

Review Report on PhD Thesis

Faculty: **Central European Institute of Technology
Brno University of Technology in Brno**

Academic year: **2019/2020**

Student: **Milena Setka M.Sc.**

Doctoral study program: **Advanced Materials and Nanosciences**

Field of study: **Advanced nanotechnologies and microtechnologies**

Supervisor: **Assoc. Prof. Ing. Jana Drbohlavova, Ph.D.**

Reviewer: **Assoc. Prof. RNDr. Juraj Dian, CSc.**

PhD thesis title: **Nanoscaled polypyrrole for sensing gaseous analytes and volatile organic compounds**

Topicality of doctoral thesis:

The submitted doctoral thesis addresses the area of sensing of chemical species in the gas phase. The topic is highly interdisciplinary and with promising applications in health diagnostics, environmental monitoring, and food quality testing. The need for chemical sensors and new sensing techniques will grow in the nowadays world and the submitted thesis represents an important contribution to this field of applied research.

Meeting the goals set:

The goal of the submitted thesis was to develop gas sensors based on nanostructured polypyrrole materials. The doctoral student had to synthesize polypyrrole structures with various nanoscaled morphology and subsequent surface modification with noble metals, to characterize the chemical composition and morphology of prepared systems and to measure sensor responses to selected analytes. All these goals were successfully achieved what is also documented both in the presented thesis and the seven published papers in journals with high impact factors (mainly Q1 or Q2 rank) as well as three conference contributions.

Problem solving and dissertation results:

Problem-solving in the field of chemical sensors is not a straightforward way from the choice of a topic through the necessary synthetic and characterization procedures to the measurements of sensor responses to selected gas analytes, followed by publishing the papers and submitting the thesis.

The main dissertation results are:

1. Synthesis of polypyrrole based nanomaterials, their surface modification with noble metals and subsequent integration into chemoresistive and Love mode surface acoustic wave transducers.
2. Characterization of the materials in the as-prepared form as well as during the sensing of gas analytes.
3. Measurements of gas sensor responses to ammonia, acetone, ethylene, and toluene and the determination of the sensor parameters and testing the sensor response in the presence of selected interferents.

Thanks to my personal experience with conductive polymers I can perceive that there were many difficulties on the road to the submission of the dissertation. I would like to appreciate the preparation of several types of polypyrrole nanostructures, the use of more than one detection technique for sensor response measurements, the effort to explain sensor response mechanism, and the ability of the doctoral student to publish in high impact journals.

Importance for practice or development of the discipline:

The presented results belong to the field of applied research with very high importance both for the practice and development of the discipline. I would like to stress that research of the chemical sensors comprises areas of material research, chemistry, and physics together with characterization techniques and chemometrics. The results obtained in the dissertation for the detection of selected gases are important for the fabrication of the new types and/or improvement of the current gas sensors in practice.

Formal adjustment of the thesis and language level:

The formal adjustment and the language level of the thesis are on a very high level.

There is – of course – a space for improvement as the larger the presented text the higher the probability of errors. The reviewer chose three formal comments concerning thesis presentation and three comments that may indicate potential problems in the future with reviewers both from the physical and chemical community.

1. Formal

- Continuous page numbering does not include published papers and appendices so the referencing to specific topics is made by both number of the specific page in the thesis and the page number in the pdf file.

- References to the literature could be in some instances more complete and referring sources commonly accessible. In the paper published in *Sensors* **2020**, 20, 1432 (p.8/11 /page 96, last line) there is a reference 32 to a book where humidity filters are mentioned. I prefer either to specify the chapter in the book (which one of the 17 chapters?) or to choose a source more available to a reader. Humidity filter is a very important topic in gas sensing and, as I was not able to follow the reference, it is worth a better explanation (see below in Questions).
- Figure 1 in Appendix A (page 1/page 140) can generate confusion to a prospective reader. It probably means that there is no sensor response to 80 ppm of ethanol, but with the units in Ω (Ohm) on the y-axis, one would expect at least some noise in the sensor response. In Figure 3 (page 2/page 141) there is probably a Copy/Paste confusion in the figure caption – there should be Au/PPy instead of Ag/PPy.

2. Physical and chemical terminology

- In the paper *“Cadmium telluride/polypyrrole nanocomposite based Love wave sensors highly sensitive to acetone at room temperature”* (page 4/page 105) the sensor response was defined as the “divergence” in the resonant frequency (...). The divergence has different meanings in mathematics and theoretical physics – here I expect that the sensor response is the “shift” in the corresponding resonant frequencies.
- Sigma bond should be denoted with the corresponding Greek letter σ and not δ (page 6). δ bonds also exist and are formed by an appropriate overlap of two d orbitals.
- Arsenate vs. arsenide (page. 13). Ending –ate indicates the oxoanion (AsO_4^{3-}), for the binary compounds ending –ide is used. Gallium arsenide is the correct name for the binary compound GaAs.

Whether the dissertation meets the conditions specified in § 47 paragraph 4 of the Act below:

(4) The study is duly completed by a state doctoral examination and the defense of a dissertation, which proves the ability and readiness for independent activity in research or development or for independent theoretical and creative artistic activity. The dissertation must include original and published results or results accepted for publication.)

The dissertation meets the conditions specified in § 47 paragraph 4. The doctoral student proved her ability and readiness for independent activity in research and development of advanced sensor systems for gas chemical species.

Questions and comments:

Comments:

1. Sensor terminology:

a/ sensitivity – the definition presented in the thesis (page 9) is rather vague and the presented unit ppm or ppb does not correspond to the standard definition (as well as to the results presented in the Tab. 7.2 on page 122).

b/ selectivity – total (full, complete) selectivity is usually called specificity.

2. The relationship between polarity and dipole moment is neither simple nor straightforward. One example: in the homological set of linear alcohols the polarity decreases with the length of the carbon chain but the behavior of dipole moment in this set is non-monotonic. For quantitative analyses in chemistry, polarity is most frequently expressed with parameters like Snyder polarity index or distribution coefficient n-octanol/water.

Questions:

1. Humidity filters (p.8/11, Sensors **2020**, 20, 1432/ page 96) would be very useful in preventing the water interferences in real-world applications and improvement. Have you checked any type of humidity filter? What level of water concentration could be achieved by such a filter? What effect do you expect the humidity filter will have on studied analytes?

2. In preparation of L-SAW sensors, volumetric ratios of CdTe QDs and PPy NPs or Ag NPs and PPy NPs are presented. These values (1:10 and 1:2) represent a simple way for the presentation of experimental results but it is difficult to imagine what is the molar ratio of CdTe and PPy or Ag and PPy nanoparticles. What are the molar ratios of the corresponding types of nanoparticles in the prepared mixtures?

Conclusion:

The submitted thesis is a result of a long time systematic effort in preparation and characterization of gas sensor systems based on the measurement of conductivity and L-SAW responses to selected gas analytes. Obtained results were published in five journal papers with impact factors in Q1 or Q2 range. The thesis results are important guides for the fabrication of nanostructured polypyrrole-based sensors for the detection of gas analytes like ammonia, acetone, ethylene and toluene in real applications.

In my opinion, the reviewed thesis fulfill all requirements posed on theses aimed for obtaining a PhD degree. This thesis is ready to be defended orally, in front of the respective committee.

In ...Prague....., date...30.6.2020.....

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Assoc. Prof. RNDr. Juraj Dian, CSc.