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Review of the doctoral thesis submitted by Yuliia Kosto

Study of cerium oxide thin films for biosensing applications

The study of the interaction of biomolecules with oxide surfaces is a very important subject due to promising biosensing applications. Thus understanding the fundamental processes taking place when glycine and sarcosine molecules interact with cerium oxide surfaces is important. Therefore the research presented in this doctoral thesis is both relevant and current.

The thesis is clearly presented and although it is rather succinct, it is well structured and it presents the subject under study in the broader context. It covers four chapters that make reference to all the important and relevant literature. Chapter 1 presents a brief description of the current state of the subject and the main goals of the dissertation. Chapter 2 describes the fundamental principles of the main experimental methods employed. In particular the author provides a clear description of X-ray Photoelectron Spectroscopy (XPS), Resonant Photoelectron Spectroscopy (RPES), Near Edge X-ray Absorption Fine Structure (NEXAFS) and the electrochemical methods employed for sensing hydrogen peroxide and sarcosine. Furthermore, the methods employed to grow the cerium oxide films as well as their complete characterization is presented. Chapter 3 discusses the results obtained in the different systems studied. The first part of the investigation deals with the interaction of glycine and sarcosine with cerium oxide thin films (section 3.1). The second part of the investigation deals with using cerium oxide as an electrode for sensing hydrogen peroxide and sarcosine (section 3.2). Chapter 4 summarizes the main findings and conclusions. Finally it should be mentioned that the work presented in this thesis resulted in one manuscript published in Applied Surface Science and in the preparation of one manuscript to be submitted for publication, in both cases the PhD candidate is the first author. Besides, the author made contributions to four different publications not related to her thesis work.

The adsorption glycine and sarcosine on different cerium oxide surfaces is reported in section 3.1. The author found that oxygen vacancies play an important role in bonding to the oxide surface. Glycine molecules adsorb via a deprotonated carboxylic group in all explored systems. Furthermore, the molecule lies almost parallel to the CeO_2 and Ce_6WO_{12} surfaces due to attraction of the amino group to the oxygen anions, whereas on the reduced cerium oxides, $CeO_{1.7}$ and Ce_2O_3 glycine binds to the surface with the carboxylate oxygens incorporated into the vacancy sites and with the amino group directed out of the surface. Finally, glycine bonding becomes stronger with increasing concentration of the oxygen vacancies on the cerium oxide surfaces. Sarcosine adsorbs on polycrystalline cerium oxide surfaces with a tilted geometry and the amino group pointing outwards. Annealing the system induces decomposition of the molecule.

Electrochemical sensing of hydrogen peroxide and electrochemiluminescent detection of sarcosine using

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polycrystalline cerium oxide thin film electrodes is reported in section 3.2. Cerium oxide electrodes give a linear electrochemical response at low hydrogen peroxide concentrations. XPS analysis before and after electrochemical cycling indicates that under applied potential the hydrogen peroxide molecules adsorb on the oxide surface interacting with the oxygen vacancies on the grain boundaries near the Ce^{+3} cations. Electrochemiluminescent measurements show that cerium oxide electrodes give a linear response in the a relevant concentration range. Thus the cerium oxide electrode could be used to detect sarcosine in the concentration range used in clinical assays.

The author performed well designed, organized and systematic experiments obtaining high quality scientific data. She analysed the data in great detailed and the interpretation generated new and sound scientific results. Therefore, this thesis demonstrates the ability of Ms. Yuliia Kosto for creative and collaborative scientific work.

Finally, I would like to present some questions that could be framed in the public defence:

1. NEXAFS measurements were carried out in the Materials Science Beamline at Elettra with partial yield Auger detection.This method is sensitive to photoemission features travelling through the regions of the Auger lines and need to be corrected as this unwanted features distort the NEXAFS spectra making the analysis and interpretation of the data very difficult. How did the author corrected the NEXAFS spectra to account for the photoemission features travelling through the regions of the Auger lines?

2. In her work the author deposited molecules by vacuum evaporation and by exposing the cerium oxide thin films to liquid solutions of the molecules of interest. These surfaces are very reactive and could adsorb not only the target molecules present in solution but also the solvent and any unwanted species also present in the solutions. Did the author quantify the level of impurities present in the solutions employed? What is the coverage of unwanted species? Did they perform blank experiments where the surfaces are exposed to blank solutions?

3. Molecules could deposit from solution as aggregates, and solvent molecules or other species present in solution could co-deposit having an impact on molecular adsorption. How uniform are the layers prepared by exposing the cerium oxide thin films to solutions? Do molecules form islands or surface clusters?

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