

MECHANISM OF TRYPTOPHAN OXIDATION ON METAL OXIDE NANOPARTICLES

Alexandra Nefedova¹, Fredric Svensson², Alexander Vanetsev¹, Peter Agback³, Tatiana Agback³, Suresh Gohil³, Lars Kloo⁴, Tanel Tätte¹, Angela Ivask⁵, Gulaim Seisenbaeva³, Vadim Kessler³

¹ *Institute of Physics, University of Tartu*; ² *Department of Solid State Physics, Ångström Laboratory, Uppsala University*; ³ *Department of Molecular Science, BioCenter, Swedish University of Agricultural Sciences*; ⁴ *Applied Physical Chemistry, KTH Royal Institute of*

Technology; ⁵ *Institute of Molecular and Cell Biology, University of Tartu*

e-mail of presenting author: alexandra.nefedova@ut.ee

One of the crucial metabolic processes for both plant and animal kingdoms is the oxidation of the amino acid tryptophan (TRP) that regulates plant growth and controls hunger and sleeping patterns in animals [1]. Here, we report a study how this process can be crucially affected by interactions with metal oxide nanoparticles (NPs). Molecular changes in TRP after interaction with ceria and titania NPs were revealed by NMR and optical spectroscopy and after interaction with polyoxometalate NPs by X-ray single-crystal study. These methods enabled analysis of TRP oxidation by NPs at a molecular level.

Depending on their redox properties metal oxide NPs were found to either act as nanozymes, specifically oxidizing TRP into 3-hydroxypyrrroloindole carboxylic acid (PIC), or, for weaker oxidants acting as photocatalysts, randomly oxidize TRP into a variety of different products by the action of photogenerated ROS. The key principle in the nanozyme action appears to be the formation of an outer-sphere NP–TRP complex based on hydrogen bonding involving the NH fragment of the TRP indole ring. The direct insight into this mechanism was obtained by combination of (HTRP)₃PM₁₂O₄₀·5H₂O, M = Mo, W, molecular model structure determination, and theoretical evaluation. The chemistry of these species clearly indicates a charge transfer mechanism [2]. The latter is then facilitated for redox-active oxide NPs due to the deprotonation of the TRP ligand under pH-neutral conditions. Thus, we can conclude that interaction between metal oxide NPs and TRP are governed by the redox potential of the former.

References

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