

Dr Renata Solarska

Summary of achievements

Annexe III to the habilitation procedure

Faculty of Chemistry University of Warsaw
Warsaw April 2019

1. First name and surname:

Renata Solarska

2. Scientific degrees:

- 2013 Diploma in **Management of Research Projects & Development Activities** –
University of Economics and Innovation, Lublin, Poland
- 2006 **PhD Degree in Chemistry** - University of Geneva, Switzerland
**« Properties and Applications of Mesoporous Semiconductor Oxide
Films »**
- 2001 **MSc degree in Chemistry** - University of Warsaw, Poland

3. Professional experience:

- since 2018 Head of Laboratory of Molecular Research for Solar Energy Innovation
(SOLEIL) in Centre of New Technologies University of Warsaw
- 2013 –
up to now Assistant Professor (*Adiunkt*) in Centre of New Technologies University
of Warsaw
- 2009 – 2016 Assistant Professor (*Adiunkt*) at Faculty of Chemistry University of
Warsaw
- 2007 - 2009 Scientist in the Institute EMPA Dübendorf (Swiss Federal
Laboratories for Materials Science and Technology), Switzerland
- 2006 - 2007 Assistant (A3) in Department of Crystallography University of Geneva,
Switzerland
- 2002 - 2006 Assistant (A2) in Department of Inorganic, Analytical and Applied
Chemistry University of Geneva, Switzerland
- 2001- 2002 Trainee in Laboratory of Supramolecular Chemistry, Institute of
Physical Chemistry Polish Academy of Science, Warsaw

4. Following the article 16 par. 2 of the act of 14th March 2003 on scientific degrees and scientific title and on degrees and title in arts (Journal of Laws 2017, poz.1789) changes) I indicate as follows:

Developing of the structural, morphological and surface changes in the semiconducting transition metal oxides to couple their properties towards enhanced solar energy conversion

as the scientific achievement to proceed the habilitation procedure.



I also indicate the following 12 publications as a base for the above-mentioned scientific achievement:

- H1** B. D. Alexander, P. J. Kulesza, I. Rutkowska, **R. Solarska**, J. Augustyński*: Metal oxide photoanodes for solar hydrogen production; *J. Mater. Chem.* 18 (2008) 2298-2303
IF₂₀₀₈ 4.464 (currently *J. Mater. Chem. A* IF₂₀₁₇ 9.931) MNiSW 40
- H2** **R. Solarska***, B.D. Alexander, A. Braun, R. Jurczakowski, G. Fortunato, M. Stiefel, T. Graule, J. Augustyński: Tailoring the morphology of WO₃ films with substitutional cation doping: Effect on the photoelectrochemical properties; *Electrochim. Acta* 55 (2010) 7780 – 7787
IF₂₀₁₀ 3.650 IF₂₀₁₇ 5.116 MNiSW 40
- H3** **R. Solarska**, A. Królikowska, J. Augustyński*: Silver nanoparticles-induced photocurrent enhancement at WO₃ photoanodes; *Angew. Chem. Int. Ed.* 49 (2010) 7980-7983
IF₂₀₁₀ 12.730 IF₂₀₁₇ 12.102 MNiSW 45
- H4** J. Augustyński*, B.D. Alexander, **R. Solarska**: Metal oxide photoanodes for water splitting; *Top. Curr. Chem.* 303 (2011) 1-38
IF₂₀₁₁ 6.568 MNiSW 40
- H5** **R. Solarska***, R. Jurczakowski, J. Augustyński*: Highly stable efficient visible-light driven water photoelectrolysis system using nanocrystalline WO₃ photoanode and methane sulfonic acid electrolyte; *Nanoscale* 4 (2012) 1553-1556
IF₂₀₁₂ 6.233 IF₂₀₁₇ 7.233 MNiSW 40
- H6** J. Brilliet, J-H. Yum, M. Cornuz, T. Hisatomi, **R. Solarska**, J. Augustyński, M. Graetzel, K. Sivula*: Highly efficient water splitting by a dual-absorber tandem cell; *Nature Photonics* 6 (2012) 824-828
IF₂₀₁₂ 27.254 IF₂₀₁₇ 32.521 MNiSW 50
- H7** J. Augustyński*, **R. Solarska**: To what extent do the nanostructured photoelectrodes perform better than their macrocrystalline counterparts? *Catalysis Science and Technology* 3 (2013), 1810-1814
IF₂₀₁₃ 4.760 IF₂₀₁₇ 5.365 MNiSW 35
- H8** **R. Solarska***, K. Bieńkowski, S. Żołądek, A. Majcher, T. Stefaniuk, P. J. Kulesza, J. Augustyński: Enhanced water splitting at thin film tungsten trioxide photoanodes bearing plasmonic gold-polyoxometalate particles; *Angew. Chem. Int. Ed.* 53 (2014) 14196-14200
IF₂₀₁₄ 11.261 IF₂₀₁₇ 12.102 MNiSW 45
- H9** M. Sarnowska, K. Bieńkowski, P. Barczuk, **R. Solarska***, J. Augustyński*: Highly efficient and stable solar water splitting at (Na)WO₃ photoanodes in acidic electrolyte assisted by non-noble metal oxygen evolution catalyst; *Advanced Energy Materials* 6 (2016) 1600526
IF₂₀₁₆ 16.721 IF₂₀₁₇ 21.875 MNiSW 45
- H10** L. G. Bloor, **R. Solarska**, K. Bieńkowski, P. J. Kulesza, J. Augustyński, M. D. Symes*, L. Cronin*: Solar-driven water oxidation mediated by an electron-coupled-proton buffer; *Journal of the American Chemical Society* 138 (2016) 6707-6710

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| | IF ₂₀₁₆ 13.858 | IF ₂₀₁₇ 14.357 | MNiSW 45 |
|--|---------------------------|---------------------------|----------|
- H11** J. Augustynski*, K. Bieńkowski, R. **Solarska**: Plasmon resonance-enhanced photoelectrodes and photocatalysts; *Coordination Chemistry Reviews* 325 (2016) 116-124
- | | | | |
|--|---------------------------|---------------------------|----------|
| | IF ₂₀₁₆ 13.324 | IF ₂₀₁₇ 14.499 | MNiSW 50 |
|--|---------------------------|---------------------------|----------|
- H12** E. Szaniawska, K. Bieńkowski, I. Rutkowska, P. Kulesza*, **R. Solarska***: Enhanced Photo-Electro CO₂ Reduction System Based on Mixed Cu₂O Nonstoichiometric-TiO₂ Photocathode; *Catalysis Today* 300 (2018) 145-151
- | | | | |
|--|--------------------------|--|----------|
| | IF ₂₀₁₇ 4.667 | | MNiSW 40 |
|--|--------------------------|--|----------|

Bibliometrics:

Number of publications: **12**Total IF in the year of publication: **125.49**Total IF at present: **146.34**Sum of Ministry points (MNiSW): **515**Number of citations: **935** (Web of Science 25th March 2019)Number of citations excluding self-citations: 916 (25th March 2019)

4.1 Description of the scientific objectives and the achieved results with an assessment of their potential implementation

Introduction

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Introduction

Multi-directional applications of semiconducting transition metal oxides in various fields of science and development, sets high-quality requirements related to their efficiency and stability within the time. [1-3]. Only in the field of solar energy these materials are used in the construction of various type of sensors [4,5], photoelectrochemical cells [1,6,H1,H4], photovoltaic devices [7] or biomimetic and artificial photosynthesis systems [8] with an aim to harvest and convert this energy to other forms of energy (chemical or electrical) or to store it for example in bonds. However, all these applications require different morphologies, specific architecture and a developed contact surface area with reaction media to achieve an application-specific and cost-effective high solar energy conversion efficiency [1,H1,H2,H4]. Therefore, since the first demonstration of water splitting in a photoelectrochemical (PEC) cell using TiO_2 as a working electrode [9], the design and controlled production of nanostructured photocatalytic materials remains a current and dynamic research trend in the field of solar technologies [1,2,10]. Others, equally important requirements which must be faced by the oxide materials result either from their electronic band structure or the surface properties, including also the phenomena occurring at the interface of semiconductor|electrolyte. These requirements include: i) right position of the valence and conduction bands in regards of their potentials which are responsible for the given process run, b) the width of the gap between them, which determines the absorption range and amount of the incident light. But not only the width of the band gap, but also its electronic structure and presence of the mid-gap electron density states affects the type of charge carrier transition (direct or indirect), thus determines the extent of light harvesting and a spectral response of the photogenerated charge carriers. Further run concerns the charge carrier transport in the bulk of the semiconductor which is determined by the degree of crystallisation of the material and the well-developed grain boundaries. These properties translate directly to quantum efficiency defined as an intrinsic ability of the system to separate the charge carriers generated upon absorption of the irradiation and to bring them to the reaction site without any recombination losses, briefly one photon accounts to one electron at the end [1,11, H1]. The behaviour of the excited charge carriers and their potential recombination paths in a n-type semiconductor [12] is shown in Figure 1:

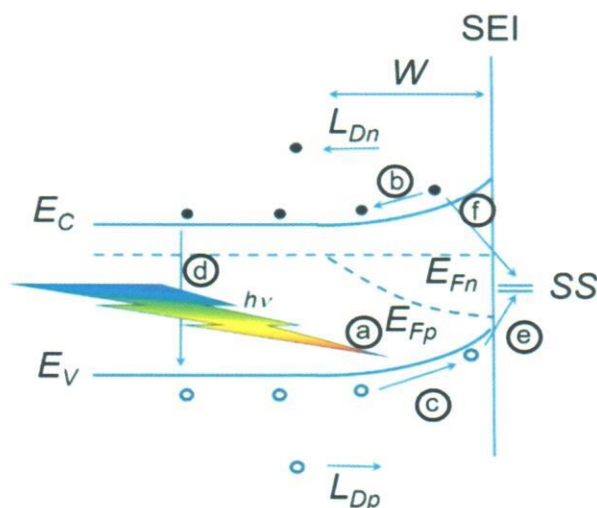


Figure 1. Schematic presentation of charge carrier behaviour after excitation. W -space charge region; a -generation of an electron-hole pair; b- electrons travelling towards the bulk; c- holes travelling towards the interface SEI; d- recombination; e- holes either react with water oxidation species or recombination centre on the surface; SS surface states; f -electrons can also recombine with holes in the SS; L_{Dn} – electrons diffusion length; L_{Dp} – holes diffusion length; E_{Fn} , E_{Fp} quasi Fermi levels for electrons and holes;

Currently, despite undoubtedly many significant achievements in construction of systems enhancing trapping and conversion of solar energy through different conceptual approaches including synthetic ones [2,13], production of nano-architectures allowing to exceed limitations resulting from *e.g.* short charge diffusion path length or integration of components in appropriate geometries [14,15], the common factor is still use of binary transition metal oxides as main photocatalytic material [1,16,H4]. Unfortunately, only a few transition metal oxides semiconductors can combine high solar light absorption with stability in electrolytes, in order to convert it to the energy allowing photoelectrochemical hydrogen production from water splitting or degradation of organic pollutants, or production of solar fuels from CO_2 . These semiconductors include tungsten trioxide WO_3 with bandwidth $E_g = 2.5$ eV, bismuth vanadate BiVO_3 $E_g = 2.4$ eV, iron oxide $\alpha\text{-Fe}_2\text{O}_3$ $E_g = 2.2$ eV or copper oxide Cu_2O $E_g = 2.1$ eV. Among this class of binary semiconductors, there are also doped titanium oxides (TiO_2), however, with very few exceptions, their activity in visible light is limited to the photooxidation of organic compounds rather than to water decomposition or other kinetically demanding photoelectrochemical processes [1,2,16,17,H1,H4,H7]. A solution might be a replacement of transition metal oxides with materials owing narrow band gap, up to *approx.* 2.1 eV [1,18]. However, most of these materials are unstable under light and undergo photocorrosion (*e.g.* GaS, GaP). The systems of three- and more components oxides owing a perovskite structure of ABO_3 are an exception. Moreover, this very stable crystal structure ensures high level of flexibility under different synthetic modifications [19]. However, these materials are much more difficult to obtain in form of a pure phase, because it is not the most thermodynamically

favoured phase. They can create many competitive, simpler phases that are stable. In this scenario, the methods of synthesis that could produce high quality layers of these materials are very limited. **Therefore, development of a conceptual coupling of intrinsic properties of metal oxides with their morphology and semiconductor|electrolyte interface properties, enabling elimination of the bottleneck phenomena and subsequently enhancement of the efficiency of the solar light driven processes, has become a goal of my scientific research described in the publication cycle H1 - H12, which is the objective of the scientific achievement.**

Research objectives

The main processes which hamper full efficiency in solar energy conversion at semiconducting materials is sluggish oxygen evolution kinetics in case of n-type semiconductors and too low electron density in the conduction band for p-type semiconductors. Both, photooxidation and photoreduction processes are limited by the charge transport dynamics of and by the reaction rates in which those photogenerated charges are involved [12, 20]. Thus, only by recognition and full analysis of transport paths of the excited charge carriers in the bulk, enabling also determination of a type of material's conductivity, and identification of the performance limiting processes one can effectively modify the photocatalytic properties of the working system and model its efficiency towards desired process. Too slow kinetics of e.g. water splitting reaction generates energy losses which manifests itself in high overpotential required to drive the reaction and a shift of photopotential towards more positive values. This measurable effect in the form of ohmic drop on the I - E curve and subsequent, lower than expected a photocurrent rise, is caused by an increased recombination of charges occurring both, in the volume and at the surface where the water oxidation process takes place [20,21,H5,H7]. The problem of excessive recombination of charges in kinetically slower processes, cannot be only solved by nanostructuring of semiconductor materials discussed in paper H7. The reason is, that although it shortens the path of the excited charges to the reaction site, which is of great importance for semiconductors owing short charge diffusion path length, the high active surface being in direct contact with an electrolyte generates a large number of surface defective states [20-22]. These surface states deficiencies act as the structural ones, trap the charges and cause losses in quantum efficiency, which translates directly into efficiency towards a given reaction [11,23]. Therefore, the morphology of the photocatalyst as well as the phase boundary between the electrolyte and semiconductor plays an equally important roles as the structure in the final efficiency of the overall PEC system. **Therefore, the aim of my research work was to explore new and those already used in current systems semiconducting materials, in order to identify fundamental processes governing the charge transfer paths, structural and surface defects, and all performance limiting**

phenomena occurring not only in the bulk but also at the interface of semiconductor|electrolyte, in order to correlate them with the efficiency of oxidation and/or reduction reactions and to develop appropriate multi-directional modifications, enabling the so-called bottleneck processes to be counteracted. Identification of structural, chemical and morphological influence of various nano-architectures of photocatalysts on their PEC behaviour related to the dissociation of electron-hole pairs, their ability to distribute, receive, trap and live time, is a key factor to a careful design of photocatalyst material that can eliminate potential routes of losses in performance. Because of the above, structural modifications consisting in changes in electrode conductivity, chemical composition, absorption range or electronic structure of the bands have been undertaken and described in the following papers: [H1,H2,H4,H6,H7,H10](#). Furthermore, surface modifications concerning of elimination of surface defects through exploration of catalytic and plasmonic properties of metal nano-particles [[H3,H8,H11,H12](#)], or by including in the working electrode an electrocatalyst of a particular reaction [[H9](#)] allowed to invert initial low performance [[H9](#)]. The main achievement of the applied research approaches was the coupling of improved semiconductor-specific properties with better surface properties [[H8, H9](#)]. The semiconductor surface does not provide only the reaction site but constitutes also the semiconductor|electrolyte interface. Thus, any improvement in surface properties was reflected by not only higher efficiency towards given reaction, but also better stability within the time and reduction of surface recombination. These improvements have been validated by the lack of transition current peaks on the CVs curves occurring upon surface charge accumulation. The same concept has also been successfully applied to construction of the p-type systems to activate CO₂ molecule towards its more efficient degradation, and also to direct the distribution of products to solar fuels, such as methanol or formic acid [[H12](#)].

4.3.2 Discussion of the achieved results

PEC cell basis

Water, like solar energy, is an easily accessible and abundant source of energy [24]. Already such a small percentage as 0.01% of global precipitation contains such an amount of hydrogen, the storage of which would enable at least an annual global energy supply [25]. However, just as concentrating and converting solar energy with cost-effective efficiency, the water splitting to oxygen and hydrogen is not a trivial process. Not only does the electrochemical transformation require as many as 4 electrons, this reaction is not privileged thermodynamically [26]:

Half-reactions in acidic medium



Half-reactions in basic medium:



In both cases the potential of the cell is $E^\circ = -1.229 \text{ V}$, and corresponds to the change in Gibbs free energy $\Delta G^\circ = + 237 \text{ kJ/mol}$, resulting from the equation: $G^\circ = - n F E^\circ_{\text{cells}}$

A positive value of the change in Gibbs free energy indicates that reaction of water splitting is an uphill reaction requiring an extra activation to drive generation of hydrogen and oxygen from water, in contrast to many others occurring spontaneously for which the Gibbs free energy is negative [25]. However, to use solar energy to force unassisted PEC water splitting, the excited photo-electrons must have an energy of at least 1.23 eV, from which the required wavelength of the incident irradiation can be calculated according to the following formula:

$$\lambda = \frac{hc}{E} \approx \frac{1240 \text{ nm/eV}}{E}$$

where λ is the wavelength of the incident photon, h is the Planck constant, c is the speed of light, and E is the required energy in eV.

According to the above equation, the photon wavelength needs to be under 1000 nm for it to have sufficient energy to enable the water splitting reaction. This covers the whole ultraviolet – visible range all the way into the near infrared region, containing 78 % of the total solar irradiance of 1000 W/m^2 [27]. However, this calculation does not give an accurate description of the efficiency of PEC water splitting. First, if one photon can only excite one electron, most of the energy contained in a short wavelength high energy photon is lost thermally. Next, the Gibbs free energy change of the water splitting reaction does not take into account the overpotential needed to overcome the entropic loss associated with the generation of conduction band electrons and the kinetic losses due to the required overpotentials for the OER and HER. All together these losses amount to approximately 0.8 eV, meaning that the photon energy should exceed 2.03 eV or have a wavelength smaller than 620 nm according to above-mentioned equation. This leads to a maximum photoconversion efficiency of 16.8 % for water splitting using a single photoanode made of a hypothetical ideal material with a band gap of 2.03 eV [17,28].

The overall efficiency of the solar to hydrogen *STH* conversion process or more generally to a given solar fuel can be calculated from the following formula [1,25]:

$$STH = J_{op} \times (1.23 V) \times \frac{\eta_F}{P_{in}}$$

where 1.23 V corresponds to the Gibbs free energy (ΔG) of the reaction, J_{op} – photocurrent density, η_F – Faraday efficiency, P_{in} – incident illumination power density;

However, the reliable measurements of the true solar to hydrogen/ fuels conversion efficiency *STH* cannot be made on the basis of three-electrode cell configuration. To calculate *STH* efficiency, a tandem cell configuration consisting of a photo-anode and a photocathode is required. Such a system in which the oxidation and reduction processes are kinetically dependent and for each H₂ molecule there are 2 electrons transferred through an external circuit, *i.e.* it is shown in the diagram below:

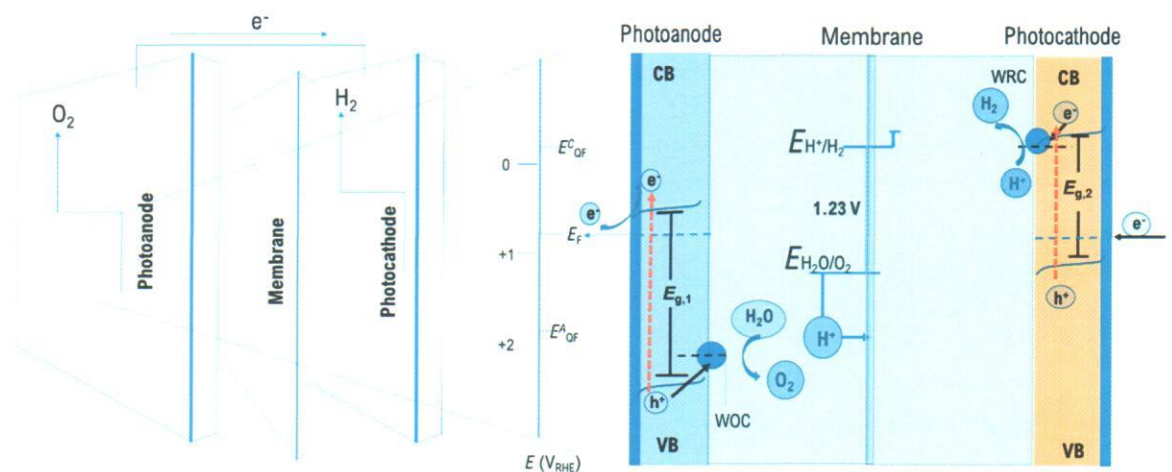


Figure 2. Schematic illustration of the working principle of the wired-type tandem cell for water splitting.

The presented tandem cell system consists of a photoanode with a band gap of $E_{g,1}$ and a photocathode with a band gap $E_{g,2}$, meeting the condition $E_{g,1} > E_{g,2}$. The processes taking place in such a cell are initiated by absorption of light by photoelectrodes, resulting in charge carriers excited. Next, the electric field generated by the depletion layer separates the electrons (e^-) excited from the valence to the conduction band from the remaining electron holes (h^+) in the valence band. In the photoanode the remaining electron holes in the valence band migrate to the phase boundary with the electrolyte, raising the photoanode's quasi-Fermi level energy sufficiently to overcome the overpotential barrier required to drive unassisted water oxidation

reaction. The photogenerated electrons travel along the external circuit to the photocathode, where they recombine with the holes in the valence band of the photocathode. The photoexcited electrons in the photocathode are concentrated in the conduction band to drive the reduction of protons to hydrogen at a water reduction catalytic site by increasing the *quasi-Fermi* energy of the cathode. Theoretically, the process of PEC water splitting could be carried out in a single electrode system or in a tandem *side-by side* geometry, however the *STH* efficiency in such configurations does not exceed 12% and 16% respectively [1,29]. In a tandem system that relies on the working electrodes with band gaps of 1.7 eV and 1.2 eV, for the first and second absorber, respectively, the efficiency may exceed 20% (Fig. 3), even considering unavoidable losses resulting from overpotential reactions or sluggish kinetics [30,31].

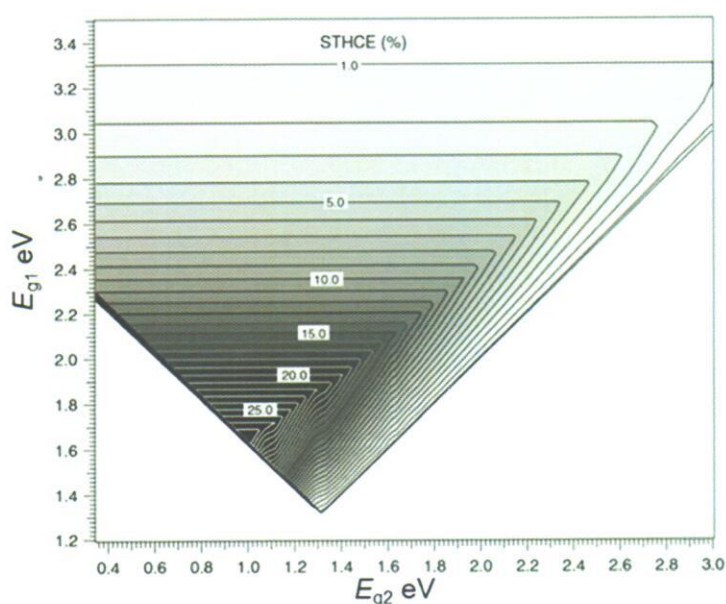


Figure 3. Schematic illustration of a principle for solar cells construction.

Requirements for photoelectrodes

Regardless of the chosen concept and geometry of the working system the driving force of the cell is the photocatalyst material. As already mentioned in the introduction, the semiconductor must meet certain requirements regarding the width of the band gap to ensure effective absorption of the incident light and the appropriate position of the energy bands to eliminate kinetic constraints due to too low oxidising or reducing potentials prior to any application in a PEC device. These requirements are described in detail in publication H1, and briefly presented in Fig. 1 in the same publication. Another key parameter pre-disposing semiconductor material for high solar energy conversion is the nature and concentration of defects in these materials such as bulk/crystal deficiencies and surface states/defects that determine the transport and an effective use of the photogenerated charges [1,2,16,17].

Despite of a large library of semiconductor materials currently used in different solar energy conversion processes [1-4,16,32,H4], only few of them combines the appropriate light absorption range with long charge carrier's diffusion path, stability under light and in often corrosive electrolyte, which are the prerequisites for high solar to fuels conversion efficiency *STFCE* [33,34]. Therefore, many strategies are used to enhance solar energy conversion by modifying either architecture of the operating system or integrating two semiconductors with different values of the work functions which affords a more efficient charge distribution and thus a higher efficiency of the overall cell. Another commonly used approach is design and modelling of the morphology properties to increase the separation of charges by shortening their paths to the reaction sites [35,36]. It has been shown that *e.g.* two-dimensional structures of nano-sheet type increase charge separation and migration by increasing photon absorption in nanostructures, which in turn favours photocatalytic activity in multi-electron processes [36,15]. Another algorithm for increasing the efficiency of solar energy conversion is the construction of heterojunctions in so-called Z-scheme systems [37]. It promotes charge separation and increases the redox potential of the photogenerated carriers. However, those systems require use of semiconductors with a high degree of crystallisation and a tight fit between the energy bands. It should be also noted, that use of materials in a PEC environment involves adsorption of transition charge density states at the electrode surface, therefore it is important to understand and identify the intermediate species at the electrode surface resulting from the electrolysis of the electrolyte itself [11,14]. Keeping in mind the above limitations, my strategy to design and construct an efficient solar energy converting system was based on careful screening of the photophysical and photochemical properties of the semiconductor materials in order to identify and eliminate bottleneck processes resulting from its intrinsic properties and next, couple these improved properties with the enhanced surface properties through of deposition of a co-catalyst of the given reaction.

My research work has been devoted to many n- and p-type semiconductors, *i.e.* WO_3 , Fe_2O_3 , TiO_2 , Cu_2O and their mixed oxides $\text{Fe}_2\text{O}_3\text{-TiO}_2$, $\text{WO}_3\text{-Fe}_2\text{O}_3$, $\text{Cu}_2\text{O-WO}_3$, but the main object of investigation was tungsten trioxide WO_3 , $E_g = 2.5$ eV, with monoclinic preferential crystal structure widely used in photoelectrochemical devices for water splitting or degradation of organic pollutants [38,39]. A motivation to its modifications was the fact of its outstanding stability under irradiation in terms of the potential of the valence band and a high theoretical value of the generated photocurrent of 6.05 mA/cm^2 [40], opening the possibility to construct a tandem cell with economically viable efficiency. Properties, structural modifications and applications of WO_3 in tandem and inorganic PEC systems have been presented in publications [H1](#), [H2](#), [H6](#), [H9](#), [H10](#) while structural and morphological modifications imposing change in intrinsic and surface related properties of the semiconductor were described in publications [H5](#), [H8](#), [H9](#). In papers [H2](#), [H8](#), [H11](#) I demonstrated the possibility of coupling the

plasmonic resonance of silver and gold nanoparticles with the spectral absorption of WO_3 , in order to generate near field electromagnetic field affecting the energy transfer and separation of the photogenerated charge carriers. These studies triggered a ramification in my research leading from structural modifications to the improvement of surface properties through development of a molecular catalyst for oxygen evolution as described in the paper [H9](#). The understanding of the electronic properties of a given material and resulting photocatalytic efficiency makes it possible to develop strategies that limit the range of phenomena that might hamper the performance of the whole system. An example of one of such strategies might be a construction of a hetero-junction in parallel with passivation of the surface, which has been described in detail based on the $\text{Cu}_2\text{O-TiO}_2$ photocathode for CO_2 reduction in the work [H12](#).

Structuring and functionalization

One of the most frequently used strategy aimed at band gap engineering is implementation of the cation combination. [1,2,15,36]. Transition metal oxides based on empty d bands (d^0 cations such as Ti^{4+} , V^{5+} , Nb^{5+} , W^{6+}) have valence band energy determined strongly by the O $2p$ levels, making the valence band low in energy and stable towards oxidation under PEC conditions. Moreover, their high ionic character enables a large separation between the band edges, but the drawback is their low light absorption coefficient resulting from too large band gap and indirect charge transition. Thus, a key challenge is to increase light absorption near the fundamental band edge through doping or adding mid-gap defect states such as for example, oxygen deficiencies. However, as the additional energy levels formed by the dopants are spatially isolated at typical dopant solubility limit of 1-2%, the transport of the photogenerated holes to the reaction site will be too slow, and in consequence the efficiency lost would be inevitable [1].

Considering the above limitation resulting from the presence of additional charge density states the semiconductor's band structure, the concentration of cations introduced to WO_3 described in the paper [H2](#) did not exceed 0.5%_{at} in order not to affect the mid-gap structure and to maintain the monoclinic structure of WO_3 , preferential for photocatalytic applications. Introduction of ion impurity into WO_3 structure was aimed at extending the range of applications of WO_3 as well as at investigating the influence of changes in electrode conductivity on photocatalytic properties of the overall working system.

In this study ([H2](#)), I showed that a small amount of 0.2-0.5%_{at} of lithium, ruthenium, silicon, molybdenum or tin ion doping did not affect the crystallographic structure itself but introduced a slight disturbance of the elementary cell. Such a disturbance introduced deformations in the crystal lattice that acted as structure defects which allowed improving in the conductivity of the active layer. This is quite successful approach for materials with sufficiently long charge diffusion path but on the other hand it might decrease the conductivity through occurrence of

charge trapping deficiencies for semiconductors with short charge diffusion path. Another issue was, that presence of cations with lower valency *i.e.* Sn^{4+} , Si^{4+} led to the formation of W^{5+} ions, responsible for the occurrence of electrochromic properties of WO_3 . Further studies have confirmed that doping with these cations introduces a significant change in the degree of crystallisation and in conductivity of the WO_3 , therefore these materials showed better performance in electrochromic applications [H2,41]. This paper [H2] presents also several structural properties such as grain size, degree of crystallisation, conductivity, defects of the structure, which can be modified depending on the type of doping cation, its amount and degree of oxidation. This work also showed how the introduced modifications might affect further applications of the working electrode. In reference to the review papers of H1, H3 characterizing the main semiconductor materials used in photoelectrochemical cells and describing the strengths and weaknesses of their specific properties, the studies performed in the paper H2, opened the possibility of adjusting the properties of the structure WO_3 to the desired application. However, the development of a well performing electrode [H1, H2, H4] does not yet guarantee high efficiency of solar energy conversion in a PEC arrangement, due to the presence of the interface semiconductor|electrolyte and phenomena occurring there, either at the surface or in the pores. Furthermore, the properties of the electrolyte itself have a significant influence on the efficiency of the entire working system. The dependency of the *STH* efficiency in PEC water splitting process on the type and concentration of a used electrolyte and its ionic conductivity have been studied and described in detail in the paper H5. The stability of the tested material in a given electrolyte in function of time was also the subject of the study, because even a well optimized selection of an electrolyte might turn out to be wrong in case of long lasting photocatalytic processes. The reason is that during photoelectrolysis run the electrolyte may undergo electrolysis itself and intermediate peroxide compounds may be formed and in result the active surface of semiconductor might be blocked [H5, 42]. Thus, the efficiency of the process decreases over a longer period, as it has been shown by performance of WO_3 in perchloric and sulphuric acids in Fig. 2 H5. Both acids are widely used in electrochemistry basic electrolytes due to their high degree of dissociation, good ionic conductivity and reasonable price. However, in both cases after certain time, the efficiency of the process towards evolution of oxygen decreases to a few percent: within the first hour of photoelectrolysis for the perchloric acid and after *ca.* 3 hours for sulphuric acid. The performed investigations made possible to select the electrolyte, which since then has been the only electrolyte used in further works and research because of its high stability. The selected, methanesulfonic acid $\text{CH}_3\text{SO}_3\text{H}$ showed high stability and lack of any intermediates under applied voltage and illumination. Stability tests for methanesulfonic acid performed under the applied potential as a function of time have been confirmed by Raman spectroscopy measurements at the beginning and at the end of the experiment. Further on, the concentration

of methanesulfonic acid was optimized by simultaneous measurements of photocurrent in function of imposed potential in PEC water splitting and by impedance spectroscopy. Both studies showed a huge correlation between the value of the generated photocurrent and conductivity of the electrolyte, up to 50% at a concentration change from 0.04 M to 1 M (Fig. 4 H5). These studies were of great importance for the next achievements, especially since the typical electrolyte concentration widely used by other researchers is the concentration of 0.05 M which strongly limit the efficiency through the ohmic drop at the surface and also in the pores. Therefore, an optimised working system consisting of a WO_3 photoanode with improved structural properties due to the addition of a very small amount of sodium cation and 1 M methanesulfonic acid made possible to drive photoelectrolysis of water with a quantum efficiency of up to 80% [H9]. Such high quantum efficiency opened a door to construction of a tandem device. Thus, prepared and optimised as described in H9, an electrode WO_3 has been interfaced to DSC electrode, consisting of dye sensitized TiO_2 , and employed as a photoanode in the tandem dual cell elaborated by Sivula's group, as described in detail in publication H6. The dual tandem system enabled unassisted PEC water splitting to hydrogen with an efficiency of 3.1 %. Design of the tandem system employing WO_3 photoanode is not trivial because the conduction band potential is too positive to allow unassisted water splitting. The overpotential required to exceed the energy barrier had to be provided by the dye cell. Optimization of the dye cell consisted in precise selection of the redox mediator, passivation of the cell surface and adjustment of a water oxidation catalyst. The schema of tandem cell and the energy level diagram are shown in Figure 1 of publication H6. Briefly, the incident light is absorbed by the photoanode within the range defined by the properties of the optimised WO_3 electrode, while the rest of the radiation is transmitted and absorbed by the DSC electrode placed in *side-by-side* configuration. While the quantum efficiency of a phot-anode is quite simple to calculate, the estimation of the quantum efficiency of a dual cell (WO_3 +DSC) providing the potential for water oxidation reaction requires consideration of the photons absorbed or reflected by WO_3 . The spectral characteristics of such a tandem cell are presented in detail in Fig. 2 of the paper H6.

Plasmon-induced enhancement

Despite of many achievements in my research regarding engineering of structural properties of the WO_3 photoanode, the reached photocurrents for oxygen evolution were stable and in range of 2.5-2.7 mA/cm^2 . Even the introduced energy bands modification through their hybridization following formation of the mixed metal oxides [H4, P12] did not allow further progress in increasing the electrode efficiency. The theoretical calculated efficiency of WO_3 is based on the photocurrent of 6.05 mA/cm^2 [40], thus photocurrent values of 2.5-2.7 mA/cm^2

left a significant discrepancy between the value obtained experimentally and the one calculated theoretically. However, it is a fact that semiconductor transition metal oxides, which exhibit indirect charge transition from the valence band to the conduction band, have low light absorption coefficients [1,36]. In this regard, next step in my research involved an exploration of plasmonic metal nanoparticles to increase light absorption by the semiconductor. By illuminating metal nanostructures (in form of inclusions or deposited on the surface of a semiconductor) with the appropriate wavelength, a localized surface plasmon resonance is induced because of collective oscillations from excited free electrons of metal, occurring upon metal interaction with a wavelength characteristic for a given metal [43,44]. The excitation of plasmons on metal nanoparticles depends on the size and shape of metal particles and on the dielectric properties of the environment [45]. The local electromagnetic field generated as a result of this interaction leads to the enhancement of the optical properties of the whole system, *i.e.* the absorption coefficient or/and the efficiency of directional light scattering [46]. Metal nanoparticles can also scatter the incident light multi-directionally and thus the irradiation can be trapped by the semiconductor (Fig. 4A). The excitation of plasmon resonance on metal nanoparticles being in direct contact with semiconductor results in separation of the charge carriers excited in the semiconductor (Fig. 4B). Finally, plasmonic excitation may occur at the metal-semiconductor interface with formation of the surface polarons. The small polarons, when coupled with the light reflecting from the rough back side of the electrode propagate in the plane parallel to the semiconductor and affect charge separation (Fig. 4C) [46]. The above specified mechanisms are shown schematically in Fig. 4:

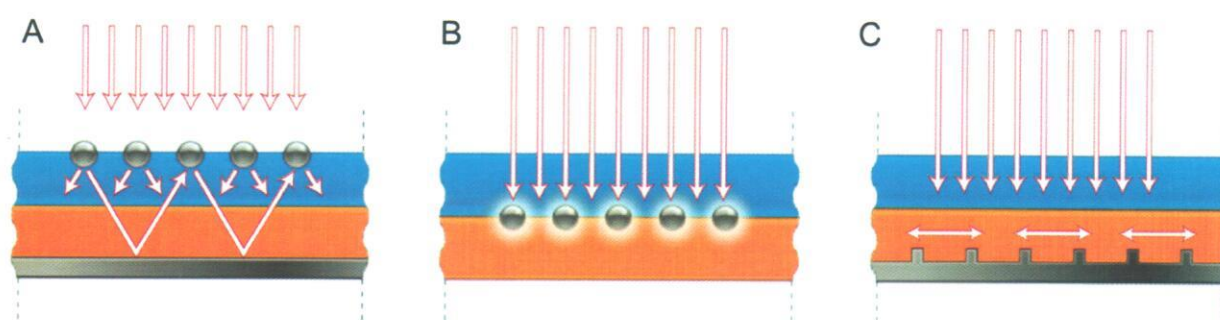


Figure 4. Schematic illustration of the plasmons interaction with light [46].

From practical point of view, the direct proof of existence of a resonant coupling between the metal nanoparticles and the semiconductor is an increased reaction photocurrent concomitant with an increased quantum efficiency. This approach has been demonstrated in paper H3 published in *Angewandte Chemie Int. ed.*, in which the silver nanoparticles were embedded within a thin WO_3 film. In this paper, I explored the ability of silver nanoparticles for enhancing sunlight-induced water splitting in the range of WO_3 absorption. Although, the plasmonic

resonance of silver do not overlap with absorption range of WO_3 , a careful optimisation of the size and shape of the metal particles verified by the UV-Vis measurement allowed to coincide it with the blue light spectral range of the WO_3 (Fig.1 H3). In my research, the silver particles of about 40 nm in size enabled the coupling of silver plasmonic resonance with the WO_3 absorption range, but the direct contact of silver nanoparticles with the corrosive acidic environment resulted in passivation of plasmonic particles. A solution could be to introduce plasmonic particles inside the semiconductor structure or to change the electrolyte to a less corrosive. But it should be noted that metal nanoparticles introduced into the semiconductor matrix may have a shifted plasmonic resonance in comparison to particles deposited on the surface, which is related to the domination of various mechanisms of plasmonic excitation. Metal nanoparticles embedded in the semiconductor may increase the absorption of light by the whole system, but it is critical to adjust tightly the electronic structure of the semiconductor so that the photogenerated charge carriers can be used effectively. Plasmonic particles deposited on the surface of a semiconductor act as light trapping antennas, while those deposited near electrical contact affect ohmic drops occurring in the semiconductor bulk [47]. Therefore, considering the advantages and disadvantages of different placement of plasmonic particles in the semiconductor, silver nanoparticles were deposited directly onto conductive glass (FTO) and electrochemically passivated with an AgCl protective layer and then coated with a WO_3 1-micron thick active layer. However, given a short range of the generated evanescent wave following the excitation of the localized surface plasmon resonance, the photoelectrode was illuminated from behind, through FTO, so that light absorption enabled first the excitation of silver plasmon resonance, and then generation and separation of charge carriers in the semiconductor. The coupling of these effects resulted not only in an increase in the values of reached photocurrents, that for a thin layer of WO_3 ca. 1 μm thick, amounted to 2.2 mA/cm^2 , *i.e.* reached the photocurrents typical for a 2.5-fold thicker WO_3 photoanode and showed an increase of quantum efficiency also at longer than usual wavelengths (Fig.3 H3). These studies, what is worth noting, were the first practical demonstration of the possibility of using the plasmonic metal particles to increase the efficiency of solar energy conversion in in PEC arrangements. These studies also gave an impulse to manufacture and use thin film of semiconducting materials, even those with a low light absorption coefficient, for high yield energy conversion in photoelectrochemical cells, and in photovoltaic or organic cells. Subsequently, many publications presenting various possible mechanisms of plasmon-induced interactions with semiconductor and their relation to the gained enhancements in energy conversion processes [48,49] have been released. Regarding my further studies on plasmonic enhancement, one of the mechanisms postulated by N. Wu [48] deserves attention. This mechanism is called PIRET: plasmon-induced resonant electron transfer and assumes a generation of an electron-hole pair in the semiconductor without any photon emission by a

plasmonic particle [48]. Energy transfer takes place even without any direct contact between the plasmonic particle and the semiconductor, which happens relatively often since the metal particles being in direct contact with the semiconductor might act as a recombination centre, thus they are passivated or encapsulated. The presented mechanism has been partially adapted to the next investigated plasmonic system based on colloidal gold nanoparticles capped with polyoxometalates (POMs), described in the publication H8. However, the typical gold plasma resonance is in the range of about 540 nm, i.e. outside the absorption range of WO_3 , and once again the problem of stability of metallic particles in direct contact with the corrosive acidic base electrolyte has arisen. A lesson taken from the previous work was that although the buffering protective layer does not impede the transfer of energy accumulated in a metallic particle, it influences its range. To prevent this scenario and with an aim to improve surface properties, gold nanoparticles have been capped by the catalytic monolayer of Keggin-type polyoxometalate: $\text{H}_3\text{PMo}_{12}\text{O}_{40}$. Polyoxometalates are a group of compounds widely employed in various electrocatalytic approaches because of their fast and reproducible redox characteristics [50]. In combination with WO_3 , they perfectly fulfil the role of both catalytic and buffer layer against corrosive and strongly acidic environment. In addition, at low pH operation conditions, the surface of WO_3 is positively charged, while polyoxometalates are present in form of anions. This is another advantage of polyoxometalate cap, because they not only prevent agglomerations of gold nanoparticles but also increase the plasmonic load at the semiconductor surface through electrostatic interactions. Besides, the $\text{PMo}_{12}\text{O}_{40}^{3-}$ anions interact with the gold through the corner oxygen atoms, thus they occupy a limited number of active catalytic sites on the gold nanoparticles surfaces. After excitation of plasmonic resonance at gold nanoparticles, the polyoxometalates contrary to other protective coatings allow charge transfer, so that all mechanisms postulated in the literature are possible to occur (Fig. 5).

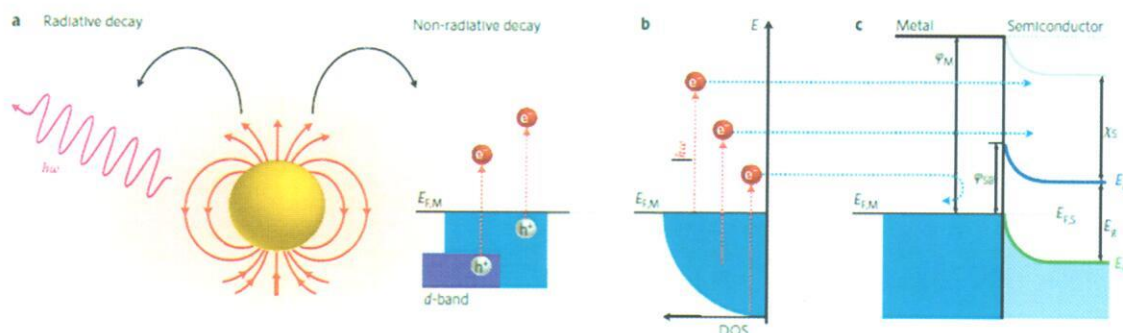


Figure 5. Schema of the energy transfer followed by the excitation of the local surface plasmon resonance (LSPR) at the semiconductor [49].

As in the previous work, the electromagnetic field induced by the appearance of localized plasma resonance on gold, allowed to increase the absorption of light by the WO_3 and affected charge separation in the bulk which all together resulted in a direct increase of quantum efficiency towards photooxidation of water. The fact of existence of a resonant coupling between gold nanoparticles and WO_3 (where the photon absorption spectra overlap) has been confirmed by investigations with use of SNOM (*scanning near field microscopy*) technique at two wavelengths: 436 nm and 546 nm, as shown in Fig. 4 in the paper H8. The occurrence of the phenomena was more intensive at the wavelength of 436 nm, that is in closer to the wavelength of maximum absorption of WO_3 (400 nm). It is important to note in this regard that, in contrast with some examples from the literature, the incorporation of Au-POM nanoparticles on the WO_3 surface did not lead to the formation of surface states promoting recombination of photogenerated charge carriers. This can be assigned to the shielding effect of the $\text{PMo}_{12}\text{O}_{40}^{3-}$ anions, which in the acidic pH of the electrolytes used in my PEC experiments are maintained close to the positively charged WO_3 solution interface by electrostatic forces.

However, on the basis of the gained results it was difficult to precisely assess the relative contribution to the observed enhanced water splitting purely to the local surface plasmon resonance induced effects especially that an overlap between the spectra of quantum efficiency IPCE and the absorption one showed differences which could not be explained only by the occurrence of LSPR although this mechanism was clearly predominant.

Identification of a catalyst

The above-mentioned subtle differences observed between the absorption spectra and IPCE diagrams must be attributed to the catalytic activity of the polyoxometalates itself. An important role in the catalytic activity of a POM (phosphododecamolybdic acid) plays the catalytic centres of molybdenum Mo^{6+} , $^{5+}$ which act as redox mediator in the reaction of photooxidation of water, allowing the electron to jump between different degrees of oxidation of molybdenum. At this stage of the research, the question which has arisen was whether such a high quantum efficiency translates into an equally high efficiency towards the photooxidation of water and whether the only product of the anode reaction is oxygen. An answer to these questions can be found in the supporting information file of the H8. In the investigated system consisting of WO_3 photoanode, supported by plasmonic and catalytic effects of Au-POM particles, oxygen was identified as the only reaction product. Next, the elaborated system for oxygen detection and quantification was also used to identify oxygen in an inorganic cell driven by reduction of highly concentrated solution of polyoxometalates [H10]. This research was conducted jointly with Prof. Cronin group from Glasgow. The polyoxometalate solution placed in the cathode compartment was used as buffer for the protons produced in the anode compartment and for the electrons derived from the photocatalytic activation of WO_3 and stored in POM undergoing

its multielectron reduction. The diagram of such a cell and the principle of its operation is presented in Fig. 2, H10. What is innovative in this system, is that the self-driven POM cell that can work continuously and steadily at 0 V potential and performs oxygen evolution at optimized WO_3 of ca. 2.5 μm thick with Faraday efficiency of up to 70%. The role of polyoxometalates in catalytic enhancement of PEC water oxidation process has been thoroughly investigated in the parallel work H9, combining the recent discoveries regarding of structural and surface modifications and their influence on active surface architecture and electronic properties of the photoanode, resulting at the end in higher efficiency in energy conversion. Although in the previous H8 paper concerning plasmonic gold induced enhancement of solar energy conversion at the WO_3 -Au(POM) photoanode, the catalytic impact of the polyoxometalates themselves was separated from the plasmonic one and estimated of about 20%, the ability to undergo reversible and rapid redox reactions providing a sufficiently high potential for water photooxidation reaction to WO_3 at 0V potential, suggested that further exploration of the catalytic properties of polyoxometalates might be promising. An additional motivation was provided by the work published in 2015 by Jaramillo group [51], which presented a library of 26 water oxidation catalysts, but mainly based on precious metals or active only in neutral or alkaline pH range, leaving empty space on the corrosive side of an acidic environment. In response to that publication, my research has been oriented towards search for a new catalyst acting in an acidic environment and not disturbing the absorption spectrum of the WO_3 . This search enabled selection of phospho-molybdic and phospho-tungstic acids, both Keggin-type polyoxometalates as molecular catalysts for PEC oxygen evolution from water [H9]. However, despite of various configurations of deposition of a POM catalyst, an increase in photocurrent towards O_2 evolution was rather moderate and did not exceed more than 25%, although the presence of POM catalyst undoubtedly had a positive effect on the degree of charge accumulation at the surface which manifested itself in reduction of recombination peaks at the polarization curves[SI H9]. To resolve this standoff, a low amount of sodium cations was introduced to the WO_3 structure which led to the increase in concentration of the oxygen deficiencies. The combination of the catalytic activity of the POM and sodium ion doping resulted in record high photocurrent densities of 4.5 mA/cm^2 under simulated sunlight (AM 1.5G) illumination. Photocurrents already reached saturation at 1-1.1 V (vs. RHE), which opened up the possibility of obtaining 5% solar energy conversion efficiency for hydrogen production (STH) using a photovoltaic cell in a tandem system (PEC-PV) in a photoelectrolyser. Such high photocurrents showed excellent agreement with the quantum efficiency spectra, and the IPCE diagram itself reflected very well the range of absorption of the modified (Na) WO_3 -POM working photoanode. An unquestionable success of this research is not only the potential application of achievements in PEC cells for hydrogen production, but

equally important is the discovery of the mechanism governing the enhanced efficiency. The predicted mechanism is shown schematically in Fig. 6:

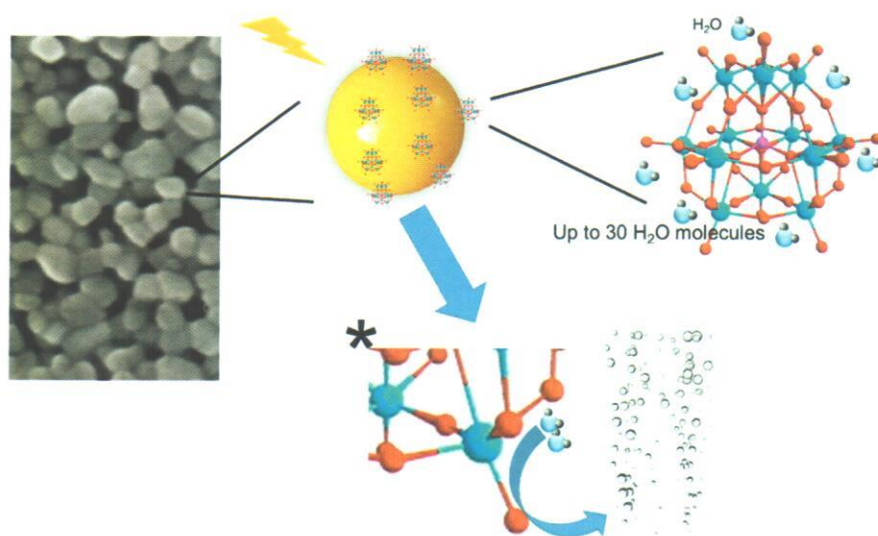


Figure 6. Proposed mechanism of increased solar energy conversion efficiency in $(\text{Na})\text{WO}_3 - \text{POM}$ system

The presence of sodium ions in the lattice of the WO_3 affected position of the Fermi band level in relation to the semiconductor conduction band, associated with the surface potential. The Fermi band level moved in the direction of more negative potentials as the absolute value of the measured photopotential increased [52]. Moreover, the isoelectric point of the semiconductor also changed due to the addition of sodium ions to WO_3 , indicating a more positive surface charge at the same pH compared to bare WO_3 . In this scenario, more molecules of the POM catalyst, were attracted electrostatically to the surface of WO_3 . However, a key to explain the enhanced efficiency of the PEC water oxidation reaction, is the ability of POM to trap water molecules in its Keggin cluster. Already one molecule of POM can absorb up to 30 water molecules. Additionally, taking into account the fact that the self-diffusion coefficient of water defined as the average residence time that a H_2O molecule spend vibrating at some equilibrium position before undergoing an activated jump to a new position in the liquid water to arrive at the reaction site, is relatively long, estimated as 1.7 ns [53], the presence of water molecule in the structure of the catalyst plays a key role in the kinetics of the whole process. It should be also emphasized here that these studies allowed to identify, define and prove the effectiveness of the POM based molecular catalyst in a corrosive acidic environment. Subsequent research described in the paper H12 represents an exploitation of the acquired knowledge and an ability to apply appropriate structural, morphological and surface modifications in order to obtain properties desired for a given process or construction of a junction. The system, described in H12, is a natural consequence of the trend in materials

search and a shift of the point of interest from the photoanode to the photocathode in order to construct an efficient system for the activation of CO₂ molecule. The operating system, consisting of Cu₂O and non-stoichiometric TiO₂, is also a kind of proof for previous works that combine structural and morphological modifications in order to increase the efficiency of solar energy use in different processes. Herein, the non-stoichiometric TiO_{2-x} layer served to passivate the Cu₂O surface, but also to counteract accumulation of holes on the surface and acted as a molecular sieve preventing a competitive oxygen reduction reaction. Furthermore, it made it possible to transport charge carriers more efficiently upon increasing in their mobility, that was confirmed by impedance spectroscopy studies.

To sum up, the selected research papers of H1-H12 showed how to combine the structure properties of a semiconductor material with its morphology and surface properties to allow a correlation of these properties with the architecture of the working system and its efficiency in solar energy conversion process. Only such parallel progress in the study of the structure and surface of a semiconductor makes it possible to a breakthrough and innovative discoveries that represent a progress in the field.

5. Description of other achievements

Apart from the presented herein cycle of papers H1-H12 regarding the scientific achievements, I am the author of 19 publications P1-P19, of which 11 were written outside the scope of my doctoral thesis. In these works, I focused on the synthesis, study of properties and structural /morphological modifications of semiconductor materials such as: WO₃ [P11, P13, P14, P15], TiO₂ [P8, P10,], mixed oxide of WO₃-Fe₂O₃ [P12], and mixed oxide of Bi₂O₃-CaO [P9]. One of the widely applied strategy towards better conductivity and charge transport dynamics in semiconducting materials is formation of ternary oxides following rational band engineering of the metal oxides through overlapping of the orbitals of component oxides, and thus introduction of new properties resulting from changes in the electronic band structure of the resulting materials. However, not only these new properties resulting from the creation of the additional electron states in the band gap itself determine better absorption or efficiency, because formation of local mixed oxide islands with often much smaller band gap than the matrix, may affect significantly charge transport properties, for example suppress low polaron conductivity which is problematic in case of Fe₂O₃. An example of such an approach is production of mixed metal oxide of WO₃-Fe₂O₃, containing inclusions of Fe₂WO₆, described in the paper P12. Mixed metal oxides are formed at high temperatures which make impossible to prepare them on FTO conductive glass. For this reason, in this work I used metal foils of tungsten and titan as conductive supports. While annealing at typical for WO₃ and Fe₂O₃ crystallisation temperature of 600°C produced films consisting of a mixture of monoclinic WO₃ and hematite α-Fe₂O₃, the heating above 1000°C afforded formation of a ferric tungstate Fe₂WO₆ ($E_g = 1.5-1.7$ eV). And

although both films exhibited optical absorption range exceeding that of $\alpha\text{-Fe}_2\text{O}_3$, only in the latter case the photocurrent value jumped from 0.5 mA/cm^2 to nearly 5 mA/cm^2 (Fig.6 P12). Apparently, at the bottom of the electrode, close to the conductive contact, the inclusions of low band gap ferric tungstate allowed to change the charge transport properties that has been confirmed further by a Mott-Schottky analysis. Another example of a mixed metal oxide is bismuth - calcium oxide, described in P9. This research was done within the frame of an individual grant of the Swiss and Japanese Science Foundations and in collaboration with Prof. Ye of the National Institute for Materials Science in Tsukuba, Japan. A high-quality functional nanoparticles of calcium bismuth mixed oxide were produced by single-step flame spray synthesis (FSS). The high temperature of the flame afforded creation of oxygen vacancies which allowed to enhance the photocatalytic activity of calcium bismuth oxide by a factor of 6, in comparison to previously reported calcium bismuth mixed oxide produced by conventional methods which required additional temperature treatment steps. Moreover, the applied investigations by NEXAFS showed a significant difference in concentration of doped holes between samples produced with different synthesis conditions. These observations were very important for further exploring of materials in view of effective environmental remediation.

The next research papers related to properties and application of WO_3 , but other than those described in the habilitation cycle, concerned: i) the use of boron cation as structure directing impurity described in the paper P11, ii) development of a new method for its production by non-water and microwave technology. Full structural and photoelectrochemical characterization together with oxygen evolution studies on this WO_3 electrode were described in the paper P13, jointly published in the framework of the Polish-Swiss grant. The comment P14, on the other hand, has been written in response to numerous misinterpretations occurring in literature concerning water oxidation and lack of oxygen identification as a product of this reaction at WO_3 . This publication has clarified many aspects of water oxidation in inorganic electrolytes and supported the approach proposed in my previous works regarding the mechanism of PEC water splitting at WO_3 . An important work in this context is P15, describing gradient and non-intentional WO_3 doping through diffusion of tin ions from the FTO occurring during the crystallization of the WO_3 film at 700°C . Electrodes WO_3 doped in this specific way with tin ions showed much better light absorption confirmed by the theoretical calculations pointing out the change in charge transition from indirect to direct. This change is because the gradient diffusion of tin ions creates additional electron states near the conduction band, changing the nature of the electronic structure of the band gap. These electrodes also showed better kinetics of water oxidation process by elimination of recombination peaks and better conductivity of the whole electrode illustrated by the lack of ohmic drops on recorded polarization curves I vs. E (Fig.1 and those in SI, P15). Improved charge transport properties also resulted from the nature of inclusions in the bulk of WO_3 , forming nano-islands of tin oxides at the grains of WO_3 . This

locally produced heterojunction afforded better charge carrier separation and their effective use in the processes, illustrated by high quantum efficiency shown in Fig.4 P15. The papers P8 &10 concern research with use of TiO₂, however represent different kinds of research objective. P8 concerns the issues of charge transport, separation and the architecture of the working system while the paper P10, was developed in cooperation with an industrial partner within the framework of a Master's thesis carried out under my scientific supervision. The aim of this work was to transfer of an optimized in transparency and photocatalytic properties titanium oxide to a flexible primer in order to create a photocatalytic ribbon.

To conclude it should be noted that all my research work was devoted to bring a marked advancement in the design, synthesis, in-depth understanding of the origin of PEC performance of polycrystalline semiconducting electrodes for their use in solar fuel production processes. Identification and recognition of the limiting steps in the desired PEC processes enabled to introduce structure and surface modifications to overcome the limited efficiency in solar energy conversion and in the future hopefully will enable to integrate the improved structure and morphology for potential applications in solar powered devices.



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