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XXXVI Cycle

Molecular quantum dots as single-molecule sensors

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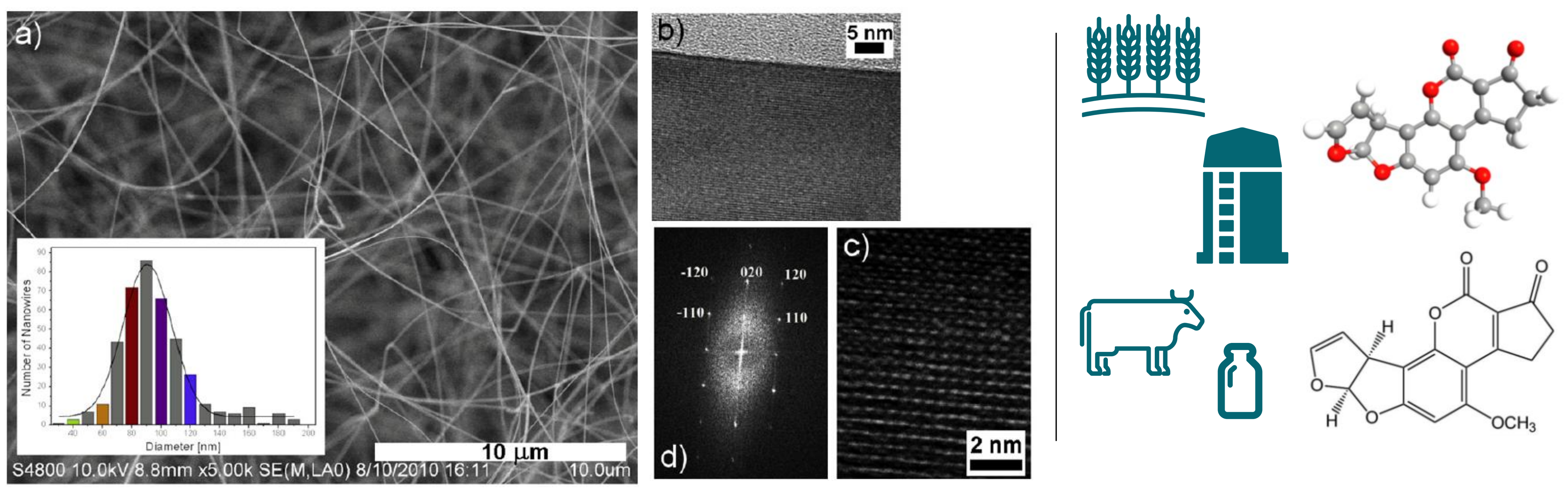
Research context and motivation

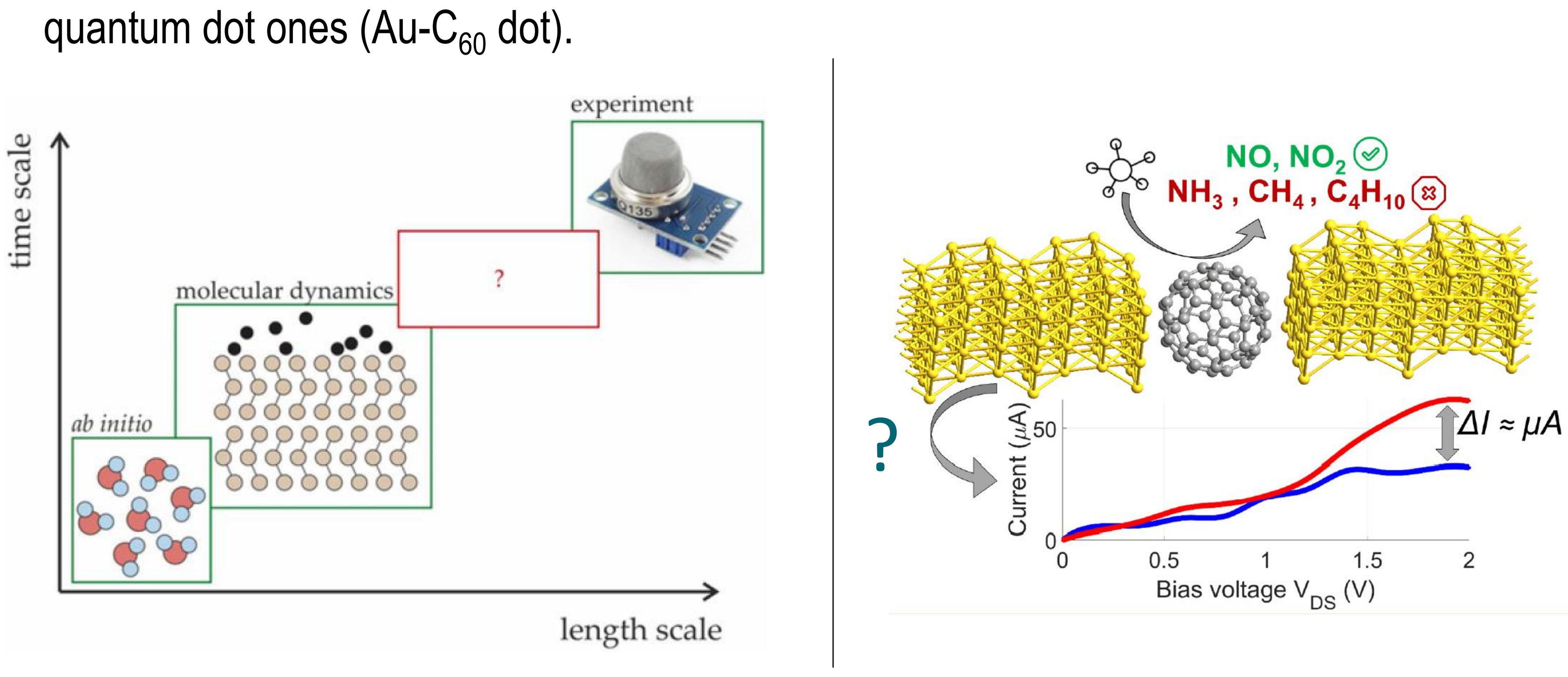
- Gas sensing is an urgent global demand, since gas pollutants are a cause of climate change and a risk to human health by provoking severe diseases.
- The current state-of-the-art gas measurement trend is toward miniaturized nanostructured metal oxides (MOX) chemiresistive sensors -e.g. nanowires- thanks to their high sensitivity, fast response/recovery time, direct electronic interface and low fabrication cost.



- Toxicants detection is as well important and topical, especially in the mass distribution food chain. Aflatoxins can contaminate food in the field and post-harvesting storage/manufacturing and cause liver/kidney diseases, chronic infections, and cancer.
- At the same time, single-entity and single-molecule detection have been recently achieved as the ultimate detection limit. Such sensors are promising because of their intrinsic high sensitivity, potentially high selectivity, and calibration-free features.

Addressed research questions/problems

- MOX (SnO_2) nanowire sensors are investigated to fill the literature gap present between the sensing principle mechanism (*ab initio* simulations and predictions already explain this aspect at a single-molecule level), and macroscopic experimental evidence at sensor device level. A simulation toolchain is developed for this purpose to start from surface kinetics information and predict the full sensor behavior.
- In addition, the aforementioned analysis is useful to compare the literature state-of-the-art gas sensors (nanostructured/nanoscale MOX sensors) with the addressed molecular quantum dot ones (Au-C_{60} dot).



- The target-sensor intermolecular interactions are proved to be effective in provoking current variations of the order of microampere in molecular quantum dots. Nevertheless, the mechanisms causing the current modulation in molecular quantum dots are not fully understood. Therefore, a methodical study of the transport modulation mechanism is carried out through device-level analyses and simulations.
- The origin of the peculiar voltage-dependent is investigated as well.
- The sensing performance under different realistic scenarios is investigated.
- Transmission mechanisms and modulation is addressed. Analogies and differences are present w.r.t. MOX nanowire sensors.

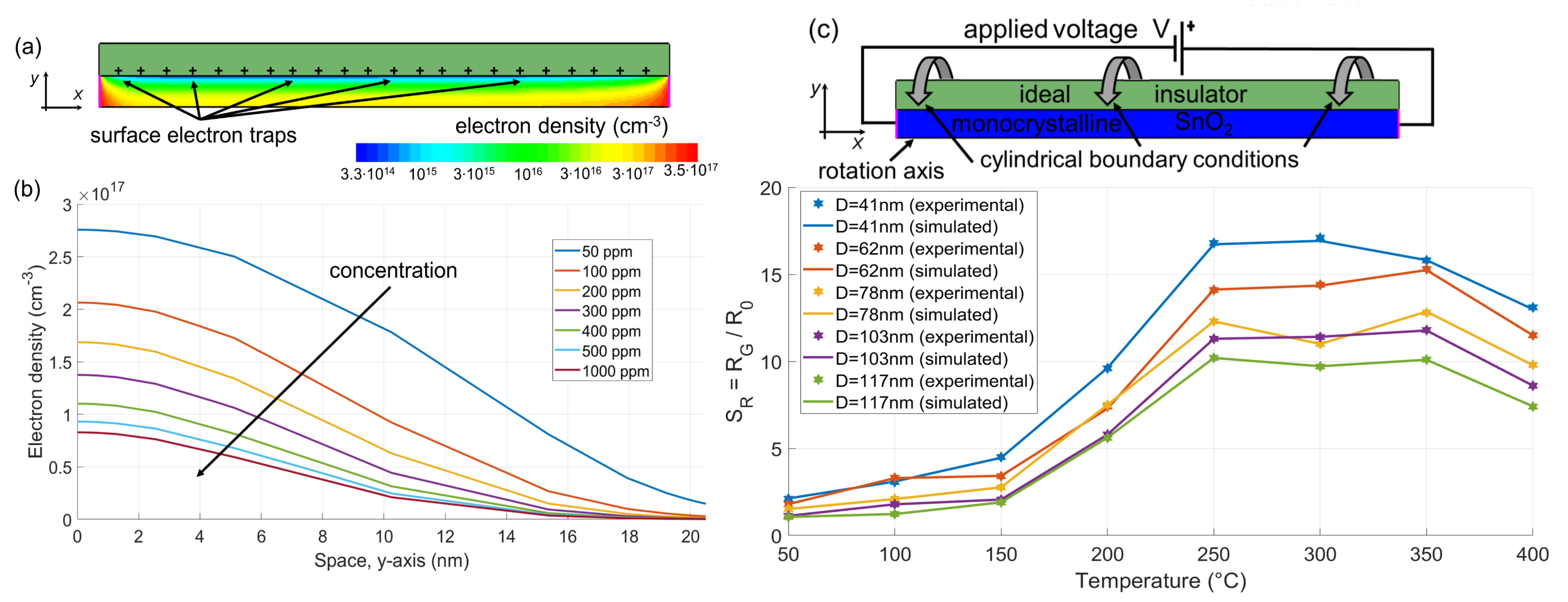
Adopted methodologies

- Theoretical investigation and study with *ab initio* simulations. Software and methods: (i) MOX nanowire simulations in Sentaurus TCAD with a customized MATLAB script to link the surface kinetics to induced surface space charge; (ii) molecular quantum dot simulations in QuantumATK with customized MATLAB codes to perform post-processing and figures of merit extraction.
- Novel methodologies were validated through comparison with *ab initio* and literature data (for molecular quantum dots) and with experimental data (for MOX sensors).

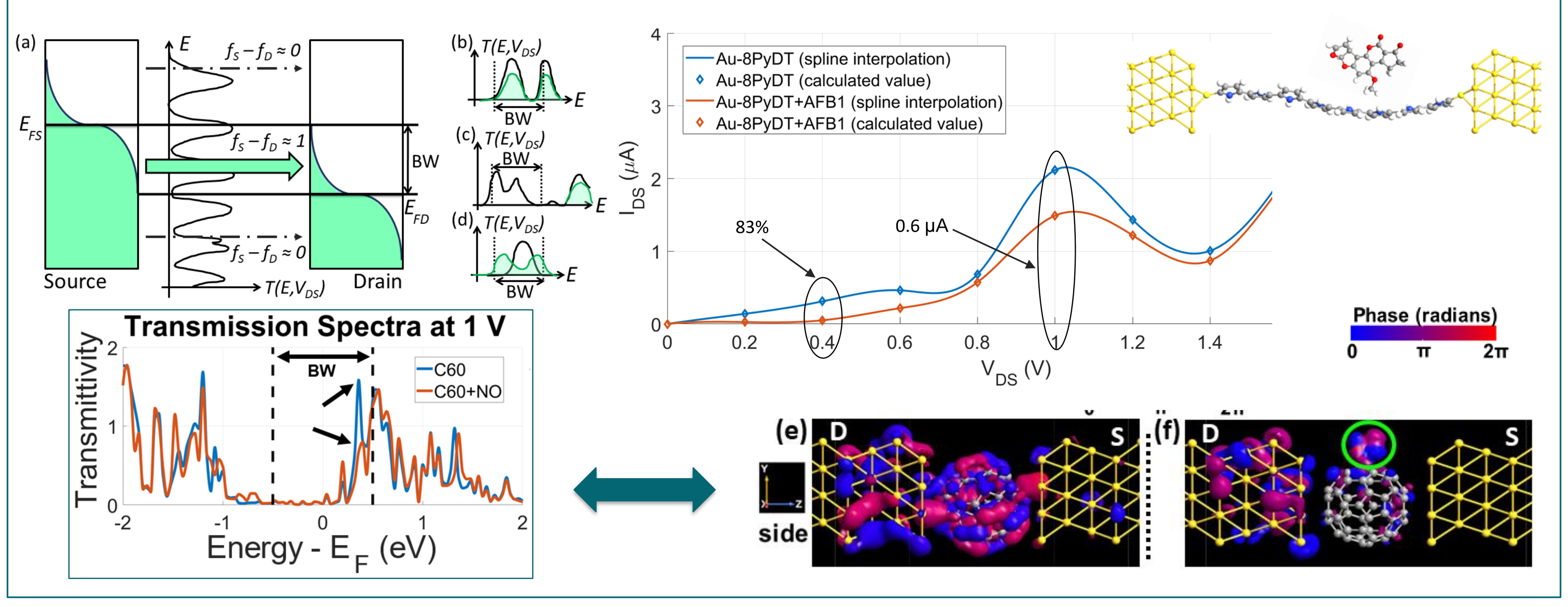
Sentaurus TCAD SYNOPSYS · MATLAB · ORCA · SYNOPSYS QUANTUMATK

Novel contributions

- Establishment of a novel methodology of analysis for the theoretical prediction and understanding of the MOX nanowire-based gas sensors, with a good match with experimental data.



- Creation of methodological analysis tools and figures of merit for the single-molecule quantum dot-based gas and chemical sensors.
- Clarification of the origin of the voltage-dependent response in molecular quantum dot-based sensors.
- Clarification of the physical mechanisms producing current variations in both gas and chemical sensors based on molecular technologies.
- Comparison between the different types of sensors studied (useful to understand if already known optimization strategies are applicable in the case of molecular quantum dots).



Future work

- Extend the MOX nanowire modeling to fabrication process and variability simulations and to polycrystalline MOX materials; experiments in collaborations with FBK institute.
- Understanding of the sensor-target properties influencing the sensitivity and selectivity of molecular quantum dot sensors, and compact modeling to highlight the most important parameters for device engineering.
- Experimental evidence of molecular quantum dot sensors in collaboration with Silesian Institute of Technology (Poland) and ASCENT+ (EU project), with Koral Technologies Srl.

Silesian University of Technology · FONDAZIONE BRUNO KESSLER · ascent+ European Nanoelectronics Access · KORAL TECHNOLOGIES

Published works

- Guarino, R., Mo, F., Ardesi, Y., Gaiardo, A., Tonezzer, M., Guarino, S., Piccinini, G., "*Modelling electronic transport in monocrystalline metal oxide gas sensors: from the surface kinetics to the experimental response*", Sensors and Actuators B: Chemical, 2022,132646, ISSN 0925-4005, https://doi.org/10.1016/j.snb.2022.132646
- F. Mo, Y. Ardesi, M. Ruo Roch, M. Graziano and G. Piccinini, *"Investigation of Amperometric Sensing Mechanism in Gold-C_{60}-Gold Molecular Dot"*, in IEEE Sensors Journal, 2022, doi: 10.1109/JSEN.2022.3203513
- F. Mo, C. E. Spano, Y. Ardesi, M. Ruo Roch, G. Piccinini, and M. Graziano, *"Single-molecule Aflatoxin B1 Sensing via Pyrrole-based Molecular Quantum Dot"*, Proceedings of the 2022 22nd IEEE International Conference on Nanotechnology. IEEE-NANO 2022, 2022, 4th-8th July, Palma de Mallorca (Spain).
- C. E. Spano, F. Mo, Y. Ardesi, M. Ruo Roch, G. Piccinini, and M. Graziano, *"Electronic Transport Study of Bistable Cr@C_{28} Single-Molecule Device for High-Density Data Storage Applications"*, Proceedings of the 8th World Congress on New Technologies (NewTech'22), Prague, Czech Republic– August 03-05, 2022, Paper No. ICNFA 138, DOI: 10.11159/icnf22.138
- F. Mo, C. Spano, Y. Ardesi, G. Piccinini and M. Graziano, *"Beyond-CMOS Artificial Neuron: A Simulation- Based Exploration of the Molecular-FET"*, in IEEE Transactions on Nanotechnology, vol. 20, pp. 903-911, 2021, doi: 10.1109/TNANO.2021.3133728

List of attended classes

- 01QTXRV – BIO/CMOS interfaces and co-design (31/8/2021, 3 CFU)
- 01TCPRV – Nano and molecular electronics (15/9/2021, 8 CFU)
- 01SHORV – Nano & Quantum Computing (16/12/2021, 8 CFU)
- 01NBTKG – Introduction to Computational Biology (12/9/2022, 6 CFU)