Highly Selective SAM–Nanowire Hybrid NO₂ Sensor: Insight into Charge Transfer Dynamics and Alignment of Frontier Molecular Orbitals

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Organic–inorganic hybrid gas sensors can offer 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 goes along with an increase of system complexity that usually hinders a predictable sensor design. In this work, an ultra-selective NO₂ 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 SnO₂ NW towards NO₂. 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 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.[12] Organo-functionalized low dimensional materials could already show improved characteristics in this field[2–9] compared to commonly used purely inorganic materials or heterostructures that usually suffer from unspecific surface interactions with the target gases.[10–14] 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 SnO₂ NWs (see Figure S1) modified with amine terminated SAMs show both extraordinary selectivity and sensitivity towards NO₂ at room temperature. This system can not only serve as a novel efficient and selective NO₂ 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 the experimentally observed extraordinary selectivity and sensitivity of the amine-terminated SnO₂ NW towards NO₂ at room temperature. This system can not just serve as a novel efficient and selective NO₂ 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 use of organic functionalities at semiconductor nanostructures in combination with a thorough simulation of the detailed chemical and electronic surface configuration thus shows a convincing potential for the development of theoretically designed selective gas sensors,[15] with flexible organic surface design and predictable response.

Gaseous nitrogen dioxide (NO₂) is one of the most dangerous and wide spread global pollutants, as it can produce ozone, acid rain and respiratory ailments.[16] Moreover it is believed to cause cancer due to its high reactivity with genetic material and organic solvents, forming nitrosamines.[17] NO₂ is produced by various ubiquitous combustion processes such as car engines, power plants and cigarette smoke and affects the human health already in tiny concentrations (ppb level).[18] Usually nitrogen oxide species in pollutant and toxic emissions are specified as NOₓ due to the diversity of possible nitrogen oxidation states.

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and the inability of current cost-effective monitoring systems to discriminate among them. However, it is critical to distinguish NO and NO\textsubscript{2}, which are the major fractions, as they exhibit different properties in terms of toxicity, biological impact and chemical reactivity.\cite{17,19} All this makes this case a paradigmatic and unsolved problem in low-cost gas monitoring technology.

2. Results and Discussion

2.1. Experimental Approach for an Initial Sensor System

To develop a strategy for coherent experimental and theoretical gas sensor design, an optimal organic functionalization of SnO\textsubscript{2} NWs for selective NO\textsubscript{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\textsubscript{2} target (Figure 1a).\cite{19} This process was supposed to affect the carrier concentration profile of the semiconductor NW and thus its resistance to give a measurable sensor response (Figure 1b).\cite{20–24} Different kinds of SAMs with primary, secondary, tertiary and mixed amine terminals were immobilized on the SnO\textsubscript{2} NW surface (Figures 1a, S1, S2).\cite{25} X-ray photoemission spectroscopy (XPS) of immobilized N-[3-(trimethoxysilyl)propyl]ethylenediamine 1 (en-APTAS) showed

![Figure 1. a) Schematic illustration of the selective NO\textsubscript{2} sensor. N-[3-(Trimethoxysilyl)propyl]ethylenediamine (en-APTAS 1) was immobilized on the surface of SnO\textsubscript{2} NWs which were directly grown on an interdigital gold electrode (5 μm spacings). The measured device resistance served as sensor signal. b) Schematic illustration of the NO\textsubscript{2} sensing mechanism by en-APTAS 1 modified NWs. The introduction of NO\textsubscript{2}, a SAM–gas interaction is established during the association process. The consequent electron transfer (Q) from the SAM to NO\textsubscript{2} is transduced to the NW and causes a charge depletion region that is monitored by an increasing sensor resistance. The depletion region is increased by additional NO\textsubscript{2}-SAM interactions until saturation is reached. The cleaving of NO\textsubscript{2}-SAM interactions by incident visible light during the desorption process leads to the initial unbound state and resistive character of the sensor. c) Scanning electron microscope (SEM) image of the en-APTAS 1 modified SnO\textsubscript{2} NWs with an average diameter of 47 ± 8 nm, grown on an interdigital electrode (scale bar, 10 μm). d) XPS N\textsubscript{1s} of the en-APTAS 1 modified SnO\textsubscript{2} NWs showing binding energies of NH/NH\textsubscript{2} groups as well as small amounts of protonated NH\textsubscript{2}+/NH\textsubscript{3} + groups that are shifted to higher binding energies in the N\textsubscript{1s} spectra. e) Binding energies of C\textsubscript{1s} spectra correspond to C–N and C–C/C–H groups of the SAM 1.](image-url)
the typical binding energies of the primary and secondary amine groups (NH/NH$_2$) in the N$_{1s}$ and C$_{1s}$ spectra, as well as a partial protonation (NH$_2^+$/NH$_3^+$) (Figures 1d,e). The successful immobilization of the amine SAM on the SnO$_2$ NW surface was further proved by Fourier-transform IR (FT-IR) analysis (Figure S1). In order to prove the selective detection of the NO$_2$ target, the gas sensing properties of all devices were tested towards small concentrations of NO$_2$ as well as high concentrations of other fossil combustion gases or interfering species (SO$_2$, NO, NH$_3$, ethanol, CO, and CO$_2$) (Figure 2a,b and Figure S2). The test gases were diluted in synthetic air and applied via a mass flow controller system into a sensor chamber with controllable gas flow. A constant current (100 nA) was applied to the sensor and the voltage was measured to monitor the resistive change of the semiconductor NWs. The sensitivity of the sensor is given as $S = \left(\frac{R_{\text{gas}}}{R_{\text{air}}} - 1\right) \times 100$ [%]. To ensure a fast and complete recovery of the sensor signal, the active surface was illuminated through a quartz window by a solar simulator with constant illumination intensity (AM1.5; 85 mW/cm$^2$). All measurements were performed at room temperature.

All amine SAMs showed a very high sensitivity and selectivity towards a low NO$_2$ concentration (400 ppb; Figure 2, Figures S2a-c), 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 (see Supporting Information), the en-APTAS$_1$ functionalization with a primary and secondary group unified the best performance in both, sensitivity and selectivity, towards NO$_2$. 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 2a,b). The low response towards 100 ppm of NH$_3$ (S = 20%) can be attributed to a protonation of the more basic amine functionalities ($pK_a \sim 10.6$) by the more acidic ammonia ($pK_a = 9.2$). Of 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.
response was proportional to the appropriate NO$_2$ concentration (Figure 2c). Average response and recovery times were 110 and 75 s, respectively. A low NO$_2$ concentration of 250 ppb (minimum concentration of the experimental setup) could still be detected with a high sensitivity of 850% which implies that the system is capable of sensing NO$_2$ selectively within the range of critical values for human health (low ppb level).

The same gas sensing experiments performed in dark conditions revealed a slower but even stronger response towards NO$_2$ with a comparable selectivity and an extraordinary sensitivity of 225 000% for NO$_2$ concentrations as low as 250 ppb. In contrast to measurements under solar illumination, the response did not reach a signal saturation and the signal recovery was much slower (Figure 3a), causing a response accumulation when further NO$_2$ pulses were introduced. The incomplete sensor response does not allow a fast and quantitative analysis of the target gas in the dark. Thus, light illumination is obviously needed to achieve a fast and reversible sensor response as well as signal saturation. These findings indicate that the intermediate SAM–NO$_2$ species can be split by incident light, returning to the initial amine and resulting in a dynamic equilibrium of binding- and removal processes (signal saturation). Without illumination, SAM–NO$_2$ binding processes are ongoing without a coincidental NO$_2$ removal and thus the signal accumulates during NO$_2$ pulses without being saturated. In order to figure out the recovery characteristics of the bound SAM–NO$_2$ state, of the incident monochromatic light was swept from 950 to 400 nm after a NO$_2$ pulse. It was found that after an almost constant phase (Figure 3b, phase I), fast recovery processes started for wavelengths from 680 and 480 nm (Figure 3b, phase II and III). Both values are above the absorption edge of SnO$_2$ (<400 nm), proving that the gas detection mechanism does not directly involve SnO$_2$ as active sensing material, since recovery processes of wide band semiconductors need higher energy UV illumination to be activated.$^{[26,27]}$ Additionally, identical pulses of NO$_2$ were applied with different wavelengths of the three recovery phases (I, II, and III), as well as in dark conditions (Figure 3c). The measurements confirmed that an illumination between 450 and 650 nm is needed to remove the NO$_2$ species bound to the SAM molecules effectively to achieve a complete and fast sensor recovery. The weak binding interaction between the SAM and gas molecules allows for an easy signal recovery with lower energy input compared to conventional NW based gas sensors without amine functionalization. Due to the amine termination of the SAM, acid–base interactions with water could possibly have a detrimental influence on the sensor response and recovery characteristics, as well as on lifetime and stability.$^{[25,28,29]}$ However, experiments in humid air show that the sensor response to NO$_2$ is slightly reduced, but stable and fully reversible when the atmosphere is changed back to dry air (Figure S3).

2.2. Theoretical Identification of Crucial Sensor–Gas Interactions

Based on the initial experimental results, a theoretical model of the complete sensor system was developed within density functional theory (DFT) to simulate (i) the chemical bonding of the en-APTAS 1 SAM to the SnO$_2$ surface, the interaction of various gas molecules with the SAM ligand in the (ii) absence...
and (iii) presence of the SnO\textsubscript{2} surface and finally (iv) the charge transfer process between adsorbed gas molecules and the SAM modified SnO\textsubscript{2} NW. In addition to the response of the sensor to NO\textsubscript{2}, the absorption of NO and SO\textsubscript{2} was also theoretically examined in order to obtain further insight into the origin of the very high selectivity. It turns out that adsorption of NO\textsubscript{2} leads to charge transfer from the NW to the gas molecule. In this respect it is quite surprising that SO\textsubscript{2} shows no sensor response (Figure 2a,b), although it has similar oxidative and structural characteristics as NO\textsubscript{2}. NO even induces a charge transfer opposite in sign to the NO\textsubscript{2} signal in agreement with the experimental findings. For both, experiment and theory, the (110) surface representing the lowest energy surface of SnO\textsubscript{2} was used.\textsuperscript{[30]} Doping of SnO\textsubscript{2} with negative charge carriers was realized via incorporation of hydrogen atoms substituting oxygen atoms in the SnO\textsubscript{2} (Figure S9).\textsuperscript{[31]}

DFT modeling revealed that bonding of the SAM to the SnO\textsubscript{2} surface via a single oxygen atom is the energetically favourable case and is used below (Figure S4). In the relaxed structure the SAM is tilted towards the SnO\textsubscript{2} surface. Different initial geometries for the free SAM–NO\textsubscript{2}, SAM–SO\textsubscript{2} and SAM–NO system were used for structural relaxations in order to find the optimal SAM–gas geometries (Figures S3–7). The lowest energy geometries have SAM–gas binding energies \( E_b = -0.44 \text{ eV} \) (NO\textsubscript{2}), 
\(-0.83 \text{ eV} \) (SO\textsubscript{2}) and 
\(-0.48 \text{ eV} \) (NO).

The optimal SAM–gas geometries were then combined with the optimized SAM-NW geometries. For the three-atomic gas molecules (NO\textsubscript{2}, SO\textsubscript{2}), bonding with the SAM at the optimal bonding site is sterically hindered by the influence of the NW surface as well as neighboring SAM ligands. As a consequence, NO\textsubscript{2} relaxes at the geometry with the second highest bonding strength near the secondary amine group with a binding energy of 
\(-0.26 \text{ eV} \) and SO\textsubscript{2} relaxes at a position near the primary amine group at the head of the SAM corresponding to configuration 5 in Figure S6, with a binding energy of 
\(-0.71 \text{ eV} \). NO relaxes at the optimal bonding geometry also in presence of the NW surface (\( E_b = -0.24 \text{ eV} \)). The charge transfer within the NW-SAM-gas system upon adsorption of the gas molecules was determined as
\[
\Delta \rho(z) = \rho_{\text{g-SAM–SnO}_2}(z) - \rho_{\text{SAM–SnO}_2}(z) - \rho(z), \quad g = \text{NO}_2, \text{SO}_2, \text{NO} \tag{1}
\]

where \( \rho_{\text{g-SAM–SnO}_2} \) is the electron density of the relaxed SAM-modified NW in the presence of the gas molecule \( g \) averaged over the SnO\textsubscript{2} (110) plane, \( \rho_{\text{SAM–SnO}_2} \) and \( \rho(z) \) are the averaged electron densities of the isolated SAM-NW system and the gas molecule with geometries from the relaxed NW-gas system. The coordinate along the (110)-direction is denoted by \( z \). As can be seen from Figure 4a, the adsorption of NO\textsubscript{2} at the SAM bound to the SnO\textsubscript{2} surface leads to charge transfer from the NW via the SAM to the NO\textsubscript{2} molecule. A charge depletion zone extending into the NW backbone is observed. Charge transfer is also found after NO adsorption. However, here charge is transferred in the opposite direction, from the NO molecule via the SAM to the NW. On the other hand, the adsorption of SO\textsubscript{2} does not induce any noticeable charge variation in the NW. Merely a localized charge redistribution in the SAM–SO\textsubscript{2} part of the system is observed. Hence, our simulations suggest that while NO\textsubscript{2} adsorption leads to a decrease and NO adsorption to an increase of negative charge carriers in the NW, SO\textsubscript{2} has no impact, although it shows the strongest bonding to the SAM–NW system. Since SnO\textsubscript{2} is an n-type semiconductor, the simulations are consistent with the experimental observation of increasing and decreasing resistance in the presence of NO\textsubscript{2} and NO, respectively, while SO\textsubscript{2} does not lead to any considerable change (Figure 2a,b).

Note that while the direction of charge transfer corresponds to the sensing measurement, the magnitude of the sensor signal being proportional to the device resistance cannot be obtained directly from DFT calculations.

Analyzing the density of states (DOS) of the SAM–NW system with adsorbed gas molecules, we found that NO\textsubscript{2} and NO adsorption lead to the formation of additional states directly at the NW–SAM Fermi level (Figure 4b). These states can be attributed to the LUMO in the case of NO\textsubscript{2}, and in the case of NO to the HOMO of the corresponding gas–SAM system. Those states are mainly formed by the LUMO and HOMO of the isolated NO\textsubscript{2} and NO gas molecules as can be seen from Figure 4c, where we show the charge densities associated with the aforementioned wavefunctions of the NW–SAM-gas systems. As the DOS from Figure 4b shows, the NO\textsubscript{2}–SAM LUMO becomes partially occupied and thus can take up charge carriers from the NW, contrary to the NO–SAM system for which the HOMO becomes partially depopulated by donating charge to the NW. Finally for SO\textsubscript{2}, none of the frontier molecular orbitals is located at the Fermi level (Figure 4b) such that the occupations of the HOMO and LUMO of the gas–SAM system remain unaffected and no charge transfer is observed in this case.

To get a clear picture, we determined the HOMO and LUMO energy levels of the isolated SAM–gas systems in the absence of the NW and aligned their positions with the energy scale of the SAM-modified SnO\textsubscript{2}. As reference for the alignment procedure the average electrostatic potentials at the cores of the carbon and nitrogen atoms at the backbone of the en-APTAS \( \text{I} \) molecule were used. As shown in Figure 4d, the LUMO of the NO\textsubscript{2}–SAM system lies below the Fermi-level of the SAM-modified SnO\textsubscript{2}. Hence charge transfer from the SnO\textsubscript{2} to the LUMO of the NO\textsubscript{2}–SAM system is energetically favoured until LUMO and Fermi-level are aligned. In contrast, the NO–SAM system has a HOMO higher in energy than the Fermi-level of the SAM-modified SnO\textsubscript{2}. Hence energy is gained by transferring charge from the HOMO of the NO–SAM system to the SnO\textsubscript{2}. Finally, the LUMO of the SO\textsubscript{2}–SAM system lies well above the Fermi-level and the HOMO lies well below the Fermi-level and so charge transfer is absent in agreement with the charge transfer simulations and sensing experiments. This analysis is extended to CO and CO\textsubscript{2} adsorbed on en-APTAS \( \text{I} \). Determining the energies of the corresponding frontier orbitals (Figure 4d), the HOMOs are well below and the LUMOs are well above the SAM–NW Fermi level. Hence, as in the case of SO\textsubscript{2}, charge transfer cannot occur for CO and CO\textsubscript{2}, in agreement with our experimental results. In total, the simulations indicate that the key to explain the selectivity of the SAM modified sensor towards different gas molecules lies in the positions of the gas–SAM frontier molecular orbitals with respect to the Fermi level of SAM-modified SnO\textsubscript{2} NWs. This property guides
the way to the tailoring of SAM–nanowire surfaces towards highly selective gas sensing.

3. Conclusion

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. Our work demonstrates that a systematic organic surface design of semiconductor nanostructures shows great potential in solving the selectivity issue, which is the main obstacle of current gas sensor technologies. On the long term, this knowledge could lead to a strategy with which a tailored and flexible design of highly precise artificial noses is enabled.

4. Experimental Section

Preparation of SnO$_2$-en-APTA S Sensors: The as-prepared SnO$_2$ NWs (average diameter 40–60 nm) grown on Al$_2$O$_3$ substrates with prepatterned interdigital gold electrodes (5 μm spacings) were cleaned in oxygen plasma for 1 min to remove surface contaminations and provide oxygen groups on the surface for the condensation reaction. Subsequently, the sample was immersed in a 1% ethanol solution of...
en-APTAS 1 (ABCR GmbH), which was stirred for 6 h. After removal, the sample was subsequently rinsed with ethanol and dried in a vacuum oven for 1 h at 60 °C.

Gas Sensing Experiments: The SnO$_2$/en-APTAS 1 samples where electrically contacted via wire bonding and placed in a gas chamber with gas-in, -outlet and a quartz window for external illumination. The gas flow was controlled by a flow control system (Goeometrics MGP-2) and the sensor signal was monitored by a SMU (Keithley 2400) that was controlled by self-programmed LabVIEW software (National Instruments Inc.). The sensor was illuminated with simulated sunlight (AM1.5, 85 mW/cm$^2$) through a quartz window. All gas sensing experiments were performed at room temperature.

DFT Simulations: The modified SnO$_2$ was modeled as slab terminated by (110) surfaces and consisting of 11 layers amounting to a thickness of 38.378 Å for the relaxed slab. Since the sensor is exposed to humidity during preparation and operation dissociative adsorption of H$_2$O on the SnO$_2$ surface has been assumed. From the relaxed SnO$_2$ bulk structure the dimensions of the surface unit cell of 6.714 Å $\times$ 6.346 Å were extracted. The considered unit cell is depicted in Figure S4a. For the charge transfer calculations one oxygen atom per unit cell in the center of the SnO$_2$ slab was substituted by hydrogen in order to model n-type doping[13]. Here, we used the PAW method and pseudopotentials[14,35] and an energy cutoff of 400 eV, a Monkhorst-Pack k-point sampling of 3 in the lateral directions, and Gaussian smearing with a width of 0.1 eV. For relaxations a force cutoff of 0.015 eV/Å was used. Dispersion forces were taken into account by using the semi-empirical DFT-D2 method of Grimme[16] as implemented in VASP. Sn atoms have been excluded from the dispersion correction in order to preserve the very good agreement between the PBE+U and the experimental values[17] of the SnO$_2$ lattice constants.

For the density of states (DOS) calculations the same DFT parameters as above were used except of using a Monkhorst-Pack k-point sampling of 9 in the lateral directions. The DOS was obtained by convolution of the DFT-eigenvalues with a Gaussian of width 0.10 eV.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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