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Strasbourg, January 16th, 2021,

to : Mrs. Urszula Kampowska,
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Concerns: PhD review on the doctoral thesis of Mrs. Zuzanna Bielan

Please find hereafter my review relative to the PhD manuscript to be defended by Mrs. Zuzanna Bielan entitled "TiO_2-based magnetic photocatalysts with core-shell structure".

Considering the work performed by Mrs. Zuzanna Bielan in the frame her PhD, I give a favorable opinion regarding the PhD manuscript, and recommend that the candidate can defend her PhD thesis in a public defense.

Yours faithfully,

Nicolas Keller
CNRS Research Director

Opinion on the PhD manuscript of Mrs. Zuzanna Bielan

The PhD manuscript defended by Mrs. Zuzanna Bielan is an interesting contribution to the development of core/shell nanostructured TiO_2-based magnetic nanocomposite photocatalysts with magnetic nanopowder recovery for use in aqueous phase applications such as notably water treatment.

The PhD work of Mrs. Zuzanna Bielan is focused on the synthesis, the characterization and the catalytic reactivity of nanostructured powdery photocatalysts with as final target the elaboration and characterization of TiO_2-based magnetic nanocomposite photocatalysts with core-shell nanostructure facilitating the viability of the implementation of aqueous phase applications like water treatment or potentially H_2 synthesis from methanol, thanks to magnetic recovery. The main innovation is related to the controlled elaboration of the double core/shell nanostructures composed of a magnetic core powder, an intermediate interfacial inorganic protective layer and an external durably stabilized TiO_2 photocatalyst, as well as to their upgrade by defects engineering and by surface modification via metal-based nanoparticle decoration. UV-vis activity towards a series of reactions requiring different surface properties with easy recycling in water is the key-targets

Mrs. Zuzanna Bielan performed an interesting broad study covering both catalyst synthesis and characterization aspects, that required the implementation of several characterization techniques for the determination of bulk and surface properties of the systems at different steps of their elaboration. She conducted promising research in a very competitive field that still requires a strong input from the scientific community. Important effort was also provided regarding the implementation of different tests reactions, including the degradation of phenol and carbamazepine refractory compounds, the acetic acid decomposition or the methanol dehydrogenation for hydrogen production, and efforts were accomplished for the understanding of the underlying (complex) phenomena involved in at the catalyst level in photocatalysis.

The PhD thesis is divided into five chapters of different importance and length. It is organized as a collection of papers supplemented by a short bibliographic introduction devoted to the context of the study and to the main challenges, a brief itemization of the research goals, a synthetic summarizing description of the research performed and a conclusive section.

First, a short general introduction aims at summarizing the global context of the PhD thesis in the field of water treatment, with focus on the bulk/surface photocatalyst properties, the research strategies followed for shifting the activity of titania nanopowders towards the visible light wavelength range, and the magnetization aspects of the photocatalysts to consider for increasing the process viability. The introduction is written in a condense and informative way, even if the reader might feel a bit frustrated by the brevity of the chapter that could have deserved a more exhaustive overview for getting a more complete understanding of the background of the field and in consequence of the issues and the challenges to overcome (among others *eg.* materials aspects, plasmonics, the associated physico-chemical mechanisms, magnetic photocatalysts).

The chapter two is devoted to the description of the research goals of the PhD thesis, and seven research goals have been itemized as points of interests to be studied during the studies performed on TiO_2-based magnetic photocatalysts for water treatment. The objectives of the PhD work have been well identified. It could have been valuable to structure and hierarchize/prioritize them in relation to the overall investigated topic.

The core research work of the PhD thesis can be found in the third, fourth and fifth chapters. The chapter three proposes a summarizing description of the research performed that consists in the canon of the thesis, formed by a collection of juxtaposed publications (six) and polish patents (three) as the chapter five. The collected articles are published in medium impact factor journals, and Catalysis Today associated to the EAAOP-6 congress (2019) displays the highest IF of 4.9 in 2020. The ranking of data in brief in Q1 is surprising.

The chapter three corresponds to the valuable attempt of Mrs. Zuzanna Bielan to provide to the dissertation a structure in terms of research strategy and in consequence a (comprehensive) logical research plan, such a necessary understanding being unfortunately not really favored by the choice of a document as publication collection. It therefore first underlines the correlation between the different gathered publications, before to summarize the studies on the enhancement of the UV-vis photoactivity of titania-based photocatalysts, on the synthesis/characterization of magnetic photocatalysts with core/shell structure, and on their activity for the degradation of persistent organic pollutants in water.

The first publication from the chapter five is a data in brief on the mono- and bimetallic Pt/Cu titanium(IV) oxide powders, with physicochemical properties and photocatalytic activity under UV-vis (phenol degradation, acetic acid decomposition, methanol dehydrogenation). While the concept of data in brief remains questionable by being in fact associated to a main publication for giving more visibility to supplementary information, the data in brief reports some partial data on the influence of surface modification of different kinds of titania with Pt and Pt/Cu metallic systems. The shell denomination from the title and the core/shell terminology from the abstract directly refer to the (main) mother article (here as independent sixth article) to which this data in brief is attached.

The second article is focusing on the photoactive titania by it-self, with the preparation and characterization of defective titania nanostructures for developing visible light activity. The article reports on an interesting strategy, according which the vacancies formation is taking place by submitting the titania precursor to different oxidizing agents such as HIO_3, H_2O_2 or HNO_3 during hydrothermal synthesis The article is reporting on the remarkable stability upon heating of the defective titania catalysts. The question of the mechanism involved in the formation of those highly stable defective titania nanoparticles remains open.

The third publication is devoted to the upgrading of the titania magnetic core/shell photocatalyst through defects formation and surface modification by plasmonic nanoparticles for visible light activity. Interface characterization would provide valuable information. Performing the catalyst recovery on the final core/shell nanostructured photocatalyst rather than the non-magnetic analogue one would strengthen the scope of the work. The question remains if the supported platinum nanoparticles are present as metal or oxide phase, and whether the concept of Schottky barrier at the metal/semiconductor interface might be applied pertinently.

The fourth article is devoted to an application of the magnetic core/shell photocatalysts for the degradation of recalcitrant chemicals from flow back water. Question remains on the origin of the difference in terms of phenol degradation rate constant for the different systems, might is find its origin in differences in terms of TiO_2 content of the photocatalyst that has not been estimated ? Following the magnetization data provided, is the recovery process efficiency via the magnetic core of the powder supported by any experimental evidence ? How the variation in terms of apparent kinetic constant rate upon catalyst cycling can be interpreted ?

The fifth article deals with the influence of the magnetic core of the titania-based core/shell photocatalyst on the properties and the activity in the degradation and mineralization of both phenol and carbamazepine substrates in water under simulated solar light. This is an interesting study based on the relationship between the surface chemistry of the core powder and the surface charge of both components to be interfaced in order to implement efficiently the surfactant- and nanoreactor (droplets)-based synthesis method. The magnetic properties of the systems are well addressed ; do they correlate well with the recovery efficiency of the powders ? Interestingly, some of the composite photocatalysts exhibit similar apparent kinetic rate constants than the TiO_2 P25 reference powder in batch slurry mode.

The sixth article is referring to the data in brief itemized in the dissertation as independent first article. It is devoted to the mono- and bimetallic Pt/Cu titanium(IV) oxide core/shell structured magnetic photocatalysts, with physicochemical properties and photocatalytic activity under UV-vis (phenol degradation, acetic acid decomposition, methanol dehydrogenation). The results reported herein are interesting and well written. The

action spectra is measured in terms of quantum efficiency using controlled monochromatic irradiation and with the 1,4-benzoquinone intermediate based method. Finally the cycling of the core/shell photocatalyst is performed through magnetic recovery and no loss of degradation for the phenol substrate is mentioned. It might have been valuable to characterize as well the photocatalyst after use during the cycling process.

A short conclusion is summarizing the main results of the PhD thesis, and highlights the main novelties of the work in terms of titania photocatalyst with defect engineering and with mono or bimetallic nanoparticle decoration, as well as in terms of elaboration of double core/shell nanostructured titania-based photocatalyst with magnetic recovery from water. Some perspectives opened by the research work might be presented.

Independently of the collected articles, for sake of clarity, some data like the time-evolution curves related to the pollutant degradation and mineralization together with the kinetic models applied, or systematic K-M analysis data would have been very valuable. It would have been appreciated to gather as well the SI with the main articles, as they contain some experimental details. A large part of the originality of the work is related to the step-by-step building-up of the metal-modified magnetic TiO_2-based photocatalyst with core/shell structure and interfacial protective layer. In consequence, a step-wise bulk and surface characterization of the materials at the different steps of the elaboration process would provide valuable information, especially in terms of morphology/nanostructure, interaction, and surface states (chemical, electronical properties). Also a clear evidence of the electronic surface state of the bimetallic systems might be helpful. The reader might be slightly frustrated by the absence of detailed discussion on some characterization and activity data. Besides, it seems that the dissertation document is peppered with some unappropriated micrographs or associated legends. Obviously, the concept of publication collection favors the existence of repetitions within the fifth chapter. By contrast, the materials characterization focuses in a selective manner on some specific catalysts.

The results have been valorized in nine (9) publications, including four-Q1 and five-Q2, four of them in the fast-publishing MDPI journal collection (the technical data in brief being associated to one Q1 article). Three polish patents have been registered. The works have been presented in 22 conferences and seminars (talks and posters), including one oral talk at an international congress and three talks at national summer school presented directly by Mrs. Zuzanna Bielan.

In conclusion, the work performed during this PhD fully deserves to be defended by Mrs. Zuzanna Bielan and I give a favorable opinion to the admission to the public defense of the dissertation of Mrs. Zuzanna Bielan, and in the possible application of her PhD thesis to the competition process for distinction.

Obviously, it raises a number of questions that emerge from the very interesting results presented. The questions will mainly be related to the synthesis of the magnetic photocatalytic nanopowders, their bulk and surface characterization during the stepwise building-up of the composite double core/shell photocatalysts and their modification by defects engineering and nanoparticles decoration, as well as the correlation between the catalyst properties and the photocatalytic behavior in water treatment, and the applicability in terms of catalyst recovery. These points will be discussed in the usual discussion session with Mrs. Zuzanna Bielan.

In my opinion, the reviewed thesis fulfills all requirements stated in Polish Law on Higher Education, in Article 13 of the Act of 14 March 2003 (Journal of Laws, No 65, item 595, with amendments).

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