Insights into Acetone Sensing by SnO_2-Porphyrin Nanocomposite Chemosensors

E. Pargoletti,[1,2] F. Tessore,[1,2] M.I. Trioni,[3] G. Di Carlo,[1,2] R. Soave[3] and G. Cappelletti[1,2]

[1] *Dipartimento di Chimica, Università degli Studi di Milano, via Golgi 19, 20133, Milano, Italy (eleonora.pargoletti@unimi.it)*
[2] *Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM), Via Giusti 9, 50121, Firenze, Italy*
[3] *National Research Council of Italy, Institute of Chemical Sciences and Technologies "Giulio Natta", Via Golgi 19, 20133 Milano, Italy*

Plethora of gas sensing systems for environmental monitoring, chemical processes, food spoilage and non-invasive medical diagnostics have been developed so far [1,2,3].
Recently, carbonaceous-based gas sensors (such as graphene, reduced graphene oxide or CNTs-based systems) have attracted huge attention thanks to their unique properties giving rise to numerous nanocomposite sensing materials [3,4,5]. However, they still suffer from several problems concerning for instance the low sensitivity, which could be overcome by coupling them with metal oxides nanoparticles (MOS), and the scarce selectivity, especially in relatively high humidity environments as the human breath. Besides, porphyrin-based macrocycles can play a dual role in gas sensing thanks to both their high chemical versatility and good electrical conductivity, especially when combined to MOS [6]. As such, boosted performances, in terms of tuned selectivity and low water interference, might be obtained.
Therefore, the present work is aimed at evaluating and comparing the sensing at mild temperatures (around or below 120 °C, also exploiting LED light) of SnO_2 matrix coupled with different porphyrins (Figure 1) towards the sensing of acetone molecules, *i.e.* the breath biomarker of type 1 diabetes. Specifically, zinc tetraphenylporphyrin (ZnTPP) and its perfluorinated derivatives were chosen [6]. Interestingly, the ZnTPP does not seem to give any significant response upon exposure to the analyte, whereas perfluorinated derivatives showed a boost of the signal with respect to pristine SnO_2. Afterwards, the effect SnO_2/porphyrins weight ratio was explored, namely 4:1, 32:1 and 64:1. In all cases, 32:1 gives the optimal performances also resulting in a detection limit of 200 ppb.

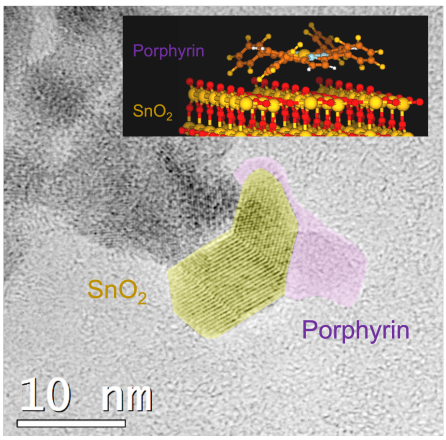

Figure 1. HRTEM image of SnO_2/porphyrin nanocomposite. Inset: DFT simulation of their interaction.

In addition, aiming at unravelling the sensing mechanism, theoretical DFT simulations were carried out. From preliminary results, we may infer that the sensing behavior of SnO_2/porphyrin composites is mainly based on a balance between the number of accessible MOS states in the conduction band (CB) and the electron transfer from the HOMO porphyrin to the CB of tin dioxide. In particular, when tin dioxide is coupled to a system that has a high tendency to donate electrons, *i.e.* ZnTPP, a saturation of the accessible states occurs, so there is no room for electrons coming from the interaction with acetone molecules, thus resulting in the signal quenching. On the contrary, when tin dioxide is coupled to perfluorinated porphyrins, which are less prone to donate electrons due to the fluorine presence, a lower amount of carriers is injected and acetone is more liable to interact with the MOS surface releasing electrons back to it and, eventually, giving rise to an observable signal.
Hence, we believe that these findings can provide guidelines to engineer miniaturized chemoresistive sensors able to selectively detect VOCs for the early diagnostics.

References

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