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dr hab. Emerson Coy, Prof. UAM
Adam Mickiewicz University in Poznan
NanoBioMedical Centre,
Ul. Wszechnica Piastowskiej 3
61-614 Poznan

THESIS REVIEW

The PhD dissertation presented by **Ayesha Khan, M.Sc.**, titled ***Titania-based heterogeneous photocatalysis for the selective oxidation of biomass-derived platform chemicals***, supervised by dr hab eng Juan Carlos Colmenares, prof ICHF-PAN and Prof. Roger Gläser (Leipzig University), shows a thoroughly performed work performed with evident attention to details and presented in an ordinated manner. The work aims to study a relevant and current issue in heterogeneous catalysis, namely the no selectivity of titanium oxide-based catalysts towards organic oxidation, attributed to the generation of highly active oxidizing species selective oxidation. The PhD dissertation focuses on improving the photocatalytic selective oxidation of biomass-derived platform chemicals into value-added chemicals and fuels, which are greatly important for the current energy and catalysis fields.

1. General assessment

The student has authored six (6) peer-reviewed publications, of which four (4) the candidate is the first author. Among the associated publications are of noticeable importance research works in reputable journals such as *Top Curr Chem (Z)* (IF=9.06), *ChemSusChem* (IF=8.92), and *ACS Sustainable Chem. Eng* (IF=8.19). The publications are additionally characterized by an active and fruitful international collaboration, with funding from various Polish national agencies (NCN and NCBR) and the European Union Horizon2020. The high citation count of the publications *Top Curr Chem (Z)* (42 citations) and *ACS Sustainable Chem. Eng.* (29 citations) are remarkable. I believe that these citations evidence the importance and reception of the presented research by the scientific community.

The first chapter of the thesis presents a well-directed introduction to the general physicochemical aspects of titanium oxide photocatalytic materials. The three (3) main structures of titanium, namely rutile, brookite and anatase, are introduced, followed by the general photon-driven process for catalysis, including the generation of reactive oxygen species (ROS) and superoxides. Noticeable, Table 1 provides quick and efficient reference material for processes and time frames in titanium oxide catalysts. The photocatalytic reduction of nitrobenzene over titania is then presented, paying careful attention to the role of the different crystalline phases (single/mixed) on the reduction of different organic compounds and the ROS involved. This section also mentions different pre-treatments of the titania-based composites and doping with different ions. This section is comprehensive, and there is a clear intention of presenting state of the art in the field. However, it is my perception that it could have been subdivided, as sometimes the information seems to overwhelm the reader and jump from crystallographic aspects to organic pathways and treatments/doping.

The drawbacks of titanium oxide materials and the strategies for solving these issues are clearly outlined and presented. Particular focus is given to ligand to metal charge transfer (LMCT) clearly, and the general aim is to broaden titania's absorption range. Moreover, the section also accurately points out that LMCT strongly depends on the titanium composites features, such as particle size, specific surface area, surface structure, hydroxyl groups, among others. A distinction on the role of 1D, 2D or 3D (porous) composites would have been profitable as support for LCMT sensitized titania. Nevertheless, the author presents a clear case for the efficiency of LMCT (page 19), where ascorbic acid (AA) and TiO_2 show absorption below 400 nm and their composite AA-TiO_2, presents an absorption well above 700 nm.

Ul. Wszechnicy Piastowskiej 3, 61-614 Poznań
tel. 48 61 829 67 04.
e-mail. cnbmadm@amu.edu.pl
http://cnbm.amu.edu.pl/

Further subsections focused on Titania/carbon composites, highlighting the importance of biomass-derived renewable materials such as lignin, cellulose, chitosan, agriculture residues, activated carbon, fly ash, and biochar. The author clearly outlines potential candidates for the preparation of photocatalytic composites. The accurate mention of the Ti–O–C structure on the electronic environment of such composites is also relevant and its role in efficient catalytic performance. The introduction of multiwall carbon nanotubes (MWCNTs), followed by the literature of nitrogen-rich compounds, such polysaccharides, and then the mention of Lignin composites, does seem a bit chaotic. However, the thought behind it becomes more evident when the composites of chitosan and lignin (CL), which can be adapted to titania nanoparticles, is introduced on page 29. The role of nitrogen-rich chemistry and π-π stacking interactions is clearly outlined as essential for this architecture.

The last section outlines the possible pathways of selective oxidation of biomass are presented in detail over different composites, such as graphitic carbon nitride (g-C_3N_4), Nb_2O_5, and over UV-radiation. Furthermore, the author summarizes the challenges and general strategies for increasing the efficiency and selectivity of the titania photocatalytic process, paving the way for the hypothesis and objectives of the thesis.

The research hypothesis is divided into two (2) main groups: *Ligand-to-metal charge transfer (LMCT)-complex formation*, and second, *preparation of nanocomposites of titania and carbon materials.* The sub-hypotheses are well outlined given the introduction of the thesis, and the objectives are clearly established, with particular attention to the experimental techniques involved. The methods section is comprehensive and describes in detail both the synthetic processes and the characterization techniques.

2. Results and discussion

One minor correction is the misuse of the word "reflex/reflexes" in this and in the appendixes section, as it should read "reflection/reflections" instead.

Ul. Wszechnicy Piastowskiej 3, 61-614 Poznań
tel. 48 61 829 67 04.
e-mail. cnbmadm@amu.edu.pl
http://cnbm.amu.edu.pl/

2.1. *In situ LMCT-sensitization of titania and its photocatalytic activity*

The comparison of the SGH-TiO_2 with commercially available compounds is compelling and shows the smaller crystalline size (5-6 nm) of the prepared compounds and the improved surface area according to the BET experiments. However, there is no information if these values are the result of an optimization process (not shown in detail in this thesis) or, due to the small size and high surface, this synthesis was good enough for this thesis. Moreover, Figure 19 shows small broad bumps at ~37° and ~43°, which could be small traces of rutile. There is no information on whether the phase's percentages were calculated automatically by the PANalytical software or by other means.

An exciting result is presented in Figures 21 and 22, where the selectivity and conversion of the nanomaterials to visible and ultraviolet light is presented. The clear increment of selectivity under visible light irradiation is a strong advantage of the process. The material's recyclability is high, and the decrement observed is well within the expected centrifugation and purification losses.

The visible change of colour after LMCT functionalization already suggests a Physico-chemical effect and broadens the absorption edge. Spectroscopic studies support the formation of LMCT complex, possibly through dissociative adsorption of CH_2OH moiety of HMF and hydroxyl groups available at the surface of the SGH-TiO_2. Additionally, important bands of Ti-O-C and Ti-O-Ti stretching vibrations were observed in the samples. One aspect that could have been added is a bad-gap estimation of the nanomaterials. This aspect would have provided a quantifiable aspect for the general enhancement of the process.

The overall attachment and presence of functional groups are well-described, and the mechanism behind the photocatalytic performance is well supported by the literature, the spectroscopic and thermal decomposition studies. As the authors have mentioned, the higher specific surface area, with its associated higher density of functional groups, might play an important and certainly exploitable role in the overall performance of the LMCT sensitized titania catalyst.

2.2. *Titania/chitosan-lignin (T/CL) nanocomposite*

The nanomaterials show different morphological characteristics, as shown by the SEM images. The elemental quantification corroborates the significant contribution of chitosan to nitrogen and lignin on the sulphur composition. There is no clarity on which technique was used to obtain the quantification of Hydrogen and Nitrogen of the samples. The XPS studies show a very complex electronic panorama, with several carbon species as well as distinctive amide and amine nitrogen compounds. An aspect that could have been illustrative was SEM images of the T/CL composites.

Especially important is the presence of N-Ti-O bonds, observed by XPS, which are indubitable are provided by chitosan. Additionally, the TEM studies show the distinctive interplanar distances of brookite and anatase in the agglomerate of nanoparticles and the congruent size distribution with the XRD experiments. Impedance spectroscopy studies show an evident change in circumference (Nyquist plots) between different samples. However, without an appropriate fitting circuit/model the overall capacity and resistance cannot be appropriately extracted.

The overall efficiency of the composites is well studied, leading to a compromise between titania content and performance. The radical conversion profiles show an interesting trend and provide insightful observation on the general mechanism under UV-light. The performance under visible light conditions shows a compelling argument towards selectivity, despite the moderate performance. In fact, as the author points out, the nanocomposites prepared from titania and renewable biomass-derived show a series of non-intuitive benefits, for instance, the indirect enhancement by nitrogen doping and the improved selectivity via mediation (scavenging) of unselective reactive radical species.

3. *Concluding remarks*

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tel. 48 61 829 67 04.
e-mail. cnbmadm@amu.edu.pl
http://cnbm.amu.edu.pl/

The PhD dissertation provides high-quality results and a methodological approach that can be extrapolated to several other studies. As the author outlines in the conclusion and perspectives sections, the methodology presented can be extrapolated to wide band-gap semiconductors and other photoactive materials. Additionally, the precise evaluation and meticulous study of the negative effect of superoxides on biomass conversion is a highly relevant topic, which, as shown in this dissertation, needs to be further experimentally studied.

To conclude, I believe that the work presented in this dissertation is of high quality, as clearly reflected by the high impact and highly cited publications accompanying this work. Moreover, It meets the conditions specified in the Article 187 of the Act of July 20, 2018 Law on Higher Education and Science (Journal of Laws of 2018, item 1668, as amended). Therefore, I recommend this dissertation for further formalities conducting to the title of Doctor of Philosophy at the Institute of Physical Chemistry (IPC), Polish Academy of Sciences (PAS) in Warsaw.

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