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On the mechanism of CNT network NH_3 sensitivity: modeling and experimental study of the density effect

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Abstract. A carbon nanotubes (CNT) network is a promising gas sensing material for "e-nose" development due to the vast methods of cross-sensitivity modification. However, the dominant sensitivity mechanism remains unclear since both the CNTs and junctions between CNTs can be gas-sensitive. In this paper to estimate the contributions of both mechanisms, we simulated CNT networks with varied densities using an equivalent electrical circuit. Density variation alters the junction's and CNT's contribution to the network resistance, and hence the total resistive response. We compared the results with the experimental resistive response of the spray-coated CNT networks toward ammonia (NH_3). A decrease in the network density results in a higher response, which indicates a likely significant role of CNTs junctions in sensitivity of a sparse networks. We also studied the effect of formic acid treatment on CNT networks, which increases both conductivity and sensitivity by removing residual solvent.

Keywords: carbon nanotube, gas sensor, spray-coating, electric circuit simulation

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Механизм чувствительности сеток из УНТ к NH_3: моделирование и экспериментальное исследование влияния плотности

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Аннотация. В работе было проведено моделирование эквивалентной электрической схемы сетки из углеродных нанотрубок (УНТ) для оценки влияния плотности сетки УНТ на вклад различных механизмов резистивного отклика на воздействие аммиака. Методом аэрозольного нанесения были изготовлены газочувствительные сетки УНТ с различной плотностью и измерена их чувствительность. Сравнение данных моделирования и экспериментальных результатов указывает на то, что изменение контактного сопротивления между УНТ, может является одним из механизмов сенсорного отклика в разреженных сетках.

Ключевые слова: углеродная нанотрубка, газовый детектор, аэрозольное нанесение, моделирование электрических схем

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Introduction

Development of “e-nose” technology promotes interest toward gas-sensitive nanomaterials. To efficiently mimic the olfactory system, an array of sensors with varied cross-sensitivity should be fitted on a single substrate. Therefore, key e-nose requirements for sensitive layers are the adjustable sensitivity toward selected gas species, miniaturization and integrability. Carbon nanotubes (CNT) fulfill these requirements and considered as a promising gas-sensing material.

Since the pioneering works in the early 2000s, the CNT’s sensitivity mechanism remains a matter of argument. A large number of studies of single CNT based field-effect transistors assert the existence of both sensitivities of CNT [1] and Schottky barrier between CNT and the electrode [2]. The apparent inconsistency of the known results rises from number of factors that determine the dominance of one of the mechanisms on the overall sensitivity in selected works. For example: presence of defects and functional groups in CNT [3], the work function of the metal that determines the height of the Schottky barrier [4, 5], the measuring temperature [6]. When studying CNT networks, the identification of the dominant mechanism is even more complicated since we should consider the presence of both metallic (m-CNT) and semiconducting CNTs (s-CNT), as well as their junctions which are also gas sensitive [7]. Sensitivity mechanisms can be localized in: 1) contact between CNT and electrode, 2) CNT channel (intra-CNT) and 3) CNT-CNT junction (inter-CNT). Taking into account that the resistance of the junctions dominates in total resistance of the low density CNT networks, especially for short CNTs [8, 9], the role of inter-CNT gas sensitivity can be essential. The dominant effect of CNT junctions in short CNT channels was already demonstrated by Boyd et al. [7] for nonfunctionalized CNTs. Inoue et al. [10] also suggest FIT model-based theory associating adsorption and contacts resistance. However, a deeper understanding of inter- and intra-CNT sensitivity contribution in large area networks of functionalized CNTs is still required since it will allow to focus on increasing the sensitivity of the dominant mechanism or vary cross-selectivity by changing different mechanisms’ contribution.

In this work, we simulated the resistive response of the resistor-based model of CNT networks and experimentally measured the resistive response of the spray-coated network to ammonia exposure. We compared simulation and experimental result to evaluate which sensitivity mechanisms prevails in fabricated gas sensing layers.

Materials and Methods

To fabricate the CNT sensor we used P3-SWCNT (“Carbon Solutions”) dispersion in a mixture of N-Methyl-2-pyrrolidone (NMP) (for HPLS “Acros Organics”) and deionized water (for HPLC, “Component-Reactive”). A multisensory chip with Ti/Au electrodes with a 50 μm gap on Si/SiO_2 substrate was spray-coated with CNT dispersion by a self-designed automated spray-coating system. To achieve uniformity of the CNT network we used ultralow dispersion flow [11]. The density of the network was varied in different segments of the chip by transferring the shadow mask while spray-coating. After deposition, chip was mounted into the PCB holder.

The morphology of obtained CNT networks was studied by atomic force microscope (AFM) Solver-Pro (“NT-MDT”) in tapping mode. The electrical characterization was carried by 2450 SourceMeter (“Keithley Instruments”). To measure CNT response to gas exposure device was preliminarily annealed in dry air by heaters integrated into the chip at 100 °C.

The gas mixture was prepared by evaporating the required volume of ammonia solution to obtain concentration of 50–400 ppm, then pumped through the device chamber with a 200 sccm flow. Chip was recovered in dry air in two steps: at first gas flow was a 2000 sccm to enhance the recovery rate, and in the second step at 200 sccm to avoid the effect of the flow rate on the response. The response was calculated as $S = (R_{gas}-R_{air})/R_{air}\cdot 100\%$, where R_{air} and R_{gas} are the resistances of the segments before and after 15 min exposure, respectively. Resistance was evaluated at 8 segments simultaneously by measuring current at a bias voltage of 5 V, the segments denoted as CNT-1–CNT-8 from the most conductive to the least one. After studying response of the as-prepared CNT network, the substrate was immersed in formic acid (FA) to reduce the residue NMP content. The CNT layers after FA treatment are hereinafter denoted as FA-CNT.

To simulate the CNT network resistive response, we randomly generated a 2-D network of randomly distributed 1-D sticks of two types denoting m- and s-CNT. The average length was 0.8 μm and the standard deviation was 0.4 similar to AFM evaluated values, the m-CNT to s-CNT ratio was 0.33 (Fig. 1, *a*). The resulting network was converted into a SPICE model of an equivalent resistor circuit. We used the following approach for equivalent circuit generation: CNT was divided into segments in intersections with other CNTs and substituted with resistors with values $R_{S,M} = \rho_{S,M}\cdot L$, where L is a segment length, $\rho_M = 6$ kΩ/μm and $\rho_S = 9$ kΩ/μm are resistivity of m-CNT and s-CNT, respectively (Fig. 1, *b*). The ρ_M corresponds to experimental results for non-sorted HNO_3 treated single-walled CNTs [12], while ρ_S is slightly higher which is observed at least for as-synthesized CNTs [13]. Since the minimal resistance of CNT is limited by resistance quantum $1/2G_0$, where $G_0 = 7.7\cdot 10^{-5}$ S is quantum conductance, the resistors with $R_Q = 1/4G_0$ were added to each junction with other CNTs. For model simplification, the junctions were also simulated with resistors, despite the non-linearity of s- and m-CNT heterojunction [14] and junctions of s-CNTs with different chirality or diameter [13]. The values $R_{M-M} = 40$ kΩ, and $R_{S-S} = 60$ kΩ corresponds to acid-treated CNTs [12]. $R_{S-M} = 200$ kΩ a few times higher than R_{S-S} as for non-treated CNTs [13]. We estimated CNT network response using a simulated circuit resistance as R_{air}, and simulated resistance with doubled values of the R_S, R_{S-S}, R_{S-M} or all of them as R_{gas}, representing a gas-induced increase of resistance of CNT junctions or s-CNT body, respectively. The doubling of the resistance corresponds in order of magnitude to CNT-metal heterojunction response to 100 ppm NH_3 exposure [6].

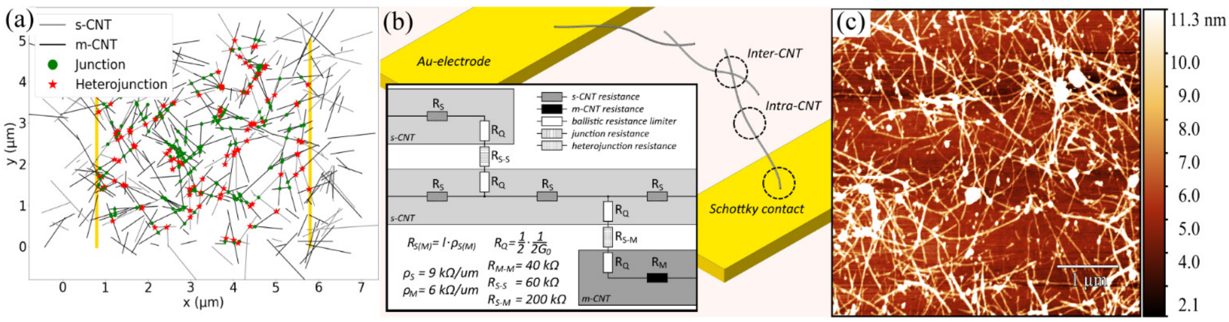

Fig. 1. Randomized CNT network (*a*); Equivalent resistor circuit of CNT and junctions (*b*); AFM image of low-density CNT network (*c*)

Results and discussion

Earlier reported method of CNT spray coating ensured high uniformity of CNT layer according to the AFM results (Fig. 1, *c*). Although, a significant number of CNT bundles was observed along with single CNTs with diameter about 3–6 nm, which were not disrupted by ultra-sonic treatment and were remaining in dispersion. It was not taken into account in the model used and may lead to overestimation of heterojunctions contribution, since the bundles may include CNTs of both types forming ohmic contacts. This effect probably was shown by A. Znidarsic et.al [12], when high-resistance junctions, which we consider to be heterojunctions, were only found for small diameter nanotubes, but not the bundles.

We counted the approximate number of CNTs in the segment with a sparse network and calculated the number in high density segments, as it is proportional to the sprayed volume. The calculated density was varied in a range 7–25 μm^{-2} from CNT-8 to CNT-1, respectively.

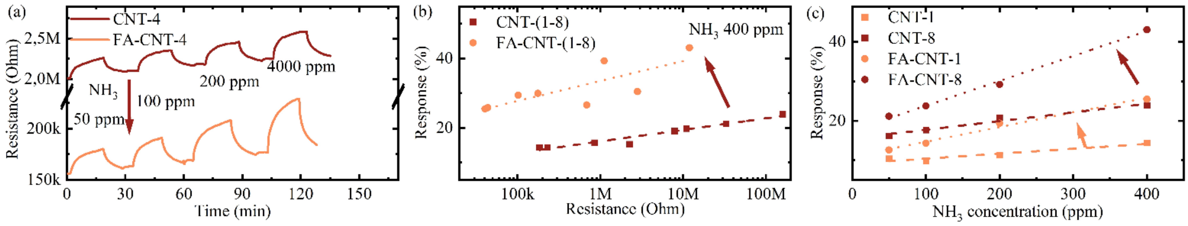

Fig. 2. CNT network response toward NH_3 exposure (*a*); Response dependence on CNT network resistance (*b*) and NH_3 concentration (*c*)

A gas sensing study has revealed a significant room temperature resistive response of CNT to NH_3 (Fig. 2, *a*). The response/recovery dynamics are close to an exponential with a time constant of about 250 s. Despite the airflow during the recovery was high, we doesn't observe a complete recovery in the used intervals, however, extrapolation allows us to expect a complete recovery in longer intervals. The response has a logarithmic dependence on segment resistance (Fig. 2, *b*) and linear on NH_3 concentration (Fig. 2, *c*).

FA treatment resulted in a significant decrease in network resistance. The before/after resistance ratio was 3 for high-density networks, and exceeded 10 for low-density networks. We consider that FA have strong hydrogen bonding with NMP [15] and therefore probably efficiently removes NMP residual thin layer from the interface between CNTs [16]. A decrease in the gap between CNTs, according to the thermal activation carrier hopping mechanism [17], leads to a resistance decrease. Greater resistance drop after FA treatment in sparse networks may correlate with greater contribution of junctions in their resistance. Removal of the solvent also leads to an increase of response up to two times, which correlates with both inter- and intra-CNT mechanisms. Intra-CNT response can be promoted by a decrease of junction' resistance contribution, while junction sensitivity also increases speculatively due to increase in changing barrier height with NH_3 adsorption at contact area.

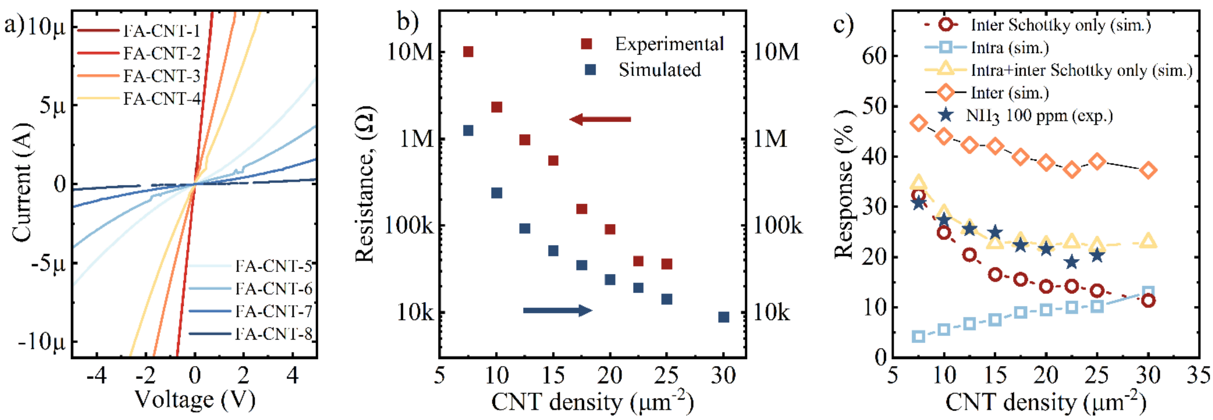

Fig. 3. (*a*) CNT networks current–voltage characteristic (*a*); Resistance dependence on CNT network density (*b*); Simulated and experimental dependence of response on CNT density (*c*)

Despite the non-linear current–voltage characteristic (Fig. 3, *a*), we exclude the influence of CNT metal contact since the same dependences are also observed in large area networks. The calculated resistance is several orders of magnitude less than experimental values (Fig. 3, *b*), probably, due to not taking into account the bending of CNTs or imprecise density approximation, higher contact resistances or influence of m-CNT on s-CNT at contact. However, both the experimental and modelled resistance have alike power dependence on density. Therefore, we plot the dependencies of the response on the density of the network (Fig. 3, *c*).

Experimental resistive response to ammonia exponentially decays with increasing network density. The same pattern is observed in simulated inter-CNT response with only heterojunction sensitivity. It originates from a growing number of heterojunctions participating in conductivity of sparse networks in the absence of bypassing by low-resistance similar-type CNT junctions.

For biosensors this effect has been already demonstrated by Thanihaichelvan et al. [18]. Inter-CNT response with both sensitive heterojunctions and s-CNT junctions also decrease but close to linear. Intra-CNT sensitivity in the opposite increases with the density, since each CNT adds only one parallel conductive channel but a growing number of parallel junctions. This leads to lowering the heterojunctions' role in a total conductivity and higher intra-CNT response. Therefore, junctions play a dominant role in sensitivity of sparse networks in the proposed model. There are just few factors improving intra-CNT sensitivity at sparse density, for example, the violation of m-CNT network percolation leading to higher s-CNT contribution into conductivity, but it is not sufficient at least in the proposed model with the taken inter-CNT and intra-CNT resistances.

For a deeper understanding, it is required to study the sensitivity of networks with different density and with a variable ratio of m- and s-CNT. Ham et al. [19] demonstrated superior sensitivity of a 90% s-CNT network over a 60% s-CNT. An increase in gas sensitivity with enrichment with s-CNT was also demonstrated by Nokano [20]. However, it can be both due to inter- and intra- s-CNT sensitivity, therefore, further study is required.

Conclusion

We have developed an equivalent circuit of carbon nanotube networks and simulated the resistive response to ammonia to evaluate the response dependence on the network density. We simulated the sensitivity of s-CNTs, the junctions of s-CNTs and heterojunctions between s-CNT and m-CNT. We have shown that a decrease in the network density should increase the contribution of the inter-CNT response and reduce the intra-CNT response. The same response dependence on density is observed in the experimental study, which hints at the dominant role of the junction's response.

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