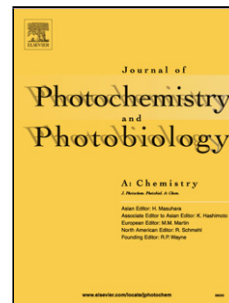


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Bioinspired Solar Cell Design: Organic Thiols as Rectifying Electron Transfer Bridges in WS₂/TiO₂ Nano Solar Cells

Jan Weiss^{1}, Markus Thomalla¹ 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

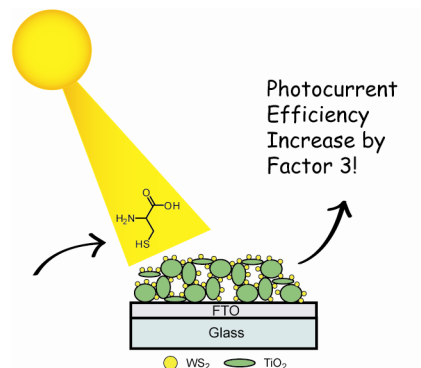
KEYWORDS (nano solar cells, thiols, electron transfer bridges, kinetically determined solar cells, quantum dots).

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 WS₂ nano-sheet sensitized TiO₂-material with organic thiols increases the photocurrent efficiency at least three fold. They bind to the WS₂ *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=10¹²W) 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.¹⁻⁵ On one hand nanomaterials are easy to prepare which suggests significant economical advantages for solar cell production.^{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.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.⁹ 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).¹⁰ 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 TiO₂ nanoparticles sensitized with WS₂-nanosheets.¹¹ 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.^{8,12} Recently, organic thiols have been used to improve the performance of photovoltaic devices (PV).^{13,14} 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%.¹⁵ 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.¹⁶⁻¹⁸ PV from ITO sensitized with PbS and PbSe showed higher efficiency when treated with ethanethiol.¹⁹ 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.²⁰ 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 TiO_2/WS_2 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 TiO_2 pores prior to sensitization *via* chemical bath deposition (CBD).²¹ First, pure sulfur was dissolved in 50 mL cymene (1-isopropyl-4-methylbenzene, $\text{CH}_3\text{C}_6\text{H}_4\text{CH}(\text{CH}_3)_2$) to obtain a 0.1 M solution. Then the TiO_2 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 TiO_2 pores), $\text{W}(\text{CO})_6$ 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 WS_2/TiO_2 solar cells was achieved by chemical bath deposition using solutions of D- and L-cysteine, thioglycolic acid, 3-mercaptopropionic acid, thiosalicylic acid and 2-thiophencarbonic acid (1w%, 5w%, sat.) for up to 90h at room temperature.

The TiO_2 layers, produced *via* the sol-gel method on a conducting substrate (fluorine doped glass, $15 \text{ !}/\text{cm}^2$), 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 TiO_2 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 Screenshot 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 nanostructured 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_2O has been used. All other chemicals for the treatment were a 5% solution in H_2O .

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 TiO₂ nanofilm produced by a sol-gel technique, during which a hydrolytic decomposition of titaniumtetraisopropylate is occurring *via* spray pyrolysis according to the reaction



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 WS₂ 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 MoS₂, which has a similar electronic and crystal structure as WS₂. 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 carboxylic 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 WS₂-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 WS₂/TiO₂ 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 WS₂. 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 WS₂ and thus increasing the photoeffect of the TiO₂/WS₂ 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 WS₂ 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_{z²}-states are protruding through the interface.²²

Holes from the WS₂ 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 MoS₂ in presence of cysteine.²⁴ A similar situation is also expected to apply to the here studied nano-WS₂ as shown in the energy diagram depicted in Figure 4. When now electrons from an electron donating redox system such as I⁻/I₃⁻ 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 WS₂-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 WS₂ 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 WS₂-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,²⁵ 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.

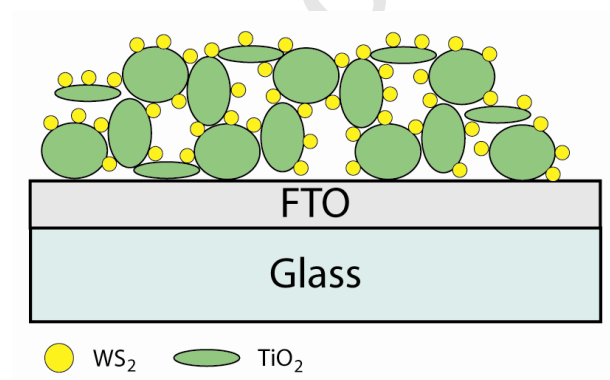
Cysteine and other thiols play the role of such rectifying electronic elements and therefore support energy extraction for power generation. The efficiency of such molecular electronic rectifiers depends on the size and structure of the molecules. Beside a thiol group for efficient adsorption onto the 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

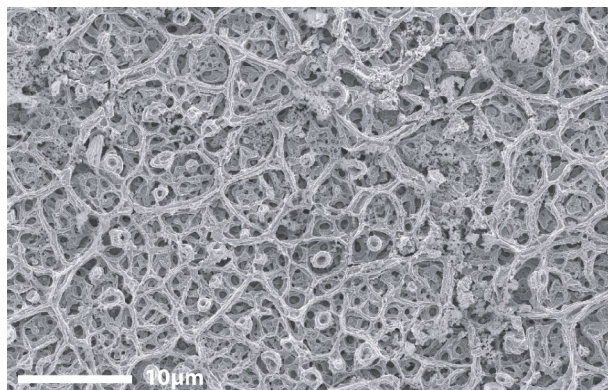
molecular environment. Such a polarization mechanism is excluded in the Marcus approach for electron transfer. But it has to be considered for uni-directional electron transfer. An electron restructures the environment during passage so that a return of the electron is made improbable. Such mechanisms, *i.e.*, self-organized or stimulated electron transfer, are apparently only accessible for phenomenological theoretical calculations.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)



b)



c)

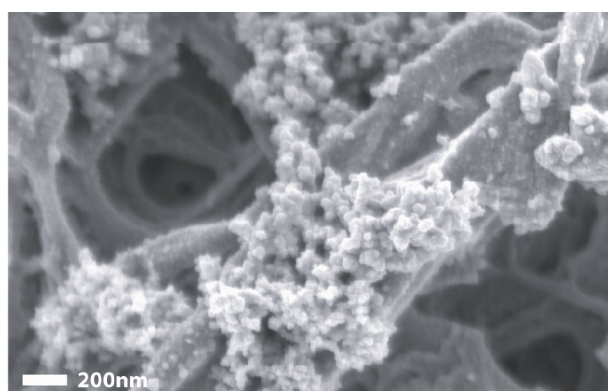


Figure 1: a) Schematic representation of the TiO₂ nano-layer on a FTO contact, sensitized by WS₂ nano-sheets; b) SEM picture of TiO₂ layers obtained by Sol-Gel techniques; c) SEM picture of WS₂ particle sensitizing TiO₂.

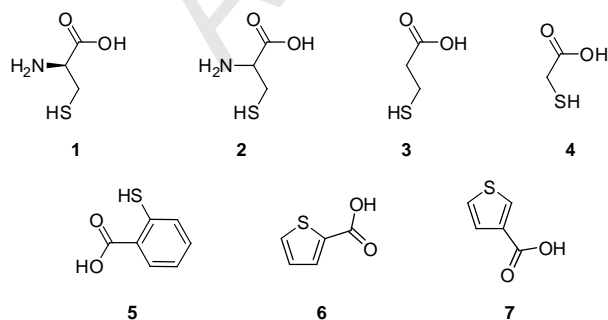


Figure 2: Thiols used for rectification of electron transfer on WS₂ nano-sheets; D-cystein (1), L-cystein (2), mercaptopropionic acid (3), thioglycolic acid (4), thiosalicylic acid (5), thiophene-2-carboxylic acid (6) and thiophene-3-carboxylic acid (7)

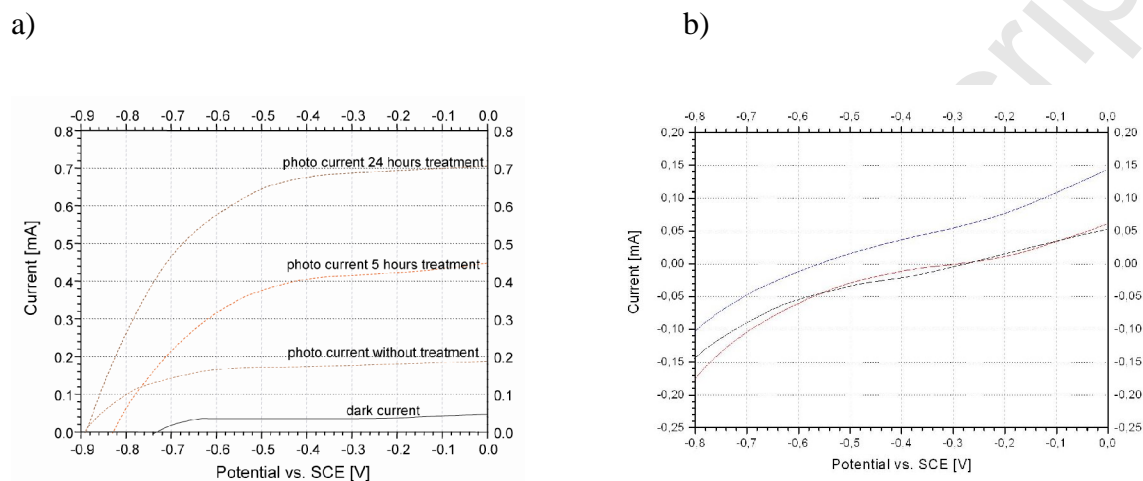


Figure 3: a) Current – voltage diagrams of WS₂ sheet / TiO₂ electrodes treated with and without L-cysteine (2) in the dark and during illumination; b) Photocurrent – voltage diagram for WS₂ – sheet/TiO₂ electrodes treated with a 5% mixture of D- and L–cysteine (1/2) in water after 18 (red) and 90 hours (blue) respectively.

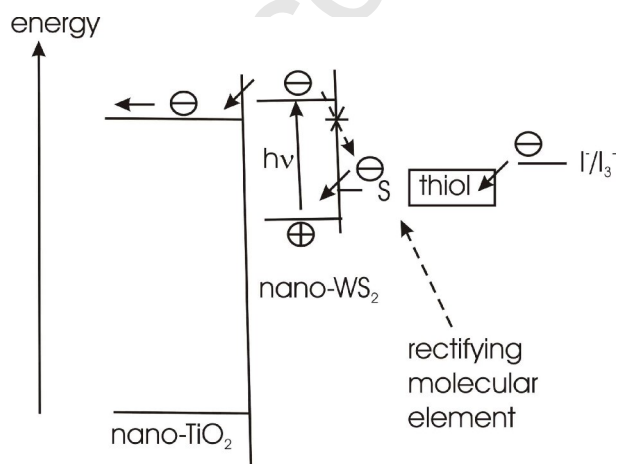


Figure 4: Energy scheme visualizing sensitization of nano-TiO₂ using nano-sheets of WS₂ and a current rectifying adsorbed thiol molecule mediating electron transfer from the iodide/iodine electrolyte. The latter can, *via* the S atom of the thiol, donate electrons to the energetically closer d-valence states of WS₂ but is unable to accept electrons from its energetically more distant conduction states.

TABLES.

Table 1: Photocurrent efficiencies of TiO₂/WS₂ nano solar cells before and after treatment with organic thiols **1-7**.

Thiol	Duration of Treatment [h]	Thiol Conc. [w%]	Before Treatment [mA]	After Treatment [mA]	Increase [%]
D/L Cysteine (1/2)	90	5	0.05	0.14	180

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

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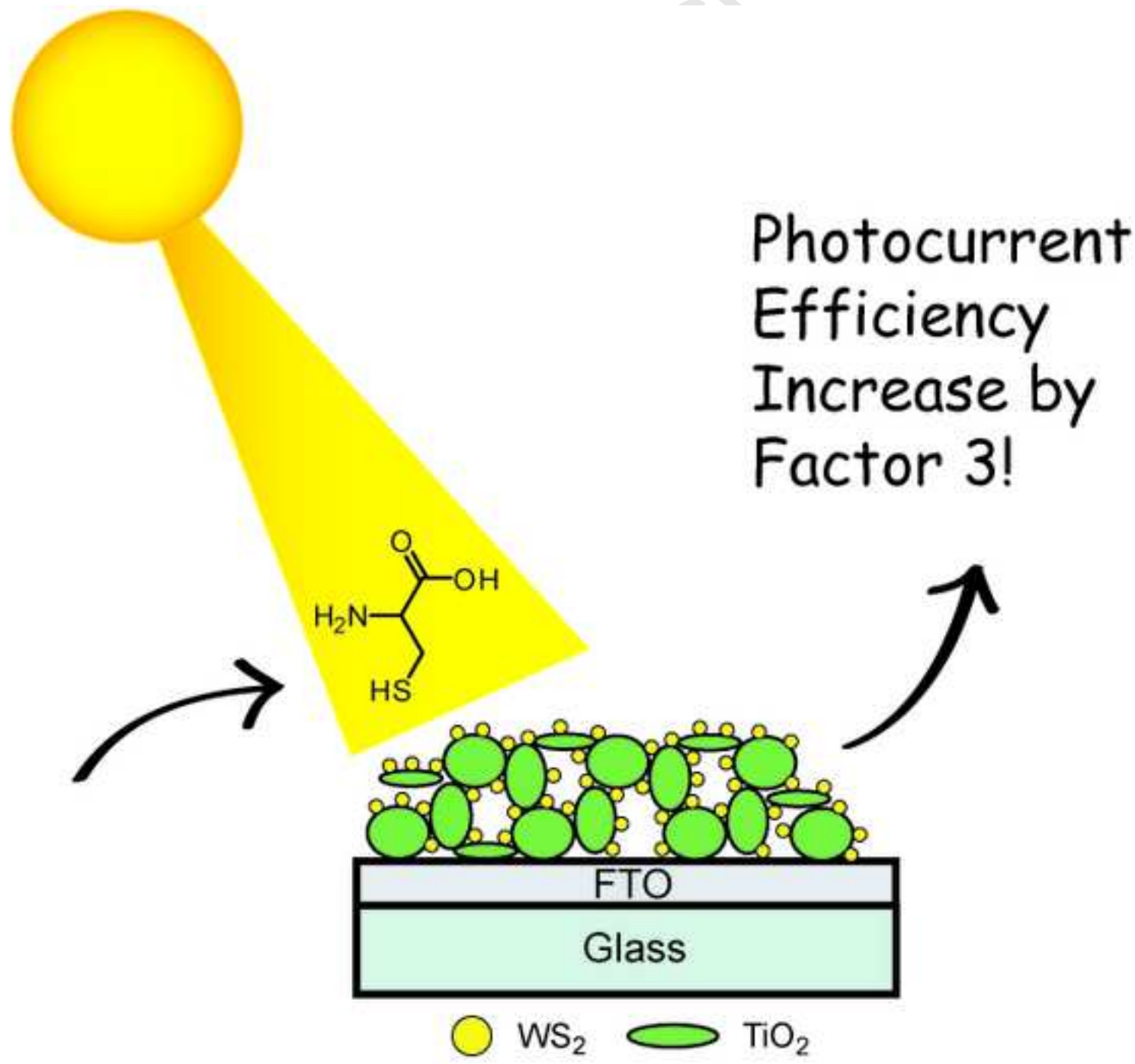


Figure 1a

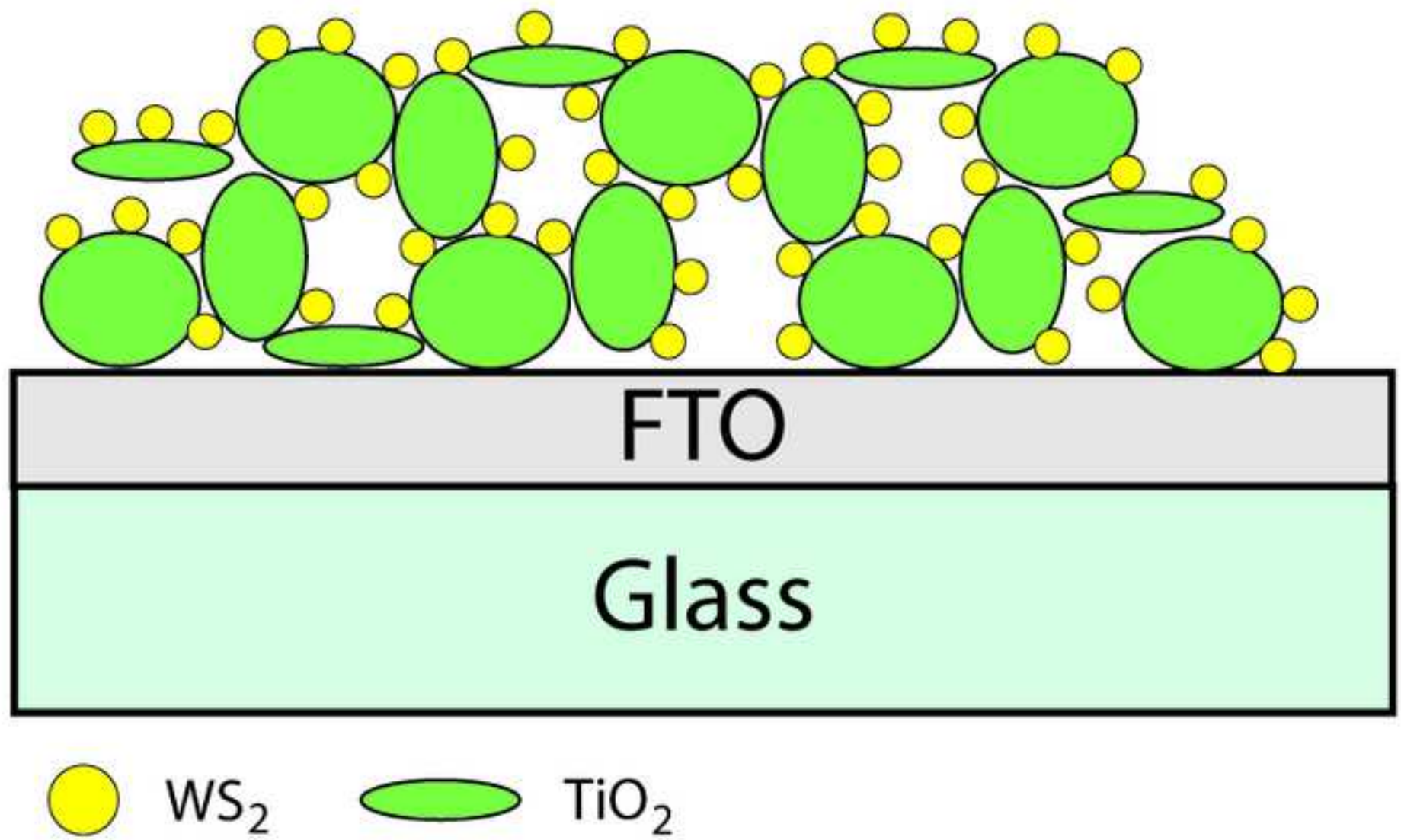


Figure 1b

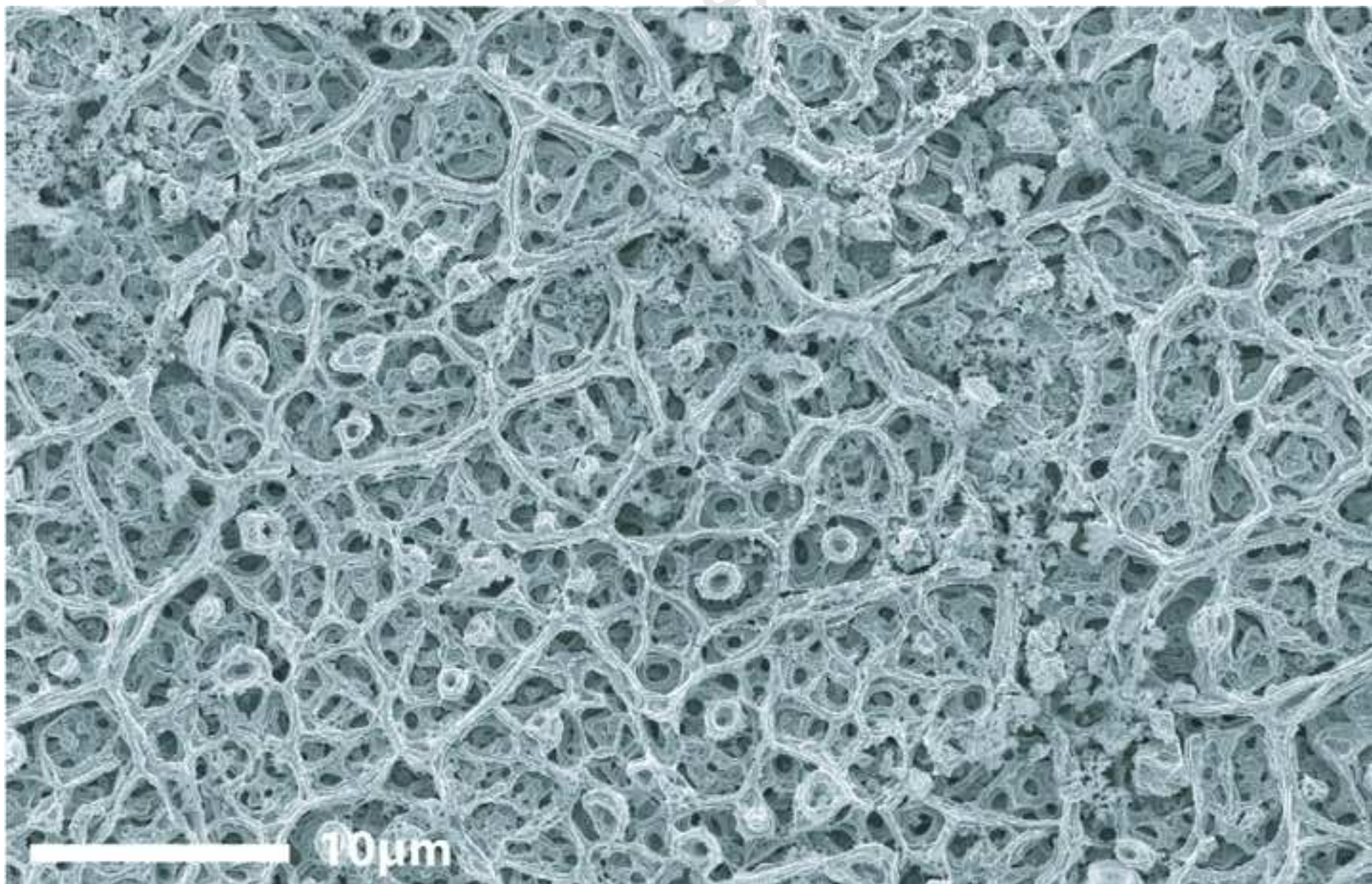


Figure 1c

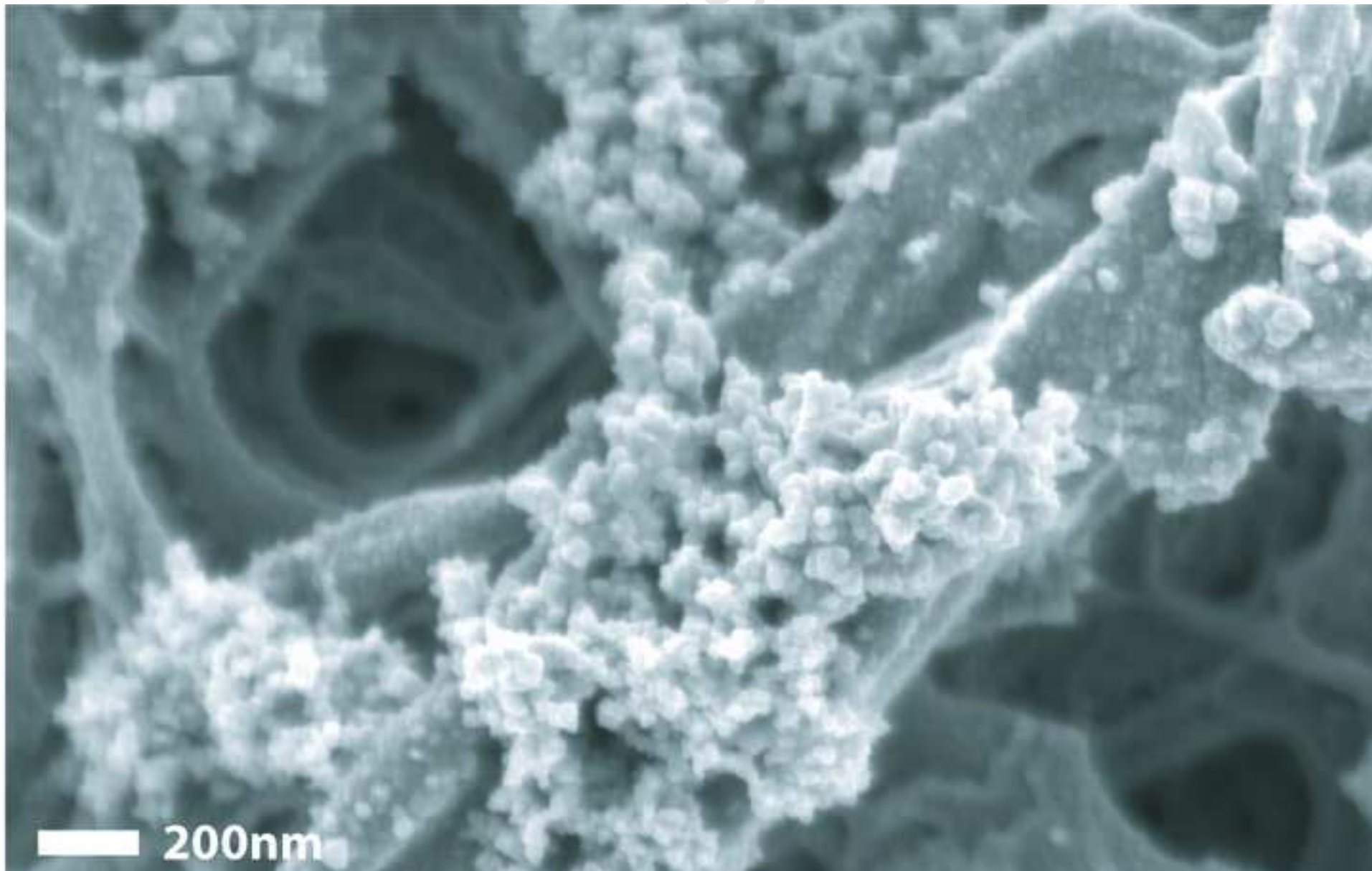
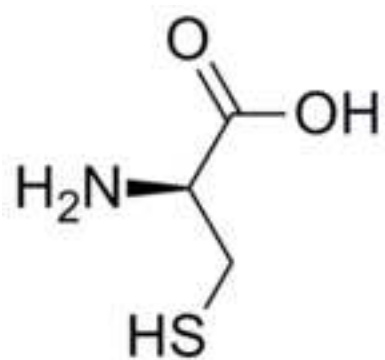
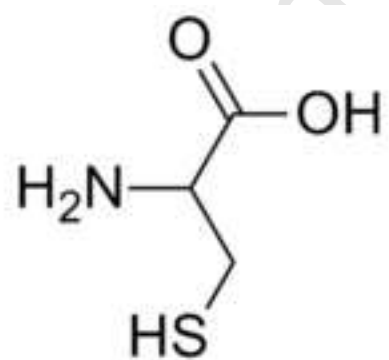


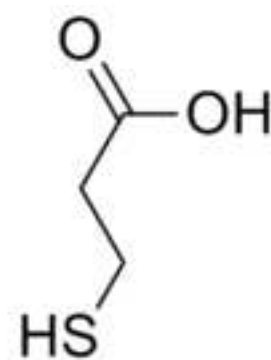
Figure 2



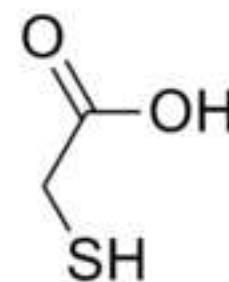
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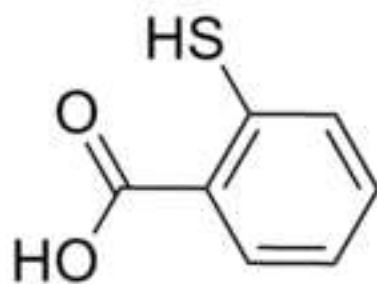
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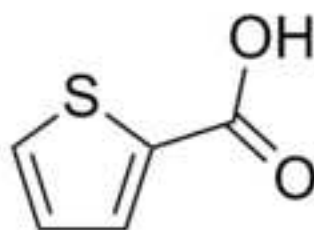
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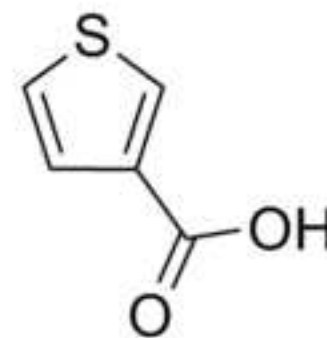
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Figure 3a

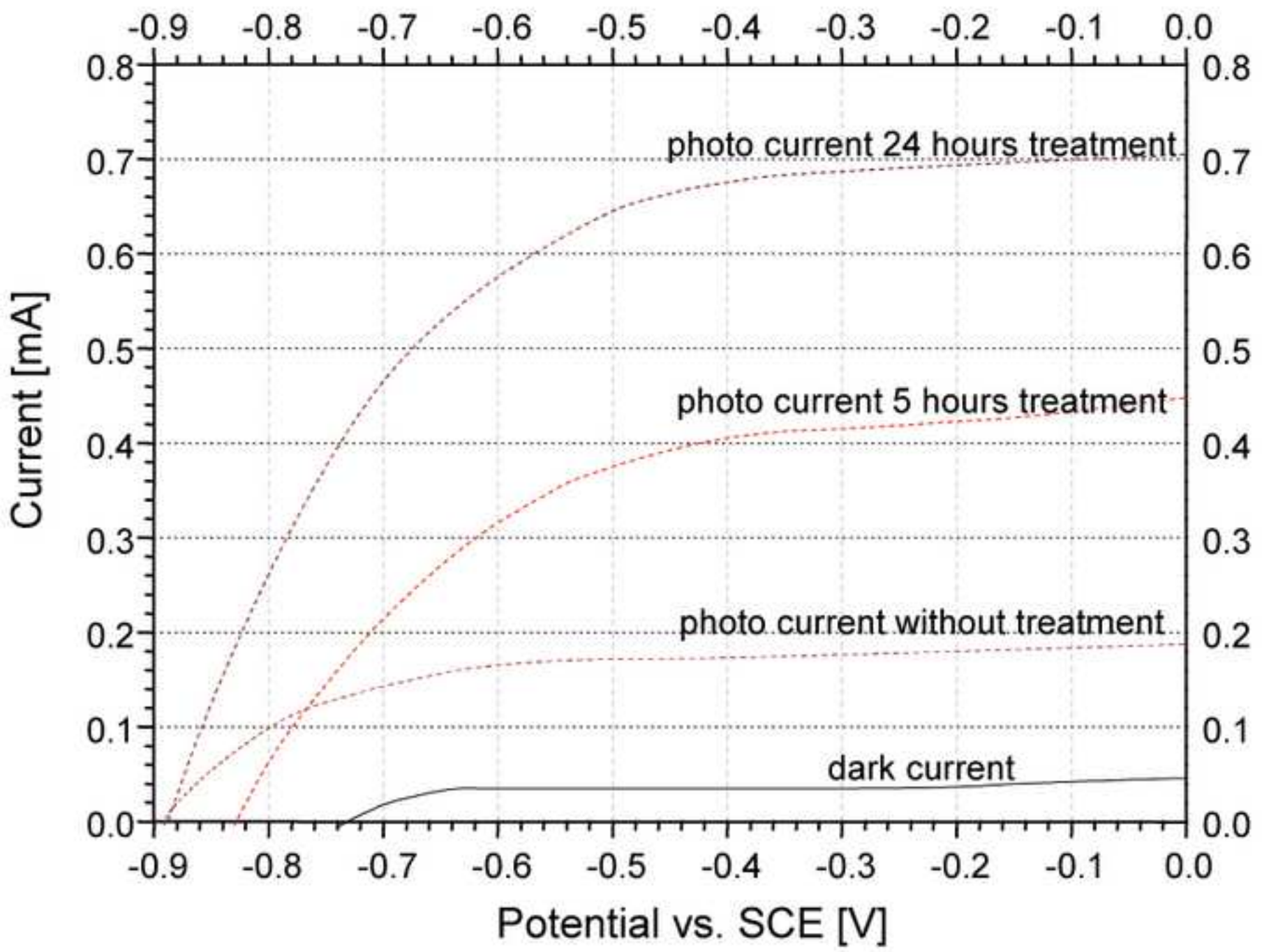
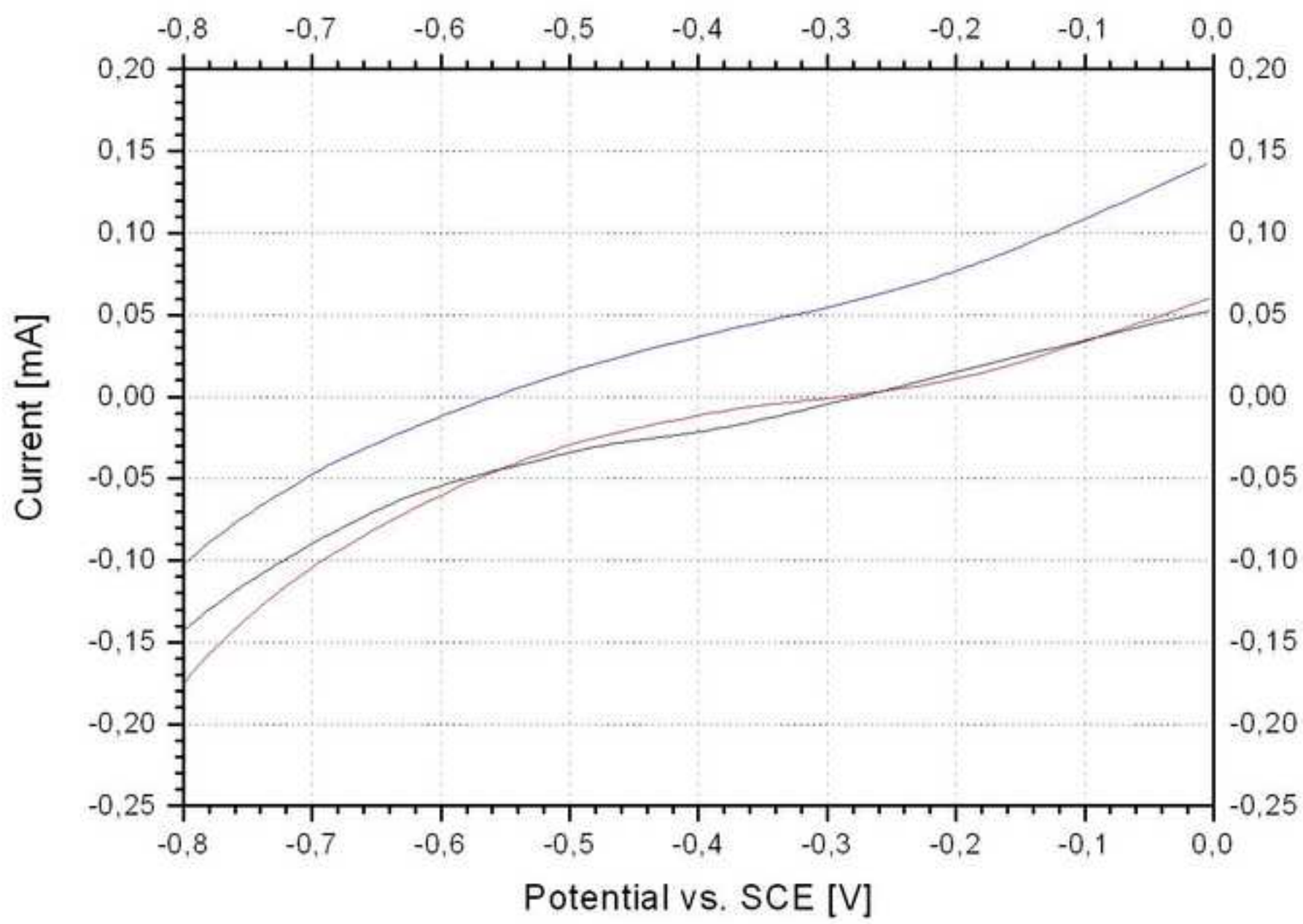
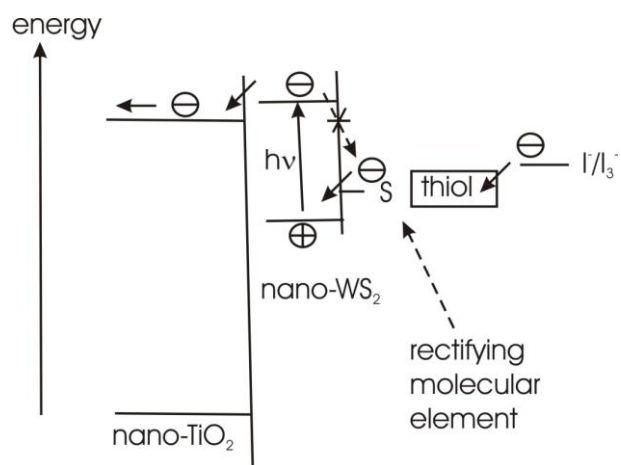


Figure 3b





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TABLES.

Table 1: Photocurrent efficiencies of TiO₂/WS₂ nano solar cells before and after treatment with organic thiols 1-7.

Thiol	Duration of Treatment [h]	Thiol Conc. [w%]	Before Treatment [mA]	After Treatment [mA]	Increase [%]
D/L Cysteine (1/2)	90	5	0.05	0.14	180
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

- 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.

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