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Doctoral Dissertation Committee
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Review

of the doctoral dissertation entitled

"Różnorodność mechanizmów fotosensibilizacji funkcjonalizowanych powierzchniowo półprzewodników tlenkowych"

submitted by

Mateusz Trochowski

The doctoral thesis of Mateusz Trochowski is focused on various aspects of mechanistic investigations of photosensitization of nanostructured TiO_2 and ZnO materials. Such materials are well established as photocatalysts, *i.e.*, materials that are capable of driving various useful chemical transformations simply by irradiation with sunlight or low-cost light sources (*e.g.*, LEDs) in the presence of ubiquitous oxidizing and reducing agents like water or aerial oxygen. Possible applications of photocatalysis range from degradation of organic pollutants in water and air, solar-driven production of fuels *via* water splitting and/or carbon dioxide reduction, to applications in medicine and sensing. However, in most of these applications the overall activity of pristine TiO_2 and ZnO materials is rather limited, particularly due to their large bandgap, which enables them to utilize only a small portion of photons (ca. 5%) in the UV range of the solar spectrum. In other words, sensitization of TiO_2 and ZnO for photoactivity in the visible range (wavelengths > 400 nm) is highly promising in terms of enhancing the light harvesting and increasing the photoconversion efficiencies. More specifically, Mr. Trochowski addresses photosensitization approaches based on *surface* functionalization. These approaches seem currently more promising than more conventional *bulk* doping methods, which have been typically shown to lead to enhanced recombination, without any appreciable increase in overall efficiencies. However, due to the inherent complexity of surface-modified nanomaterials, clear design rules for the development of highly active and stable surface-functionalized photocatalysts are still elusive. Significant research efforts are therefore currently underway worldwide to counteract this lack of knowledge which hampers the

development of novel photocatalytic systems. The dissertation project of Mr. Trochowski is thus located in the very center of one of the most expanding and competitive fields of contemporary chemistry and materials science.

The thesis is well written and clearly structured. It starts with a very helpful overview of the current state of our knowledge about all fundamental topics related to photophysics and photochemistry of semiconductors that have some bearing on topics of this dissertation. This allows the reader to identify clearly the "added value" of the findings presented in this thesis. I would like to emphasize that all these literature-based parts of the thesis are written in an impressive style, drawing on large amount of published literature data from the past as well as from the most recent papers. Here Mr. Trochowski clearly proves that he is able to sort out the wheat from the chaff, identifying the most fundamental aspects of each problem, and showing thus a genuine depth of knowledge of this highly interdisciplinary research field. After this introductory part, a short and helpful outline of major scientific questions that the thesis addresses is presented, followed by an elaborate and well-written overview of experimental techniques used in this PhD project.

The research part of the thesis is divided into four sub-chapters, dealing with different topics related to photosensitization of TiO_2 and ZnO. As the topics of these sub-chapters are rather different, in what follows, I will try to highlight the major strengths and weaknesses of these parts separately, before I evaluate the thesis as a whole. In Chapter 4.1, Mateusz Trochowski investigates a very interesting question whether the deposition of thin layers of TiO_2 by atomic layer deposition (ALD) can increase the photostability of several organic (*e.g.*, catechol) and one inorganic $[PtCl_6]^{2-}$ sensitizers that are known to increase the visible light photoactivity of TiO_2 photocatalysts. Such a strategy seems promising, since it has been reported, for example, that encapsulation of organic sensitizers at TiO_2 by ALD-grown alumina can increase the stability of dye-sensitized photoanodes for water oxidation (*e.g.*, Wasielewski et al., *J. Phys. Chem. C* **2017**, 121, 7, 3752-3764). Mr. Trochowski found out that though minor improvements of stability can be achieved, these are unfortunately traded off by decreased activity of sensitized materials. In other words, the photoactivity in the visible range seems to be mostly based on the oxidative degradation of the sensitizers. This photodegradation could be nicely followed by recording the changes in the electronic absorption spectra using the diffuse reflectance spectroscopy. Interestingly, it has been found that in case of catechol, the photodegradation products can still act as effective sensitizers, before they are degraded completely. It should be noted that a large variety of different TiO_2 materials combined with different sensitizers has been investigated, and the results show that precise behavior of the sensitized systems depends very much on a complex interplay between the sensitizers and the various TiO_2 substrates with different surface properties. In this context, I wonder why (*in situ*) vibrational spectroscopy (DRIFTS and/or Raman) has not been employed to follow the light induced changes at the surface of modified TiO_2 in more detail. Such a study could possibly reveal a more detailed picture of the photodegradation in all investigated materials, including the specific chemical changes (amount of OH groups, identification of degradation products, their desorption, *etc.*) occurring during irradiation. The same holds for the following Chapter 4.2 which brings some otherwise very interesting results confirming enhanced activity and stability of sensitizers based on dihydroxyanthraquinone, as compared to, say, catechol. In my view, the use of vibrational

spectroscopy could again give a much better insight into what is happening during photodegradation, and perhaps even provide some hints about how to tackle this problem. In this context, I was also missing a more detailed discussion of the photocatalytic mechanism of sensitized materials under visible light irradiation. In general, Mr. Trochowski discusses the photodegradation rather vaguely as caused by the "reactive oxygen species". However, it is clear that if an electron is injected from the sensitizer to the conduction band of TiO_2 *via* the CT mechanism, this leaves an oxidized equivalent ("hole") in the sensitizer or at the sensitizer/TiO_2 interface. This means that, in order to stabilize the sensitizer, this hole should be transferred to the reactive substrates in the solution. In case of the ALD-grown protective layers, this is not impossible as it is known that holes can tunnel through very thin TiO_2 layers (see, for example, the work of Lewis et al. on TiO_2-protected Si photoanodes), but I would expect that such issues should be at least briefly discussed. In a similar vein, the reader is presented with a Figure 71, from which it is clear that pristine anatase TiO_2 (UV100) can induce significant degradation (ca. 35%) of 4-chlorophenol (4-CP) under *visible* (> 420 nm) light irradiation, which is rather surprising since UV100 itself does not absorb in the visible. It is known that this degradation is based on formation of a charge-transfer complex between 4-CP and TiO_2 (S. Kim, W. Choi, *J. Phys. Chem. B* **2005**, 109, 5143 –5149), and I believe that the reader would be better served if a short discussion of this phenomenon were provided.

For me the most interesting part of the thesis is Chapter 4.3 that draws on some findings from Chapter 4.1 which suggest that even presumably negligible changes induced at the surface of TiO_2 by few cycles of ALD deposition of TiO_2 can have a significant impact on the photoactivity, especially in the visible range. Notably, here Mr. Trochowski was able to follow the changes in the distribution of the density of (surface) states in the materials using a method developed recently in the lab of Professor Macyk. Though, as for now, clear trends (number of cycles *vs.* activity, *etc.*) are difficult to capture, these findings are highly significant as they highlight the crucial impact of the surface conditions of the photocatalyst on their activity. This is further exemplified by a huge impact of the deposition method of the sensitizer/modifier, which, for example in case of photodeposition, clearly plays a more important role than the presence or absence of the modifier itself (Figure 91). Due to their importance, I anticipate that these findings, when published, should find a significant resonance in the scientific community.

The last Chapter 4.4 is chiefly devoted to investigation of the mechanism of surface plasmon resonance sensitization by Au nanoparticles on ZnO. Based on the photoluminescence measurements (Fig. 101), Mr. Trochowski concluded that the visible light photoactivity is related to hot electron injection, rather than to plasmon-induced resonance energy transfer (PIRET). In my view, this part of the thesis is still a bit premature and open to other interpretations. For example, the only result on the basis of which the PIRET mechanism has been ruled out is the missing emission in the range 350-400 nm. However, what if the emission related to the electron-hole recombination is red-shifted and occurs at, say, 600 nm? This cannot be ruled out. Moreover, the fact that only negligible photocurrents (Figs. 97 and 98; I was missing a blank experiment with FTO/Au only in Figure 98) were observed under visible light irradiation (one would expect a photoaction spectrum with a similar shape like the absorption spectrum), makes one ask

if alternative explanations of the photocatalytic activity in the visible were possible (*e.g.*, combined effects of defects and thermal effects, *etc.*)

I have also few minor comments on some specific issues in the thesis:

a) Figure 6 (page 29) shows the band edge positions at pH 7 (caption) but the figure reads "@ pH = 0"; also the standard reduction potential of O_2/O_2^- couple is here given as –0.74 V vs. NHE, whereby otherwise it is taken as –0.28 V vs. NHE, which is completely puzzling.

b) Figure 81 (page 120): error bars are missing.

c) Page 105: the author says that the intensity of light during the IPCE measurements was corrected for light not absorbed by the sample. This means that the reported values, in this particular case, are not IPCEs (*incident* photon to current efficiencies) but rather APCE (*absorbed* photon to current efficiencies), assuming, obviously, that scattering is neglected.

d) Reference 53: Volume and page numbers are missing.

Taken as a whole, the doctoral dissertation submitted by Mateusz Trochowski is an original, well presented, and in many ways interesting piece of scientific work contributing to a highly important field of scientific research. Apart from the excellent introductory part, the major strength of the research part of the thesis is that it brings several very important and unexpected results. A certain weakness is that some research opportunities (*e.g.*, the use of vibrational spectroscopy) that could have provided a significant insight have been missed, and that not always a thorough and in-depth discussion of the results was provided. To give a brief summary of my evaluation, I would say that the significance of Mr. Trochowski's thesis lies more in the new questions and scientific problems it opens than in the answers it provides. But, after all, this is in no way a bad outcome for a doctoral dissertation!

Based on my above evaluation, I recommend the original and interesting doctoral dissertation of Mateusz Trochowski to be accepted, and recommend the Committee to continue the process of awarding the doctoral degree.

Prof. Dr. Radim Beránek