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Ultra-High Selective Gas Sensors: novel approaches and future developments

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Abstract

Purely inorganic gas sensors are generally facing the problem of a low selectivity. Systematically overcoming this problem would put sensor technology on a whole new level of performance. Organic–inorganic hybrid gas sensors are potentially offering outstanding performance in terms of selectivity and sensitivity towards single gas species. The enormous variety of organic functionalities enables novel flexibility of active sensor surfaces compared to commonly used pure inorganic materials, but on the other hand the hybrid combination of different materials goes along with a substantial increase in system complexity. Even today a sensor design with predictable selectivity and sensitivity is not yet possible. In this work, a strategy for the development of highly selective gas sensors is proposed and demonstrated. As an example, an ultra-selective NO_2 sensor is realized based on self-assembled monolayer (SAM)-modified semiconductor nanowires (NWs). The crucial chemical and electronic parameters for an effective interaction between the sensor and different gas species are identified using density functional theory simulations. The theoretical findings are consistent with the experimentally observed extraordinary selectivity and sensitivity of the amine-terminated SnO_2 NW towards NO_2. The energetic position of the SAM–gas frontier orbitals with respect to the NW Fermi level is the key to ensure or impede an efficient charge transfer between the NW and the gas. As this condition strongly depends on the gas species and the sensor system, these insights into the charge transfer mechanisms can have a substantial impact on the development of highly selective hybrid gas sensors.

1. Introduction

The modern anthropogenic environmental hazards, like toxic gases, are implicated in a range of impacts on human health. The selective detection of a certain predefined gas species is the most critical requirement in different fields like pollution and food control, health care, security or industrial process control. However, predictive strategies towards the development of highly selective nanostructured gas sensors are still missing [1].

Organo-functionalized low dimensional materials could already show improved characteristics [2] in this field compared to commonly used purely inorganic materials or heterostructures that usually suffer from unspecific surface interactions with the target gases. Here, we present a sensor system composed of semiconductor nanowire (NW) surfaces with defined organic self-assembled monolayers (SAMs) in order to accomplish exclusive chemical and electronic conditions for the selective detection of a single gas species. We demonstrate that SnO_2 NWs modified with amine terminated SAMs show both extraordinary selectivity and sensitivity towards NO_2 at room temperature. This system can not only serve as a novel efficient and selective NO_2 sensor, but also as a model system for the theoretical reconstruction of crucial sensor-target interactions. Our simulations reveal that an energy level alignment of the SAM-gas system with the Fermi level of the SAM–NW system is the key to understand and achieve high detection selectivity and are consistent with our experimentally observed results. The here reported results show a convincing potential for the development of theoretically designed selective gas sensors, with flexible organic surface design and predictable response [3].

3. Results and discussion

To develop a strategy for coherent experimental and theoretical gas sensor design, an optimal organic functionalization of SnO_2 NWs for selective NO_2 detection was first evaluated experimentally. The identified system then served as starting point to build up a theoretical NW–SAM–gas model and define critical parameters for selective sensing interactions. Amines, due to their electron donating character, were chosen as functional units to achieve strong surface–gas interactions with the electron affine NO_2 target. Amine SAMs showed a very high sensitivity and selectivity towards a low NO_2 concentration (400 ppb; Figure 2), whereas only small or mostly no response was observed for higher concentrations of the other gases (SO_2, NO, NH_3, ethanol, CO, and CO_2; concentrations between 2 ppm and 5%). Among all amines, the en-APTAS 1 functionalization with a primary and secondary group uni-

fied the best performance in both, sensitivity and selectivity, towards NO_2.

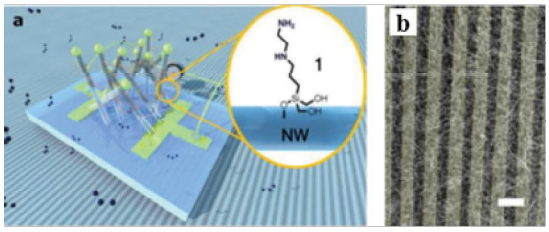

Fig. 1 a) Schematic illustration of the selective NO_2 sensor. b) SEM image of the *N*-[3-(Trimethoxysilyl) propyl]ethylenediamine (en-APTAS 1) modified SnO_2 NWs.

With the introduction of 400 ppb NO_2, the resistance instantly increased to give a sensitivity of 2100%, whereas the other gases did not show any response (SO_2, CO, and CO_2) or very low values (NH_3, NO, ethanol) (Figures 2 a,b). Particular interest was the low and negative sensitivity value towards 2 ppm NO gas (S = −6%). Cross sensitivity of NO_2 and NO is up to date a major issue in the analysis of NO x mixtures produced in various combustion processes. The identification of a single nitrogen oxide species, here NO_2, is featured by our system in a very simple and cost effective configuration.

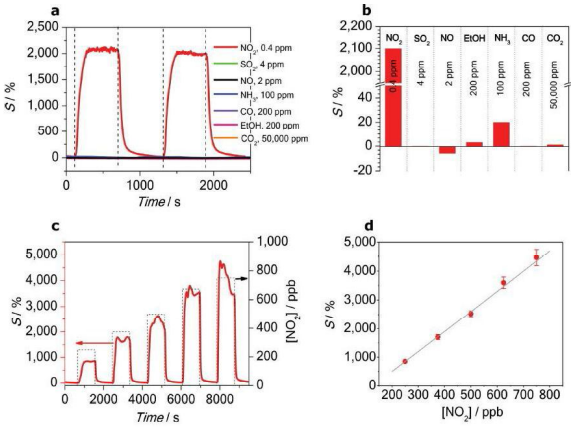

Fig. 2 The en-APTAS **1** functionalized SnO_2 NW sensor measured under solar illumination. a) Pulses of 0.4 ppm NO_2, SO_2 (4 ppm), NO (2 ppm), NH_3 (100 ppm), ethanol (200 ppm), CO (200 ppm) and CO_2 (50,000 ppm). b) Summary of sensitivities towards the tested gases. c) Sensing response vs. different NO_2 concentrations ranging from 250 to 750 ppb in synthetic air. d) Linear behavior of the sensor response with different NO_2 concentrations.

The theoretical density functional theory (DFT) modeling was used to explain the ultra-high selectivity of the sensor; it was concluded that the positions of the gas/SAM frontier molecular orbitals with respect to the Fermi level of SAM/modified SnO_2 NWs was the key factor for the observed selectivity. The adsorption of gas molecules at the SAM/NW system leads to the formation of additional states (mainly formed by the LUMO or HOMO of the isolated gas molecules) directly at the NW/SAM Fermi level (see figure 3a, b). Depending on the positions of the LUMO or HOMO of the gas/SAM system with respect to the Fermi level of SAM/NW, charge transfer can take place either from NW to the LUMO of gas/SAM (as in case of the NO_2/SAM where the LUMO can take up charge carriers from the NW, i.e. leads to an electron depletion at NW surface) or from the HOMO of gas/SAM to the NW (as in case of NO/SAM system where HOMO becomes partially depopulated by donating electrons to the NW, i.e. leads to a higher electron density at the NW surface).

In case of lack of proper alignment between the NW Fermi level and the HOMO (LUMO) orbitals of gas/SAM, the charge transfer between the gas/SAM and the SAM/NW systems is blocked (as in case of SO_2, i.e. no sensing response)

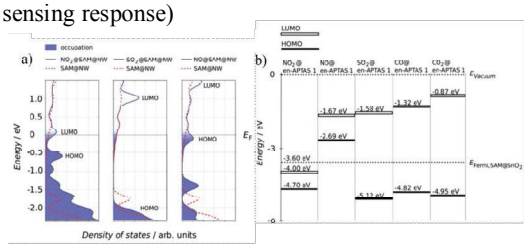

Fig. 3 a) Density of states (DOS) of the SAM/SnO_2 NW with adsorbed NO_2, SO_2, and NO. The Fermi levels of the different systems are set to 0 eV. For comparison the DOS of the SAM modified NW without an adsorbed gas molecule (dashed red line) is shown in each graph. b) Energy diagram of the frontier orbitals of different gases adsorbed on en-APTAS (gas/SAM).

3. Conclusions

In conclusion, we demonstrated that the theoretical prediction of a SAM–NW hybrid sensor system is capable to provide an effective strategy for designing functionalized gas sensors through electronic structure calculations. The selectivity of the hybrid sensor is caused by a suitable alignment of the gas–SAM frontier molecular orbitals with respect to the SAM–NW Fermi-level. The present sensor is capable of detecting very low NO_2 concentrations in the ppb range qualitatively and quantitatively with relatively fast response and recovery time at room temperature. It fulfills the criteria for environmental pollution monitoring systems based on a very simple and cost effective device. The strategy demonstrated here for a NO2 sensor can now systematically be extended to other gas species.

References

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