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REVIEW OF DOCTORAL DISSERTATION

of Ms. MSc. Anna Jakimińska

Under the title: ***"Process of energy and electron transfer in photocatalytic systems containing metallic nanostructures."***
carried out at the Department of Inorganic Chemistry at the Faculty of Chemistry at the Jagiellonian University under the supervision of **professor dr hab. Wojciech Macyk.**

Substantive analysis of the work

The doctoral thesis submitted for review by Ms. Anna Jakimińska concerns the understanding of elementary phenomena occurring in photocatalytic processes using systems based on titanium dioxide and nanometallic structures. The focus was put on the mechanisms of plasmonic photocatalysis and the role of metallic nanostructures. This is a very important and vastly developing area of research. The doctoral thesis of Ms. Anna Jakimińska is also an excellent example of the use of the knowledge and achievements of the team led by prof.

Wojciech Macyk to develop her own research ideas in an original and creative way. She defined the aim of her work as the determination of the factors influencing the photocatalytic activity and the efficiency of the energy/electron transfer between plasmonic nanostructures and semiconductor through the example of the several catalytic systems. In order to realize her aim, she was responsible for the synthesis and broad characterization by many techniques like SEM, EDS, XRD of several photocatalytic systems based on titania or Ag/AgCl. She evaluated the photo and photoelectroproperties for chosen systems. Ms Anna Jakimińska tested for example the behavior of different dyes degradation (transformation) on the photocatalysts, investigated their activity in photocatalytic water splitting accompanied by methanol photoreforming. These tests allowed her to propose new mechanistic approaches for the studied catalytic systems in above mentioned processes.

I will mention only a few of the most important achievements of Ms. Anna Jakimińska, which, in my opinion, have a very significant contribution in expanding the knowledge in the field of photocatalysis:

- For photocatalytic transformation of Rhodamine B to Rhodamine -110, it was find out that neither holes nor the radicals are responsible for the N-deethylation process, and the process competes with the non-selective oxidation reaction. It was also shown that the process is driven by the photoinduced electron transfer between the dye molecule and the titania support. That stays in contrast to often stated mechanisms description of this process and therefore this new knowledge broadens strongly the process understanding.
- For the photocatalytic water splitting accompanied by methanol photoreforming performed on TiO_2/Ag_2O, the role of silver photo-transformation was explained.
  The improved photocatalytic activity of the TiO_2/Ag_2O during photo-transformation does not relate, according to the PhD student, with the establishment of commonly believed p-n junction but with the new intrinsic properties of the photocatalysts and the Conduction Band edge shift towards lower potential.
- In the case of the Ag/AgCl systems, its photocatalytic activity was assigned to the formation of reactive chlorine species like HCl and HClO, therefore it was concluded

that the photochemical transformation is crucial in the photocatalytic activity of this system.

Formal analysis of the thesis

The doctoral dissertation submitted for assessment is prepared in a hybrid mode. The dissertation is based on a thematically-related collection of scientific articles, but also contains additional chapters including material that has not been published yet. The dissertation is written in English. The dissertation contains a literature introduction, a clearly defined research goals, a description of the attached publications together with the description of unpublished results and ends with conclusions.

The literature introduction is quite concise, but very clear and clearly introduces the topics of the PhD thesis. The PhD student explained the basic phenomena occurring in photocatalysis, the catalysts used in this process, the mechanism of the process and discussed the properties of indicators used in the catalytic process. The properties of titanium dioxide, one of the most frequently used and best-known semiconductors in catalytic processes, are also described. Ms. Anna Jakimińska also discussed the most important issues related to the use of metallic structures in photocatalytic processes. The literature chosen by the doctoral student when preparing this part is mostly from the last decade, which highlights the innovative nature of the work.

Ms. Anna Jakimińska very clearly formulated the aim of her work, which was to determine the factors influencing the photocatalytic activity and efficiency of the energy/electron transfer between plasmonic nanostructures and semiconductor on the example of the several catalytic systems. When setting these research goals, the PhD student approached the issue in the very ambitious way. I must also say that the doctoral student focused on important and valid research topic.

The research part of the thesis is thematically divided into two parts. First one is dedicated to remote excitation of the photocatalytic system. The PhD student clearly described this process by explaining that it can take place through the involvement of surface plasmon polaritons, and that energy can be transferred at much longer distances than the incident light at a given wavelength. In that case the photocatalytic system is excited without

the direct implication of the incident irradiation. She clearly provided the motivation of the sample choice which was based on silver nanowires coated with semiconductor layer and the choice of fluorescent probe. In the first part of the thesis different kinds of dyes were used as a fluorescent probe that allow to monitor the photocatalytic process in solid state applications. The detailed mechanistic approach is very nicely explained and elaborated on the example of the photocatalytic transformation of Rhodamine B to Rhodamine 110. In the next part there is nice discussion and experimental data provided concerning the remote excitation of the photocatalytic systems, firstly the proof of principle study on single nanostructures and further the remote excitation experiments are described. Second part relates to the role of plasmonic nanostructures in semiconductor-based systems under direct irradiation. Here the description concerns silver and gold nanoparticles as plasmonic nanostructures used for the titania modification. Ms. Anna Jakimińska describes and discuss both their preparation methodology as well as characterization of the physicochemical properties mainly by SEM, XRD and DRS techniques. She also convincingly explains the photo- and photo-electro properties for the chosen systems. In subsequent part she compares the influence of the modification of titania with plasmonic (with the example of gold) and non-plasmonic (with the example of palladium) nanostructures. And she explains based on the presented results that both modifications (not only with the plasmonic nanostructure) can have positive implications concerning activity. For example, the presence of palladium can have beneficial effect in water splitting process by its ability to catalyze the hydrogen evolution.

The attached papers present very interesting and valuable information concerning photoactivity of the TiO_2/Ag_2O in water splitting accompanied by the methanol photo-reforming. Second one concerns the photochemical transformation of AgCl. This thematically forms nice scientific story.

Comments and remarks:

Despite the nice concept of the hybrid thesis combining both published and unpublished works that I personally find interesting as a new way of PhD thesis formulation, there are few comments that I have to mention:

- It would be easier and more consistent if the additional chapters (namely with non-published results) would have the same manuscript-like structure, e.g. introduction, experimental and results parts. In contrary in the thesis, the description of those chapters is merging all information - which is also not typical even for the traditional way of presenting the thesis.

- The results are characterized by their highly ambitious nature, and all the chapters consisting of both published and non-published works are building a nice part of a consistent story. This story could be even nicer whether the published work could be summarized in at least few sentences.

- Some fonts (particularly in the case of some figures) and some figures themselves are too small e.g. fig. 28, fig.33, fig. 36.

Driven by the curiosity, I would be happy to discuss during the public defense the following issues:

(1) For the measurements of the particle size presented on the Fig. 36, the count presented on the histograms is in [%] or this is the actual number of the particles given? What is the possible accuracy of the measurements in that case? To which extent that accuracy can influence the interpretation of the results, given the known highly sensitive dependence of the plasmonic properties (plasmonic band maximum, intensity, width) against the particle size. The same remark applies for the shape of the particles, that unfortunately it is not possible to estimate from the SEM measurements; could it also influence the photoactivity?

(2) When the catalysts have different metal particle sizes, we can have also different interactions between the metal and the support (well identified in heterogeneous catalysis), which in consequence is influencing the electronic properties of the metal, and therefore possibly also the plasmonic properties of the metal and the recombination rate in the catalysts. How important can be the influence of the metal – support interaction on the photocatalytic activity of the tested materials in the different reactions investigated in the thesis?

(3) In the complex process of water splitting accompanied by methanol photo reforming, to which extent it is possible to discriminate and quantify both reactions (namely, the H_2 production by true water splitting and by reforming of methanol)?

To sum up, in my opinion, these studies contain very interesting material, characterized in detail. The doctoral student tried to understand the research topic very thoroughly, which deserves a special recognition.

I also rate the PhD student's scientific achievements very high. Ms Anna Jakimińska is co-author of 5 publications directly related to this thesis, and two of them were published very recently after the thesis submission. It is worth to highlight that in all of them she is the first author. Additionally, she is the co-author of three other publications not related directly with the thesis topic. What is more she was very actively presenting the results of her thesis on many international and national conferences (15 contributions).

Final conclusions

I believe that the doctoral dissertation that I had a pleasure to assess meets the requirements set for doctoral theses by the Act of July 20, 2018 - Law on Higher Education and science (Journal of Laws of 2018, item 1668, as amended). The reviewed scientific work contains significant elements of scientific novelty, and the comments provided are polemical in nature and do not diminish my very high assessment of the work as a whole. Therefore, I am asking the Discipline Council of Chemical Sciences of the Jagiellonian University to admit Ms. Anna Jakimińska, to the next stages of the doctoral program.

Moreover, taking into account the excellent research skills of the doctoral student, the very valuable research results described in the doctoral thesis, the outstanding achievements of the doctoral student (co-author of 8 publications, 15 conference achievements), I ask the Disciplinary Council of Chemical Sciences of the Jagiellonian University to award the doctoral thesis if the doctoral student meets the other requirements for distinguished candidates at the Jagiellonian University.

Łódź, 15th December 2023 Agnieszka Ruppert

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