

Referee opinion on the PhD dissertation of Abdul Wafi: „Preparation and characterization of nitrogen-doped TiO<sub>2</sub> semiconductors for photocatalytic degradations” submitted for PhD defence for Doctoral School of Chemistry and Environmental Sciences of University of Pannonia

The dissertation is suitable for the following step of the PhD process, and after successful defence to award the degree. The English is quite acceptable, understandable and clear with very few typing errors. (A bit frustrating that the first line in the abstract, also understandable, is far from the perfect construction.) The 94 pages text (with further 11 pages of Attachment) contains approx. 47 (+12) well-made figures and 9 (+1) informative tables. The 206 references testify the candidate thoroughly studied the corresponding scientific literature, and help the reader to get an overview of the scientific field. The dissertation is based on two articles, in both he is the first author and those are published in proper, reasonably good journals. (Consequently, the dissertation also contains two separate but cohesive part, which feature, I think, is proper.) In the 7<sup>th</sup> chapter (the “Thesis Points of PhD Dissertation”) there are 5 statements, together with the 2-4 additional explanations for each item, and all of them are proper and acceptable for me.

It should be emphasis that the dissertation is better than most studies in the literature. The thesis describes the catalysts prepared by the author in a versatile way and then characterizes their photochemical properties by thorough experimental work. The choice of the N-doping is a suitable idea to improve the absorption properties of TiO<sub>2</sub> in the visible light range, even more because it keeps the modified material stable in use and similarly environmentally friendly than the original one. Its versatility and sophistication set it apart from similar works.

However, it is my obligation to look for uncertainties or weaknesses in the text, so, I would like to rise some questions.

- i.) First of all, although the candidate write about it, I would emphasize more that the primary aim is not to develop a potential wastewater purification system, but learn more about the material- and photochemistry of  $\text{TiO}_2$  based semiconductor photocatalysis, i.e. it is a basic science study. Must be mention that there are several other than mentioned drawback of the heterogeneous photocatalysis, as the low quantum efficiency, the potential color and the often-enormous amount of TOC (which competes with the low concentration poisonous contaminant) in the dust water. The reduction in the oxidation efficiency of otherwise often inert active pharmaceutical ingredients (APIs) is also noteworthy when the bandgap of the semiconductor catalyst is artificially reduced to make it suitable for use with visible light. Even more, the necessity to remove the colloidal (and not environmental friendly) catalyst from the purified water, and probably to regenerate it, etc.
- ii.) The equations 3.8 – 3.12 are not fully consistent in respect which species or reaction occur on the surface or in homogeneous phase. For example 3.11 seems to be homogeneous reaction, while 3.12 probably both, i.e. the pollutant a adsorption on the surface of the catalyst may be a key step as well.
- iii.) Similar way at the end of page 16 would be worth to mention that the surface metal loading may change the adsorption efficiency (and that way the exchange current density) of the key reacting species (as for example the pollutant, or the reduction side the  $\text{H}^+$  or  $\text{O}_2$ ).

iv.) I would prefer a more critical review of the literature, to tell us that very difficult to compare those results, when model compounds and their concentrations are different (with different reduction and oxidation properties), and of course the lamps spectra and photon efficiency, as well as the construction of the set-up also differ very much. (Of course, it is not the candidate's fault, even more his work is much better in this respect.)

1. page 21. 540 min instead of 540-min
2. page 35. End of Ch. 5.1: it is missing whether it is an approximation or an evidence from the literature.
3. page 37. I wonder if these results have been reproduced or if they were just a carefully executed series of experiments.
4. page 47. Figure 5.9. It would be useful for the reader to indicate that 3.18 eV band-gap energy means that the semiconductor absorbs the light has bigger energy than 390 nm.
5. page 52-54. see question a.)
6. page 56.  $pK_a$
7. page 60. 3 valuable digits for the percentage values would be enough
8. page 76. Table 5.7. ... other reactive species **than OH radical**. (Is it OK ?)

Questions:

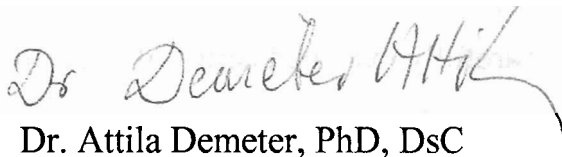
- a.) Please discuss more detailed the experiments corresponds to Figure 5.13 to 5.16. It is not clear for me while in Fig. 5.13 the rate of formation of 7-OHC is twice as much in presence of air (more triplicate if we consider the initial rate, probably two at 60 min while it is oxidized further), while at Fig. 5.15 the part degraded via OH radical is the same. Seems to be, the total

- degradation of coumarin triplicate with air saturation in agreement with Fig. 5.14, but the 7-OHC derived part is practically the same, although the Fig. 5.13 indicates an increase contradicting the last but one sentence on page 53.
- b.) Please discuss whether the trends, shown in page 57, is contaminated with the continued oxidation of 7-OH at longer irradiation, or isn't it?
  - c.) There is literature of the TiN/TiO<sub>2</sub> composite photocatalysts, do you see any relation of your work and those?

In summary, the questions and comments I have asked do not affect my good opinion, but rather serve to clarify some of the findings. Thus, in the event of a successful defence, I recommend the award of the degree.

**(A disszertációt és a téziseket elfogadásra javaslom.)**

Budapest, 03<sup>th</sup> of June 2021.

  
Dr. Attila Demeter, PhD, DsC