

Exploring the influence of Zn(II) porphyrins on the electronic properties of SnO₂ chemiresistor toward acetone detection

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Plethora of gas sensing systems for environmental monitoring, food spoilage and non-invasive medical diagnostics have been developed so far [1,2].

Recently, carbonaceous-based gas sensors have attracted huge attention thanks to their unique properties giving rise to numerous nanocomposite sensing materials. However, they still suffer from several problems concerning for instance the low sensitivity, which could be overcome by their coupling with metal oxides (MOS), and the scarce selectivity, especially in relatively high humidity environments as the human breath [3,4]. Besides, porphyrin-based

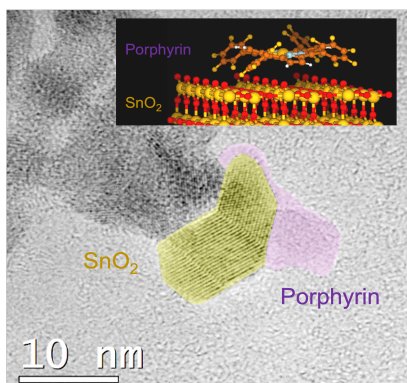


Figure 1. HRTEM image of SnO₂/porphyrin nanocomposite. Inset: DFT simulation of their interaction.

macrocycles can play a dual role in gas sensing thanks to both their high chemical versatility and good electrical conductivity, particularly when combined to MOS [5].

The present work is aimed at evaluating and comparing the sensing at mild temperatures (120 °C) of SnO₂ coupled with different porphyrins, toward the sensing of acetone molecules *i.e.* the breath biomarker of diabetes type 1. Specifically, zinc tetraphenylporphyrin (ZnTPP) and its perfluorinated derivatives were chosen [5]. Interestingly, the ZnTPP does not seem to give any significant response upon exposure to the analyte, whereas perfluorinated derivatives showed a boosted signal with respect to pristine SnO₂. In addition, the effect SnO₂/porphyrins weight ratio was explored (4:1, 32:1, 64:1). In all cases, 32:1 gave optimal performances also resulting in a detection limit of 200 ppb.

Hence, aiming at unravelling the sensing mechanism, DFT calculations were performed. From preliminary results, we may infer that the sensing behavior of these nanocomposites is mainly based on a balance between the number of accessible MOS states in the conduction band and the electron transfer from the porphyrin's HOMO to the CB of SnO₂. In particular, when SnO₂ is coupled to a system that has a high tendency to donate electrons (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. Conversely, when SnO₂ 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.

Therefore, we believe that these findings can provide useful guidelines to achieve a boosted light-free gaseous sensing.

References

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