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The Interplay between Zn(II) Porphyrins and SnO_2 in Boosting the Sensing of Gaseous Acetone

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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 sensors have attracted huge attention thanks to their unique properties giving rise to various nanocomposite 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[1,2]. 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[3].

The present work is aimed at evaluating and comparing the sensing at mild temperatures (120 °C) of SnO_2 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[3]. 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 SnO_2. In addition, the effect SnO_2/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 unveiling the sensing mechanism, DFT calculations were performed. From preliminary results, we may infer that the sensing behavior of theses 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 SnO_2. When SnO_2 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, resulting in the signal quenching. Conversely, when SnO_2 is coupled to perfluorinated porphyrins, that are less prone to donate electrons due to the fluorine presence, a lower number 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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