
Jan Weiss$^1$, Markus Thomalla$^1$ and Helmut Tributsch$^{1,2}$

1) Helmholtz Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, 14109 Berlin, Germany

2) Retired from Free University Berlin with address: helmut.tributsch@alice.it

KEYWORDS (nano solar cells, thiols, electron transfer bridges, kinetically determined solar cells, quantum dots).

ABSTRACT

Nano solar cell materials cannot sustain imprinted thermodynamic potentials yielding electrical fields for a charge separation. They have, therefore, to rely on kinetic mechanisms for current rectification and energy conversion. It is shown that treatment of WS$_2$ nano-sheet sensitized TiO$_2$ material with organic thiols increases the photocurrent efficiency at least three fold. They bind to the WS$_2$ via the thiol sulfur to produce a charged surface state, which converts into an efficient electron transfer bridge in presence of suitable electron donors. These thiol bridges essentially operate in anodic direction. Thus they increase both the photo induced chemical affinity, which is proportional to the photovoltage generated, and the interfacial reaction rate which is proportional...
to the photocurrent. The results underline the importance of studying unidirectional electron transfer processes for innovative solar cell applications.

GRAPHICAL ABSTRACT

INTRODUCTION

The solar energy reaching our planet (reflected light deduced) amounts to 121,000 TW (1TW=10^{12} W). It is about the 8,000-fold of the world’s energy consumption in 2010. However, to date solar energy devices still suffer from low efficiencies or comparably high costs despite the ongoing research within this field. Nanocomposite solar cells have attracted considerable interest within this context.\textsuperscript{1-5} On one hand nanomaterials are easy to prepare which suggests significant economical advantages for solar cell production.\textsuperscript{6,7} On the other hand the resulting nano solar cells are still facing significant problems with respect to instability.

Most problems encountered with nanostructured solar cells appear to be related to an only partial understanding of the mechanism involved. Molecular kinetic mechanisms have to be functioning to facilitate current rectification and unidirectional electron transfer.\textsuperscript{8} The importance of kinetic effects became, for example, visible with the work of Hodes et al. demonstrating that
the same nanocrystalline film exhibits n- as well as p-type behavior, depending on the hole or electron scavenger used as electrolyte. However, a more fundamental understanding of nanocomposite solar cell function on the basis of kinetic electron transfer rectification is needed. This has recently been attempted by deriving the nano solar cell function from the principle of least action, as applied to irreversible thermodynamics (principle of minimum entropy production). The most straightforward strategy to increase the power output of a kinetically determined solar cell would be to rectify electron transfer by suppressing reverse reactions. For nano solar cells, interfacial electrochemical properties need therefore to be developed, which favor unidirectional electron exchange.

The present work aims at investigating the advantage of thiols for this purpose by adsorbing them to TiO$_2$ nanoparticles sensitized with WS$_2$-nanosheets. The thiols should enhance unidirectional electron transfer and thus current rectification. The idea of using thiols was derived from biology, where cysteine, a thiol group containing amino acid, has been playing a significant role in electron transfer since early evolution. Recently, organic thiols have been used to improve the performance of photovoltaic devices (PV). For instance, a few volume per cent alkanedithiols incorporated into a polymer/fullerene solution before spin-casting led to an increase of power-conversion efficiency by about 100%. The results were explained by an increased efficiency in mobile-carrier-generation as well as an increased mobile-carrier lifetime due to changes within the heterojunction morphology. Moreover, quantum dot PV have been treated with organic thiols. PV from ITO sensitized with PbS and PbSe showed higher efficiency when treated with ethanethiol. The effect was explained by surface passivation due to the adsorption of organic thiols. Furthermore, Chen et al. reported on the use of n-butanethiol to improve the performance of P3HT/CdSe PV. They concluded that monofunctional thiols are
better in order to improve the efficiency of hybrid solar cells than the commonly used bifunctional thiols due to enhanced charge transport between nanocrystals.

Herein we present a series of organic thiols as organic rectifiers for a TiO₂/WS₂ nano solar cell and discuss their function with respect to their chemical structure.

EXPERIMENTAL

Unless otherwise noted, all chemicals were purchased from Fluka. All samples were heated to 150°C in order to remove water residues from TiO₂ pores prior to sensitization via chemical bath deposition (CBD).²¹ First, pure sulfur was dissolved in 50 mL cymene (1-isopropyl-4-methylbenzene, CH₃C₆H₄CH(CH₃)₂) to obtain a 0.1 M solution. Then the TiO₂ samples were carefully placed at 45° inclined to the vertical wall into a glass container with sulfur solution. Then the solution was heated up to 170°C until the boiling point was reached. After 20 min (to allow the dissolved sulphur to penetrate the TiO₂ pores), W(CO)₆ was added (0.05M) and the container was covered with a glass top. The colour of the solution changed to dark brown immediately. After waiting for additional 30 sec to 2 min the substrates were removed from the container and dried in air. Then they were washed with acetone and distilled water and dried in vacuo.

Sensitizing of the WS₂/TiO₂ solar cells was achieved by chemical bath deposition using solutions of D- and L-cysteine, thioglycolic acid, 3-mercaptopropionic acid, thiosalicylic acid and 2-thiophencarboxonic acid (1w%, 5w%, sat.) for up to 90h at room temperature.

The TiO₂ layers, produced via the sol-gel method on a conducting substrate (fluorine doped glass, 15 1/cm²), were purchased from SGLux. The electrodes were contacted with the help of Elecolit Panasol 353, a two compound silver epoxy glue. A small part of sensitized TiO₂ was removed from the electrode. Then the conducting glue was placed on the conducting glass with a
piece of copper wire and allowed to dry. The electrodes were carefully sealed with Screentec RTV silicon rubber to avoid short circuits between FTO and liquid electrolyte. The electrically accessible surface had an area of approximately 2 cm$^2$. All SEM images were taken using LEO 1530 Scanning Electron microscope at 2 kV equipped by an Energy Dispersive X-Ray Fluorescence Analyser (EDX) to quantify the composition of the samples.

For the electrochemical measurements a three electrodes setup was used. The counter electrode was platinum wire and the reference electrode was SCE (saturated calomel electrode). The nano-structured TiO$_2$ electrode was illuminated from the front (which means from the FTO/TiO$_2$ side, which is the usual dye solar cell set-up). The electrolyte used for electrochemical measurements was 0.5 M LiI dissolved in propylene carbonate. For the determination of photocurrents a Schott KL 1500 LCD has been used as a light source. The electrolytic contact was just used for testing the photoelectrical quality of the layers, since the final aim was to develop an all solid nanostructured cell. For chemical treatment and edge site passivation of the samples, a 1% TWEEN 80 (polyethylene glycol sorbitan monooleate) solution in H$_2$O has been used. All other chemicals for the treatment were a 5% solution in H$_2$O.

RESULTS AND DISCUSSION

A schematic picture of the nanostructured TiO$_2$ electrode sensitized with WS$_2$ nanosheets is shown in Figure 1a. An iodide/iodine electrolyte maintains the electrolytic contact to the counter electrode. During illumination electrons are excited within the WS$_2$ to stimulate electron transfer to the TiO$_2$ and regeneration from the iodide/iodine redox electrolyte.
Figure 1b shows the characteristic scanning electron microscopic structure of the TiO$_2$ nanofilm produced by a sol-gel technique, during which a hydrolytic decomposition of titaniumtetraisopropylate is occurring via spray pyrolysis according to the reaction

$$Ti(C_3H_8OH)_4 + 2H_2O \rightarrow TiO_2 + 4C_3H_7OH$$

(1)

This nanofilm could be further functionalized with tungsten disulfide nanoparticles by a chemical bath deposition (CBD) method (Figure 1c). In a similar way, thus by CBD, organic thiols can chemisorb to the WS$_2$ particles, providing a rectifying electron transfer relay. The thereby changed photocurrent density was expected to be a measure for photocurrent rectification.

The property of thiols to rectify electron transfer to the layer material has been experimentally deduced from photoelectrochemical studies$^{22,23}$ of cysteine on MoS$_2$, which has a similar electronic and crystal structure as WS$_2$. If electrons are taken from a thiol sulfur that is attached to a metal, the electron density will be lowered and redistributed over the whole molecule. In contrast, donation of an electron to the sulfur is not possible which renders electron transfer through cysteine essentially rectified. The organic thiols used in the present work are summarized in Figure 2. Beside cysteine itself (1,2) we chose two derivatives similar to cysteine but without amino group, namely 3-mercaptopropionic acid (3) with a C2-spacer and thioglycolic acid (4) with a C1-spacer between the thiol and the carboxylic acid function. Furthermore, we tested thiosalicylic acid (5) bearing an aromatic C6-ring as well as thiophenes carrying a carboxlic acid in 2 and 3 position (6,7).
Figure 3a shows a current potential diagram, which compares the behavior of dark current and photocurrent in absence and presence of L-cysteine (2) after exposure lasting 5 and 25 hours, respectively. Interestingly, the photo effect of the cysteine treated nanoelectrode is significantly increased. By using a 5% mixture of D–cysteine (1) and L–cysteine (2) in water for the treatment of the WS$_2$-layer, no significant increase of photocurrents is observed after 18h (Figure 3b). However, after 90 hours a three times increase of the photocurrent develops. Long-term treatment apparently improves the photo-efficiency significantly. Comparative studies show that cysteine and thioglycolic acid (4) yield good improvements of the photoeffect, but the promoting effect disappears when the 3-mercaptopropionic acid (3) or thiols with longer alkyl chains are used. Aromatic compounds like thiosalicylic acid (5) improve the photocurrents but two tested thiophene carbonic acids (6,7) decreased the photocurrent output. The low performance of the thiophene derivatives 6 and 7 may be explained by the reduced ability of the thiophene sulfur to bind to the WS$_2$/TiO$_2$ surface due to the absence of a thiol group. Table 1 shows, under comparable conditions, the effect of different thiols on the performance of the nanophotocathode sensitized with WS$_2$. The relationship between the chemical structure of the organic thiol and its ability to improve the photocurrent is not fully clear at the moment. As indicated by the drop of efficiency when thiophenes are used, the thiol group seems to be important for effective binding of the molecule onto the surface. Surprising is the dramatic drop of photocurrent output when 3 was used instead of cysteine, indicating the importance of the amino group for efficient rectification.

From earlier studies of cysteine-molybdenum disulfide interaction and its effect on the photoelectrochemistry of the system$^{22,23}$ it could be expected that cysteine is also attaching to WS$_2$ and thus increasing the photoeffect of the TiO$_2$/WS$_2$ nanocomposite electrode. The present work has confirmed this expectation. Cysteine is functioning as a rectifying molecular bridge
which is suppressing a reverse reaction of electrons from the WS\(_2\) conduction states. As Figure 4 visualizes the relevant interaction is expected to occur via the thiol sulfur with metal d-states on edge sites of the layer-type material as well as on to the Van der Waals surfaces where d\(_{z^2}\)-states are protruding through the interface.\(^{22}\)

Holes from the WS\(_2\) nano sheets are efficiently trapped via the thiol-S within the cysteine molecule to form a positively charged adsorbed molecular layer. Such a situation could convincingly be demonstrated by combining photoelectrochemical and microwave conductivity measurements of MoS\(_2\) in presence of cysteine.\(^{24}\) A similar situation is also expected to apply to the here studied nano-WS\(_2\) as shown in the energy diagram depicted in Figure 4. When now electrons from an electron donating redox system such as I\(^{-}\)/I\(^{3-}\) are available, the positive charge of the cysteine molecule is neutralized and the captured electron is available for renewed electron transfer to the valence states of WS\(_2\)-sheets. In this way the adsorbed thiol molecule is acting as an electron transfer bridge. This can be deduced from the significantly increased photocurrent density observed. The function of the bridge is highly asymmetric. When electrons are deduced from the sulfur atom of the thiol group and drawn into the WS\(_2\) the electron density distribution within the thiol molecule will change accordingly and facilitate an electron recovery from the redox donor. However, the function of the electron transfer bridge cannot easily be reversed since it is not at all favorable for donating an electron to the sulfur of the thiol group, which is chemisorbed on WS\(_2\)-sheets. In this way the thiols work as asymmetric electron transfer shuttles and contribute towards a rectification of photocurrents in the nano composite structure. A comparison of the action of different organic thiols suggest that thiols, which combine a thiol group with carbonic acid are favorable with respect to a stimulation of unidirectional electron transfer. Longer alkyl chains interfere drastically with this effect, since they reduce the electron
transfer probability (or electron conduction). Equally, molecular structures, which interfere with a favorable positioning of the absorbed thiol species are expected to reduce the photocurrent efficiency.

CONCLUSIONS

As shown in a previous publication, nanocomposite solar cells are controlled by a power output law, which is proportional to the product of chemical affinity and reaction rate. The chemical affinity (proportional to the Gibbs-free energy) of a photochemical reaction acts as a thermodynamic force. The reaction rate is acting as a thermodynamic flux. Both reach a high value when the reverse reaction is suppressed, i.e., electrons are preferably channeled into one direction only. Thus, both the chemical affinity and the reaction rate take advantage of an inhibited reverse reaction which leads to an improvement of the power output conditions.

Cysteine and other thiols play the role of such rectifying electronic elements and therefore support energy extraction for power generation. The efficiency of such molecular electronic rectifiers depends on the size and structure of the molecules. Beside a thiol group for efficient adsorption onto the surface, as indicated by the drastic drop of photocurrents when thiophenes were used, the spacer type and length between thiol and carboxylic acid appeared to be of high importance. While an aromatic ring shows good results, aliphatic spacer of C2 or more have even negative effects on the cell performance.

Unidirectional electron transfer can not easily be described via the standard Marcus theory of electron transfer, since the relevant quantum processes allow a facile inversion of the mechanism. To make electron transfer directional, feedback processes on molecular electronic level are required. This means, the electron transfer should be accompanied by a polarization of the
molecular environment. Such a polarization mechanism is excluded in the Markus approach for electron transfer. But it has to be considered for uni-directional electron transfer. An electron restructures the environment during passage so that a return of the electron is made improbable. Such mechanisms, i.e., self-organized or stimulated electron transfer, are apparently only accessible for phenomenological theoretical calculations.\textsuperscript{26-33} One reason is that a quantum process does not know time, a “before” and “after”, needed for feedback mechanisms (the time in the time-dependent Schrödinger equation arises from classical perturbation theory). Many details have still to be learned about the chemical requirements of photovoltaic membranes, which only allow photocurrents into one preferred direction. The results presented in this work serve as examples, which should attract interest in the fundamentals of such kinetically determined solar cells.

FIGURES

a)

\begin{center}
\includegraphics[width=0.5\textwidth]{figure1}
\end{center}

b)
Figure 1: a) Schematic representation of the TiO2 nano-layer on a FTO contact, sensitized by WS2 nano-sheets; b) SEM picture of TiO2 layers obtained by Sol-Gel techniques; c) SEM picture of WS2 particle sensitizing TiO2.
**Figure 2**: Thiols used for rectification of electron transfer on WS2 nano-sheets; D-cystein (1), L-cystein (2), mercaptopropionic acid (3), thioglycolic acid (4), thiosalycilic acid (5), thiophene-2-carboxylic acid (6) and thiophene-3-carboxylic acid (7)

![Diagram showing thiols used for rectification of electron transfer on WS2 nano-sheets](image)

**Figure 3**: a) Current – voltage diagrams of WS$_2$ sheet / TiO$_2$ electrodes treated with and without L-cysteine (2) in the dark and during illumination; b) Photocurrent – voltage diagram for WS$_2$–sheet/TiO$_2$ electrodes treated with a 5% mixture of D- and L-cysteine (1/2) in water after 18 (red) and 90 hours (blue) respectively.

![Diagram showing current-voltage and photocurrent-voltage diagrams](image)
**Figure 4:** Energy scheme visualizing sensitization of nano-TiO$_2$ using nano-sheets of WS$_2$ and a current rectifying adsorbed thiol molecule mediating electron transfer from the iodide/iodine electrolyte. The latter can, *via* the S atom of the thiol, donate electrons to the energetically closer d-valence states of WS$_2$ but is unable to accept electrons from its energetically more distant conduction states.

**TABLES.**

**Table 1:** Photocurrent efficiencies of TiO$_2$/WS$_2$ nano solar cells before and after treatment with organic thiols 1-7.

<table>
<thead>
<tr>
<th>Thiol</th>
<th>Duration of Treatment [h]</th>
<th>Thiol Conc. [w%]</th>
<th>Before Treatment [mA]</th>
<th>After Treatment [mA]</th>
<th>Increase [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>D/L Cysteine (1/2)</td>
<td>90</td>
<td>5</td>
<td>0.05</td>
<td>0.14</td>
<td>180</td>
</tr>
</tbody>
</table>
L Cysteine (2) & 18 & 5 & 0.05 & 0.1 & 100 \\
3-Mercapto propionic acid (3) & 19.5 & 5 & 0.2 & 0.1 & -50 \\
Thioglycolic acid (4) & 19.5 & 5 & 0.1 & 0.14 & 40 \\
Thiosalicylic acid (5) & 69 & 1 & 0.05 & 0.08 & 60 \\
2-Thiophene carbonic acid (6) & 19 & sat. & 0.08 & 0.07 & -12.5 \\
3-Thiophene carbonic acid (7) & 19 & sat. & 0.16 & 0.1 & -37.5 \\

ASSOCIATED CONTENT

Supporting Information. Photocurrent – voltage diagrams for all experiments listed in Table 1.

AUTHOR INFORMATION

Corresponding Author

*Dr. Jan Weiss

Current address: Institute Charles Sadron, UPR22-CNRS 67034 Strasbourg (France)

E-mail: Jan.Weiss@daad-alumni.de
References

Graphical Abstract (for review)

Photocurrent Efficiency Increase by Factor 3!
Figure 1a

The diagram illustrates a layered structure with the following components:

- **Glass**
- **FTO**
- **WS\textsubscript{2}**
- **TiO\textsubscript{2}**

The diagram shows the layers from top to bottom: WS\textsubscript{2} and TiO\textsubscript{2} on top, followed by FTO and then Glass.
Figure 3a

Plot showing the relationship between current (mA) and potential (V) vs. SCE with different treatment conditions:

- **Photo current 24 hours treatment**
- **Photo current 5 hours treatment**
- **Photo current without treatment**
- **Dark current**

The graph demonstrates the increase in current with potential for each treatment condition.
Figure 3b
TABLES.

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<td>5</td>
<td>0.05</td>
<td>0.14</td>
<td>180</td>
</tr>
<tr>
<td>L Cysteine (2)</td>
<td>18</td>
<td>5</td>
<td>0.05</td>
<td>0.1</td>
<td>100</td>
</tr>
<tr>
<td>3-Mercapto propionic acid (3)</td>
<td>19.5</td>
<td>5</td>
<td>0.2</td>
<td>0.1</td>
<td>-50</td>
</tr>
<tr>
<td>Thioglycolic acid (4)</td>
<td>19.5</td>
<td>5</td>
<td>0.1</td>
<td>0.14</td>
<td>40</td>
</tr>
<tr>
<td>Thiosalicylic acid (5)</td>
<td>69</td>
<td>1</td>
<td>0.05</td>
<td>0.08</td>
<td>60</td>
</tr>
<tr>
<td>2-Thiophene carbonic acid (6)</td>
<td>19</td>
<td>sat.</td>
<td>0.08</td>
<td>0.07</td>
<td>-12.5</td>
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<td>3-Thiophene carbonic acid (7)</td>
<td>19</td>
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</tr>
</tbody>
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Bioinspired WS₂/TiO₂ nano solar cells treated with organic thiols are presented.

An increase of the photocurrent efficiency by a factor of three is observed.

Organic thiol bridges act as rectifying electronic elements.

Unidirectional electron transfer is important for innovative solar cell applications.