemical flexibility, such a system may be appropriate for testing and identifying suitable candidates for generating photocurrent rectification in nanosolar cells.

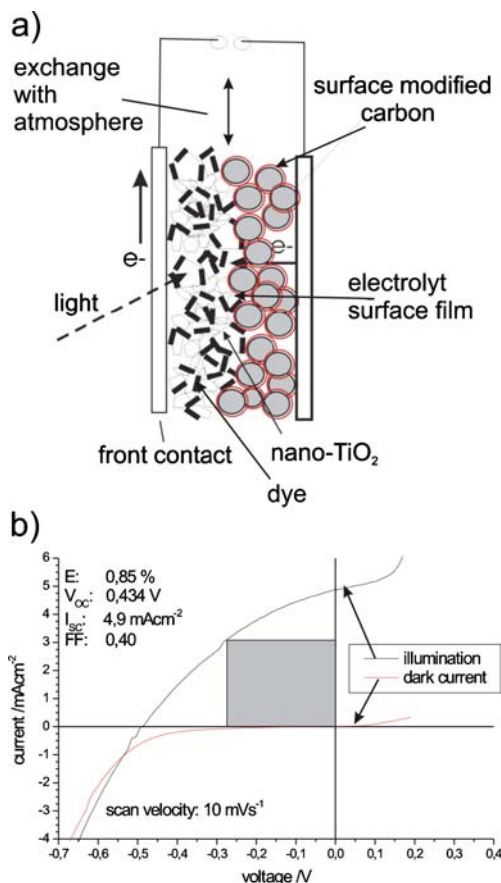
Dye solar cells that operate with a quasi-stationary surface electrolyte film interacting with the environment (SCSC cells) offer a big opportunity because they avoid problems with confined liquid electrolytes. Simultaneously they offer favorable opportunities for chemical experimentation toward kinetically determined mechanisms for current rectification.

#### New frontiers for hot carrier and quantum dot devices

During the past two decades, there has been a lot of research activity aiming at hot carrier and quantum dot devices for solar energy conversion [39, 40]. Hot carrier devices attempt to utilize the excess energy of photo-excited electronic charge carriers (above the energy gap), which is usually lost in the form of heat, for energy purposes. Quantum dot devices use small (dot like) material accumulations to create quantum states and quantum wells for electronic and energy conversion purposes. However, only moderate progress has been made up to now. In our opinion, one reason is that electrical potential gradients and resulting electrical fields have to be provided for hot carriers and electrons in quantum dots to react laterally, thereby contributing to



**Fig. 6** Scheme showing  $TiO_2$  nanoparticles sensitized by  $WS_2$  nano-sheets (top) and energy scheme showing rectifying electron transfer action of cysteine molecules (below)



**Fig. 7** **a** Set up and function of the liquid phase free surface conductivity dye solar cell (SCSC cell), which transfers positive counter ions only via a thin surface electrolyte film on the nanoparticles. **b** Example of power output characteristic

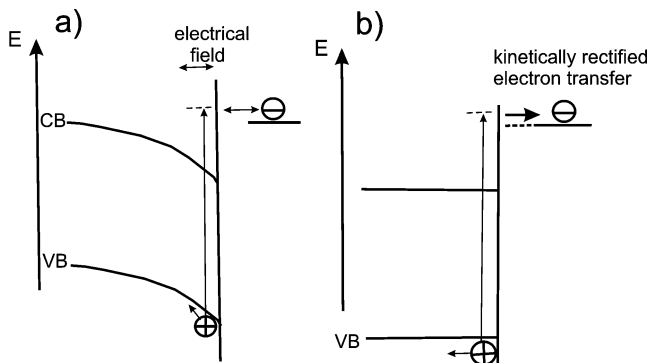
the current turnover. Such electrochemical potential gradients in interfaces pose the problem of instability and interfacial degradation because mechanisms will proceed, which tend to neutralize the gradients by ion transfer, diffusion, and chemical reactions.

As visualized in Fig. 8a, a better way to cope with interfacial stability and to make hot carrier processes more efficient would be to operate hot carrier turnover as kinetically determined charge transfer and charge separation processes. Electrons reacting with properly tailored molecules should, first, avoid a reverse reaction and, second, pass on to a next acceptor under conservation of most of the energy involved. This way, the chemical affinity  $A$  involved in the hot carrier reaction and the reaction rate  $w$  of the interfacial hot carrier reaction could become sufficiently large to support a significant power output according to relation 10. A big challenge, as to be discussed below, of course remains to be the tailoring of appropriate molecules, which not only guarantee current rectification but also adjust to a fluctuating input of excitation energy.

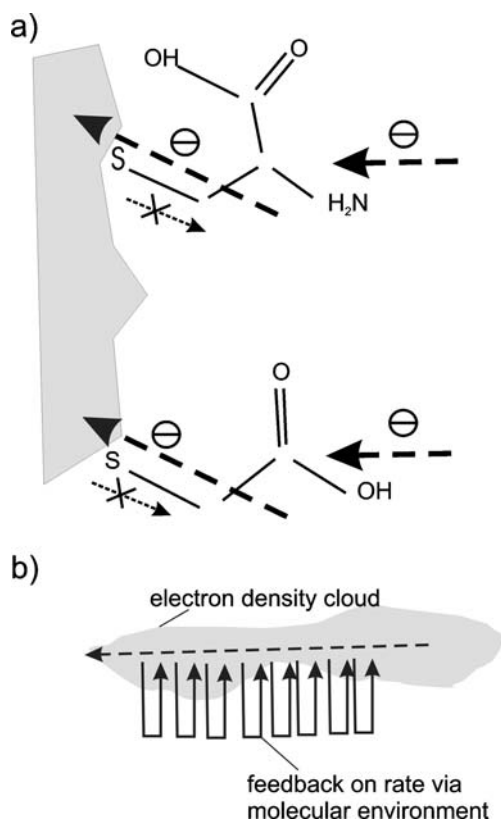
**Electron transfer theory for kinetic current rectification**

Throughout the discussion of kinetically determined solar cells in this work, it became clear that generation of unidirectional electron transfer is a crucial mechanism, which we have to much better understand in order to control it. Molecular structures able to rectify electron transfer are the simplest building elements of solar cells. They can provide the selectivity for electron passage of a selective membrane, which we call solar cell. That finding ways to rectify molecular electron transfer is not an easy challenge is already demonstrated by the quite sophisticated photo-induced nuclear spin polarization technique (Fig. 2), which photosynthetic systems have adapted and maintained throughout evolution to provide unidirectional electron transfer.

The difficulties science is facing with unidirectional electron transfer are twofold. One challenge is that appropriate mechanisms for electron transfer rectification by molecular bridges have to be identified. First, inspirations may be obtained from molecular biology where numerous elements of electron transfer chains dynamically react with respect to electron transfer. The previously discussed role of the amino acid cysteine and of similar thiols (see also [7] and Fig. 6) may be one example. Figure 9a is visualizing how L-cysteine and thioglycolic acid adsorbed to a semiconductor particle via the thiol-sulfur support anodic but not cathodic electron exchange. An electron extracted from the thiol sulfur leads to a reorganization of electron density over the remaining molecule, which supports regeneration of the electron. However, the opposite reaction pathway for an electron is blocked. This peculiar non-symmetrical electron transfer behavior of cysteine has been continuously used in biological systems for electron transfer bridges in ferredoxins since early evolution. Molecules like these two examples are needed as model substances to learn about unidirectional electron transfer for kinetically determined nanosolar cells.



**Fig. 8** Energy scheme comparing hot electron capture via inbuilt electrochemical potential gradient (a) and via molecular kinetic rectification processes (b)



**Fig. 9** **a** Cysteine and thioglycolic acid adsorbed to a nanomaterial via the thio-sulfur with explanation of rectification of electron passage, **b** scheme explaining how electron charge density can feedback interact to stimulate and rectify electron transfer

The second challenge is that today's well established and dominating electron transfer theory, Marcus theory, is not at all suitable for addressing this task from theoretical points of view. The main reason is that it does not consider polarization of the molecular environment while the electron is transferred. This however is necessary if the way back for the electron should be made less probable or be entirely blocked. Marcus theory can, to some extent, however contribute to irreversible electron transfer pathways when several steps are involved and reorganization energies and concavity parameters (of the reaction parabola) of the reactants involved are optimized and also a reverse reaction via the Marcus inverted region is considered [7].

However, a much more straightforward way to make an electron transfer unidirectional would arise via a polarization of the electronic and molecular environment. In a passing electron, equivalent to a passing charge density cloud, the electron density could induce a feedback on the molecular environment and break a bond or stimulate a structural change, which could make the reverse reaction much less probable or even impossible. This is schematically indicated in Fig. 9b. The electron should be able to exert a feedback reaction on the molecular environment

(indicated as bent arrows in Fig. 9b). Such an interaction is not permitted by the Marcus theory and also meets fundamental problems. A feedback reaction is a process well defined in time. There is a time before the feedback and a time after. Quantum physics does not accept a time concept, and time-dependent quantum processes only arise from interactions with classical perturbation.

However, a phenomenological theory of feedback-cooperative and feedback-stimulated electron transfer has been developed [25, 26–28, 41, 42]. A multi-electron transfer process can be treated in such a way that one electron exerts a feedback on the next electron and so on. The obtained set of equations can be reduced to one equation, which shows that one electron is “slaving” the following, making the process to proceed in a synergetic way. If such a mechanism of feedback interaction is calculated via the electron density of an individual electron cloud as a continuous model considering infinitesimal feedback steps, the self-organized behavior of an individual electron, while interacting with the molecular environment, can be calculated [41]. It turns out that molecular feedback for electron transfer may not only make the process directional. It can also become significantly faster [41]. Such an electron transfer mechanism, which was named “stimulated electron transfer,” supports kinetic electronic charge separation because it is directional and efficient, leading to a large  $w$  in relation 10. The challenge is that it has to be learned how appropriate feedback mechanisms during electron transfer can be activated and implemented in the form of appropriate electron transfer bridges.

## Discussion

The presented solar cell model, derived from irreversible thermodynamics, has yielded two possible fundamental mechanisms involving both the classical solar cell principle (with imprinted thermodynamic potential gradients and charge transfer via drift or diffusion) and an additional principle that involves purely chemical-thermodynamic quantities. It turned out to describe the operation principle of nanocomposite solar cells. It includes the photochemical affinity of the excited nanomolecular system as the thermodynamic force and its chemical reaction rate as thermodynamic flux (relations 2, 4, and 11). The photo-generated chemical affinity, which corresponds to the Gibbs free energy turnover with respect to the extent of the reaction, is related to the photovoltage generation (relation 11) and the reaction constant to the photocurrent generation (relation 15). For both quantities to become large for an optimal nanosolar cell efficiency, it is essential that the reverse reaction of photo-transferred electrons is kept very low, transforming the solar cell into a membrane with

selective properties for electron passage. The expected photovoltage output will be related to the difference between the highest occupied electronic level (HOMO) of the donor and the lowest reduced (excited) state of the acceptor (its acceptor strength or first reduction potential). But additionally, the photovoltage will be reduced by light-intensity-dependent entropy losses (Eq. 13). They will be smaller the higher the light intensity. Such a behavior essentially seems to match properties observed with polymer–fullerene solar cells [43]. It is important to note that the kinetically determined nanosolar cell mechanism involves the generation of photochemical free energy, which is subsequently turned over via the electrochemical cell principle (leading to relation 11). The similarity with a photogalvanic cell is obvious, which, via its metal electrodes, reacts to the free energy change (or chemical affinity) of an illuminated surrounding medium. However, there is an important difference. By incorporating a kinetic current rectification, it can become much more efficient. However, in principle, the photo-generated free energy (chemical affinity) in combination with a mechanism for electronic charge transport provides the driving force. This occurs in analogy to an electrochemical cell with two concentrations of a redox species, e.g.,  $\text{Fe}^{2+/3+}$  (separated by a diaphragm), into which metal electrodes are dipping. A corresponding electromotive force will be generated, which drives a current.

It was emphasized and shown that natural primary photosynthetic processes work as kinetically determined solar cells, as well as the nanocomposite dye and polymer–fullerene solar cells. However, the classical solar cell principle (with inbuilt thermodynamic potential gradients generating electrical fields) and the kinetic solar cell principle do not exclude each other. Both principles for photovoltaic electricity generation can operate simultaneously, depending on the degree of crystallinity and nanostructure involved (Fig. 5). In nanostructured solar cells (Fig. 5c), where thermodynamic potentials cannot be sustained, only the kinetic mechanism for charge separation will be working or must be considered by providing appropriate kinetic current rectification.

All presently known kinetically controlled nanosolar cells suffer from photo-degradation. This can be explained. A critical factor, according to our irreversible thermodynamic model, is related to the role of photo-induced chemical affinity (proportional to the Gibbs free energy change) as a thermodynamic force for electrical power generation (relation 10). This, of course, involves the danger that the photo-induced reaction can engage in other than sustainable electron transfer, which would here be the only useful mechanism. Photochemical mechanisms are well known for not only engaging in electron transfer. They may also involve energy transfer to form singlet oxygen;

they may induce bond breaking or photo-induced conformational changes. Fullerenes can, under illumination, also irreversibly react with oxygen so that reaction sequence (Eq. 7) would have to be extended to yield a different affinity and a different rate. Obviously, such side reactions will cause a deterioration of solar cell performance and may generate accumulating irreversible photo-damage. Like in the photosynthetic membranes, inbuilt protective and repairing molecular mechanisms will have to be considered in technical nanosolar cells.

There is also a peculiar photo-degradation phenomenon observed with organic solar cells, which may be explained based on the derived model. The phtalocyanine/fullerene solar cell is highly unstable, even though phtalocyanine itself is photochemically known to be very stable and the fullerene reasonably stable. What can the reason for this increased instability be? The explanation is that the process of energy conversion occurring (Eq. 12) is not a pure photochemical one but that the photochemical reaction is driving an electricity-generating solid-state electrochemical process. It is in this case ultimately sacrificial, leading to irreversible product formation. The process may be compared to one proceeding in a non-rechargeable battery but with the difference that light was used to store the primary energy. The only way out in this case would seem to be a re-design of the photoelectrochemical system, with the aim to make it rechargeable (by light)

Another example of strong photo-induced degradation of the photoactive system, which generates the affinity  $A$  and the reaction rate  $w$  for power generation (relation 9) was observed in solid-state  $\text{TiO}_2/\text{dye}/\text{CuI}$  solar cells [38]. The electron, injected by the Ru-sensitizer into  $\text{TiO}_2$ , reacts back to irreversibly reduce hydrothiocyanate, which acts as an electron transfer bridge. As a consequence,  $\text{H}_2\text{S}$  is liberated and the electron transfer through the interface degrades. In liquid dye solar cells, generation of a high chemical affinity  $A$  and a high directional reaction rate  $w$  may be counteracted by a photo-induced dye degradation and photochemical reactions with iodine. It is clear from these examples that a profound experience with electricity generating photoreactions will have to be gained to handle the complex problem of nanomaterial preparation, photovoltaic efficiency, and long-term stability. For this purpose, a theoretical model explaining the function of nanocomposite solar cells will be helpful.

## References

1. Grätzel M (2003) *J Photochem Photobiol C Photochem Rev* 4:145 doi:10.1016/S1389-5567(03)00026-1
2. Sommerling PM, Späth M, Smit HJP, Bakker NJ, Kroon JM (2004) *Photochem Photobiol A* 164:137 doi:10.1016/j.jphotochem.2003.12.017

3. Tributsch H (2004) *Coord Chem Rev* 284:1511 doi:10.1016/j.ccr.2004.05.030
4. Gunes S, Sariciftci NS (2008) *Inorg Chim Acta* 361:581 doi:10.1016/j.ica.2007.06.042
5. Jorgensen M, Norrman K, Krebs FC (2008) *Sol Energy Mater Sol Cells* 92:686 doi:10.1016/j.solmat.2008.01.005
6. Barkschat A, Moehl T, Macht B, Tributsch H (2008) *Int J Photoenergy*. doi:10.1155/2008/814951
7. Tributsch H (2006) *CR Chimie* 9:596
8. Meier H (1965) *J Phys Chem* 69:719 doi:10.1021/j100887a003
9. Gerischer H, Michel-Beyerle ME, Rebentrost F, Tributsch H (1968) *Electrochim Acta* 13:1509 doi:10.1016/0013-4686(68)80076-3
10. Tributsch H, Gerischer H (1969) *Ber Bunsenges Phys Chem* 73:850
11. Tributsch H (1968) An electrochemical technique for the study of spectral sensitization and of heterogeneous photochemical reactions on ZnO electrodes. PhD Thesis, Technical University Munich
12. Tributsch H, Calvin M (1971) *Photochem Photobiol* 14:95 doi:10.1111/j.1751-1097.1971.tb06156.x
13. Tributsch H (1972) *Photochem Photobiol* 16:261
14. Tsubomura H, Matsumura M, Nomura Y, Amamya T (1976) *Nature* 261:402
15. Alonso-Vante N, Beley M, Chartier P, Ern V (1981) *Rev Phy Appl* 16:5
16. Matsumura M, Matsudaira S, Tsubomura H, Takata M, Yanagida H (1980) *Ind Eng Chem Prod Res Dev* 19:4157 doi:10.1021/i360075a025
17. O'Regan B, Grätzel M (1991) *Nature* 353:373 doi:10.1038/353737a0
18. Yu G, Gao J, Hummelen JC, Wufl F, Heeger AJ (1995) *Science* 270:178 doi:10.1126/science.270.5243.1789
19. Sariciftci NS, Heeger AJ (1997) In: Nalwa HS (ed) *Handbook of organic conductive molecules and polymers*, vol. 1. Wiley, New York
20. Bockris JO'M (1980) *Energy options: real economics and the solar—hydrogen system*. Australian and New Zealand Book Company, Sydney
21. Würfel P (2005) *Physics of solar cells. from principles to new concepts*. Wiley, Weinheim
22. Smestad G, Ries R (1992) *Sol Energy Mater Sol Cells* 25:51 doi:10.1016/0927-0248(92)90016-I
23. Luque A, Marty A (1997) *Phys Rev B* 55:6994 doi:10.1103/PhysRevB.55.6994
24. Nicolis G, Prigogine I (1977) *Self-organization in nonequilibrium systems*. Wiley, New York
25. Pohlmann L, Tributsch H (1997) *Electrochim Acta* 42:2737 doi:10.1016/S0013-4686(97)00078-9
26. Tributsch H, Pohlmann L (1995) *J Electroanal Chem* 396:53
27. Tributsch H, Pohlmann L (1997) *J Electroanal Chem* 438:37
28. Tributsch H, Pohlmann L (1998) *Science* 279:1891
29. Hoff AJ (1984) *Quart Rev Biophys* 17:153
30. Jeschke G, Matysik J (2003) *Chem Phys* 294:239
31. Jeranko T, Tributsch H, Sariciftci NS, Hummelen JC (2004) *Sol Energy Mater Sol Cells* 83:247
32. Rispen MT, Meetsma A, Rittberger R, Brabec CJ, Sariciftci NS, Hummelen JC (2003) *Chem Commun* 17:2116
33. Kuang D, Klein C, Ito S et al (2007) *Adv Mater* 19:1133
34. Tributsch H (1994) *Solar Energy Mater Solar Cells* 31:548
35. Tributsch H (1997) *Catal Today* 39:177
36. Moehl T, Abd El Halim M, Tributsch H (2006) *J Appl Electrochem* 36:1341
37. Thomalla M, Tributsch H (2006) *J Phys Chem B* 110:12167
38. Sirimanne PM, Tributsch H (2003) *J Solid State Chem* 177:1789
39. Nozik AJ (2002) *Physica E* 14:115
40. Luque A, Marti A, Nozik AJ (2007) *MRS Bulletin* 32:236
41. Pohlmann L, Tributsch H (1992) *J Theor Biol* 155:443
42. Pohlmann L, Tributsch H (1992) *J Theor Biol* 156:63
43. Brabec CJ, Cravino A, Meissner D, Sariciftci NS, Rispen MT, Sanchez L, Hummelen JC, Fromherz T (2002) *Thin Solid Films* 403–404:368