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Referee report on the doctoral thesis "Study of cerium oxide thin films for biosensing applications" by Ms. Yuliia Kosto.

The submitted doctoral thesis represents a highly innovative study of biomolecules interactions with cerium oxide films.

The thesis begins with a detailed overview of the physicochemical properties of cerium oxides and their potential applications in biomedical applications. In biosensor applications, the interaction between cerium oxide and amino acids plays a pivotal role, therefore, its understanding provides well-formulated arguments for the investigation of adsorption behavior of these biomolecules on model cerium oxide surfaces. The techniques described in the second chapter are well-suited experimental methods selected by the author for achieving the goal of the present work.

The first experimental part of the thesis is focused on the investigation of two representative amino acids (glycine and sarcosine) bonding to cerium oxide model films by state-of-art surface science techniques. Adsorption chemistry and thermal stability of the molecules on the oxides, with different degrees of chemical and structural complexity, were studied in relation to the oxidation state of ceria cations, film morphology, and molecular deposition method (vacuum and solution). In particular, the results revealed that the molecular film deposited from an aqueous solution, in contrast to deposition in vacuum, induces continuous reduction of the cerium oxide during thermal annealing. Moreover, the experimental results show that oxygen vacancies in the cerium oxides affect the adsorption geometry and stability of adsorbed molecular systems. The obtained results provide fundamental insight into the complex processes at the interfaces between biomolecules and inorganic solid surfaces at the atomic scale.

In the second part of the PhD work, the author used polycrystalline cerium oxide thin films as an electrode for electrochemical and electrochemiluminescent detection of hydrogen peroxide and sarcosine and showed that the cerium oxide deposited on a glassy carbon substrate can be efficiently used for sarcosine detection in biomedical applications.

Finally, the reported results have been published in high-impact international journal *Applied Surface Science*. Another publication is in preparation for *Physical Chemistry Chemical Physics* journal. Besides these, Ms. Yuliia Kosto is co-author of other publications in her field of interest. In summary, Ms. Yuliia Kosto has demonstrated the ability to conduct high-quality experimental work, data analysis and manuscript writing.

Thereby, I recommend Ms. Yuliia Kosto to be awarded the PhD title.

To the content of the thesis, I have the following questions:

1) Section 3.1.1.
(Page 38). Which molecular levels are occupied or become empty upon charge transfer at the organic/oxide interface.
(Page 44). What is the thickness of the Gly film?
(Page 45). Which energy is required to deprotonate the Gly molecules in the gas phase? Does this energy change in comparison to the energy of the deprotonation reaction of Gly on the surface? Do the oxide surfaces facilitate the reaction?
(Page 51). The charge transfer from the molecules to the substrate would change the electronic structure, with the emptying of the HOMO of Gly. Is this confirmed by spectroscopic data? Does the change in the N K-edge NEXAFS measured after annealing, and the presence of new π resonance, suggest this?

2) Section 3.1.2.
(Page 59) What is the pH value of the solution used? Will different pH values affect the neutral/zwitterion ratio of the molecular system in solution?
(Page 70) The features in the NEXAFS data reported in Fig. 3.1.20 associated with the decomposition products have a higher intensity for the deposition in UHV than for deposition in solution. Do the products form in the Knudsen cell (thermal-induced phenomena), or the decomposition of molecules is taking place on the oxide surfaces (surface assistant reactions)?

3) Section 3.2.2.
(Page 91) Can the CeO_2/GC electrode be used for the detection of other amino acid molecules, or even can be applied for different class of organic systems? Should the molecules contain the oxygen or amino groups for this detection approach?

Jülich 29.03.2021
Dr. Vitaliy Feyer