Research Article

Enhanced Ammonia Adsorption on Directly Deposited Nanofibrous Carbon Films

Alexander G. Bannov, Ondřej Jašek, Jan Prášek, Jiří Buršík, and Lenka Zajičková

1Central European Institute of Technology, Masaryk University, Kamenice 5, CZ-62500 Brno, Czech Republic
2Department of Chemistry and Chemical Technology, K. Marx 20, Novosibirsk State Technical University, 630073 Novosibirsk, Russia
3Department of Physical Electronics, Faculty of Science, Masaryk University, Kotlářská 2, CZ-61137 Brno, Czech Republic
4Central European Institute of Technology, Brno University of Technology, Technická 3058/10, CZ-61600 Brno, Czech Republic
5Centre of Sensors, Information and Communication Systems, Faculty of Electrical Engineering and Communication, Technická 3058/10, CZ-61600 Brno, Czech Republic
6Institute of Physics of Materials, Academy of Sciences of the Czech Republic, Žižkova 22, CZ-61662 Brno, Czech Republic

Correspondence should be addressed to Alexander G. Bannov; bannov_a@mail.ru

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The ammonia adsorption on the nanostructured carbon thin film was significantly influenced by the choice of deposition temperature and deposition time of thin film synthesis. The thin films were prepared on Si/SiO2 substrates by chemical vapour deposition in Ar/C2H2 gas mixture using iron catalytic nanoparticles. The analysis of the grown layer by the scanning and transmission electron microscopy showed the transition from long multiwalled nanotubes (MWCNTs) to bamboo-like hollow carbon nanofiber structure with the decrease of the deposition temperature from 700 to 600°C. Further, the material was analyzed by energy-dispersive X-ray spectroscopy and Raman spectroscopy confirmed the transition from graphitic sp2 structure to highly defective structure at lower deposition temperature. The resistance of the prepared layer strongly depends on deposition temperature (T_d) and deposition time (t_d). High resistance layer, 38.6 kΩ, was formed at T_d 600°C and t_d 10 min, while at T_d 700°C and t_d 60 min, the resistance decreased to 860 ohms. Such behaviour is consistent with MWCNTs being responsible for the formation of the conductive network. Such system was studied using chemiresistor ammonia gas sensor configuration. The sensor resistance increased when exposed to ammonia in all the cases, but their response varied considerably. A decrease in deposition time, from 60 to 10 min, and the deposition temperature, from 700 to 600°C, led to the 10-fold increase in the sensor response. The measurements carried out at room temperature showed the higher sensor response than the measurements carried out at 200°C. This behaviour can be explained by the change in adsorption-desorption equilibrium at different temperatures. Analysis of dependence of the sensor response on the ammonia concentration proved that the underlying resistance change mechanism is chemisorption of ammonia molecules on the carbon network corresponding to the Langmuir isotherm.

1. Introduction

A safety and sustainable development require creation of new highly sensitive devices for the detection of toxic and flammable gases along with the control of environmental pollution. Such devices require new materials which extend the number of detectable gases and lower their detection limits. One of the most dangerous gases that have a negative influence on human health and environment is ammonia (NH3). According to US OHSA (Occupational Safety and Health Administration) and CDC (Centers for Disease Control and Prevention) regulations, the long-term exposure limits are 25–35 ppm for
workers. The smell threshold of ammonia ranges from 5 to 15 ppm. The concentrations above 50 ppm induce irritation to the mouth, nose, wheezing, etc. The concentrations from 300 to 500 ppm are dangerous for life. In industry, ammonia can be detected at higher concentrations (from 1000 ppm to 40000 ppm, depending on rooms, facilities, etc.).

Therefore, study of ammonia adsorption on nanostructured surfaces and development of new materials for ammonia gas sensors attracted a lot of attention of scientific community. Single-wall carbon nanotubes (SWCNTs) and multiwall carbon nanotubes (MWCNTs) belong to one of the most promising candidates in the gas sensing field [1–9] because of their ability to change the electrical properties (e.g., resistivity) under gas adsorption. This fact is complemented by the enhanced adsorption of gases by carbon nanomaterials [8]. There are a wide range of gases on which the carbon nanotube- (CNT-) based sensors can be used, such as NH3 [4, 10–16], NO2 [17, 18], CH4 [19, 20], H2 [21], H2S [22–25], CO2 [26], ethanol [25], methanol [25], hydrocarbons [7], and other gases.

Commercially available sensors require a high temperature for their operation. For wider use of such devices, the room temperature operation of ammonia gas sensors is an important requirement and was recently studied by several authors. In [27], the authors created HCl-doped MWCNT/polyaniline composite sensors with good sensing response and high reproducibility. In [28], the authors created SWCNT- (40% metallic and 60% semiconducting) based ammonia sensors using inkjet-printed electrodes which possessed the maximal response of 27.3% for 500 ppm at room temperature. Cui et al. [29] developed the room temperature ammonia sensor based on Ag nanocrystal-functionalized MWCNTs that exhibited enhanced response of 9% and fast response at room temperature with the full recovery within several minutes in air. In [12], the authors created the room temperature sensor based on SWCNT for ammonia sensing with the extremely low detection limit (3 ppb). The enhancement of the response was realized by two techniques: drop casting and sonication.

In this paper, a promising potential of managing the NH3 gas sensor performance by the control of nanofibrous carbon (NFC) chemical vapour deposition (CVD) synthesis conditions is investigated in detail. Up to now, the CNT-based NH3 gas sensors were closely investigated from the performance point of view but the influence of the synthesis conditions of these materials on the sensing properties has not yet been studied. Previous studies were based on the creation of the sensors by the direct deposition of CNTs using only certain conditions [30–33] without detailed investigation of their synthesis role in the formation of sensor response. The influence of NFC deposition parameters (growth temperature and time) on the materials’ properties and NH3 sensing characteristics is determined. The interconnection between the sensor resistance and response has been found.

2. Materials and Methods

2.1. Nanofibrous Carbon Film Preparation. NFC layers were grown by atmospheric pressure chemical vapour deposition using an iron catalyst. Polished single-crystal Si (c-Si) pieces (8 mm × 8 mm) coated by a thermal SiO2 film, 92 nm in thickness, were used as substrates. Nanoparticles (NPs) of iron catalyst were deposited by a microwave (MW) plasma torch from the iron pentacarbonyl, Fe(CO)5, vapours mixed with argon. The experimental set-up is described by Synk et al. [34, 35] in detail. The c-Si/SiO2 substrates were put in a special holder for 4 samples. The flow rate of argon through the central part of the nozzle was 700 sccm. The outer concentric part of the nozzle was used to deliver Fe(CO)5 vapours (0.1 sccm) carried by Ar flow of 28 sccm. The MW torch was ignited with the power of 210 W. The deposition time of the nanoparticles was 15 s. Direct deposition of nanoparticles was used as preferred form of the catalyst because it enabled us to form a sparse network of fibrous carbon. In case of the thin film catalyst, dense structure of the nanofibrous carbon network with low resistance and negligible response was formed. NFC growth was carried out in a quartz tubular furnace. The processes started by heating the furnace from the room temperature to deposition temperature (Td): 600°C, 650°C, and 700°C, under the argon flow of 1400 sccm. The heating speed was 25°C/min. Then, the catalytic nanoparticles were reduced in Ar/H2 flow (1400 sccm of Ar and 500 sccm of H2) for 10 min. After reduction, the hydrogen flow was switched off and NFC growth was carried out in Ar/C2H2 mixture with the flow rates of 1400 and 25 sccm, respectively. The growth lasted for 10 min, 40 min, and 60 min as summarized in Table 1.

The reactor was cooled down to the room temperature under argon flow. The samples were taken out and placed in a vacuum evaporator for the deposition of 6.65 mm × 2.33 mm gold contacting pads overlapping by 1 mm with the field of NFC (Figure 1). Thickness of the Au layer was 350 nm, and a 15 nm thick Ni/Cr layer was used to improve Au adhesion to the substrate. Such prepared substrates were used as sensors for measurement of resistance change under various gas atmospheres.

2.2. Investigation Methods of NFC Films. The as-prepared catalytic NPs and NFCs on c-Si/SiO2 substrates were investigated by scanning electron microscopy (SEM) with MIRA II

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reduction and deposition temperature (Td), °C</th>
<th>Reduction time, min</th>
<th>Deposition time (td), min</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNF600-10</td>
<td>600</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>CNF600-40</td>
<td>600</td>
<td>10</td>
<td>40</td>
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<tr>
<td>CNF600-60</td>
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<tr>
<td>CNF650-60</td>
<td>650</td>
<td>10</td>
<td>60</td>
</tr>
<tr>
<td>CNF700-10</td>
<td>700</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>CNF700-40</td>
<td>700</td>
<td>10</td>
<td>40</td>
</tr>
<tr>
<td>CNF700-60</td>
<td>700</td>
<td>10</td>
<td>60</td>
</tr>
</tbody>
</table>
TESCAN, Brno, Czech Republic) equipped with the EDX detector (Oxford Instruments, UK). Raman spectra of NFCs were obtained using the Renishaw inVia (Renishaw, Gloucestershire, UK) spectrometer in the range 100–3200 cm\(^{-1}\) (\(\lambda = 514\) nm). Raman spectra were treated using Lorentzian fitting. Structure and morphology of carbon nanomaterials and catalytic nanoparticles were additionally investigated using the CM12 STEM transmission electron microscope (Philips, Eindhoven, Netherlands).

Gas sensing characteristics of the sensors were determined by measuring the changes of sensor resistance during ammonia exposure in a custom-built system equipped with two gas channels and a measurement chamber (Figure 1). Synthetic air (80% \(\text{N}_2\), 20% \(\text{O}_2\), Linde, Brno, Czech Republic) was used as a gas carrier in one gas channel. Along with it, the second gas line was flowed by ammonia diluted in nitrogen (calibration gas 5000 ppm of \(\text{NH}_3\) in \(\text{N}_2\), Linde, Brno, Czech Republic). Total volume flow rate of gases was set constant at 500 sccm for all stabilizations and measurements, but the concentration of \(\text{NH}_3\) in the mixture with synthetic air and \(\text{N}_2\) was changed. The additional channel for oxygen was used in the setup, and oxygen was admixed when increasing ammonia concentration in order to keep the concentration of air and nitrogen mixture the same as in synthetic air.

Gas distribution system was made of stainless steel (connections, tubes). The volume of the chamber where the sensors were examined was 160 cm\(^3\) (length: 10 cm, width: 8 cm, height: 2 cm).

The sensor was placed on a heater inside the measurement chamber, and the measurements were carried out at two temperatures: room temperature (25 ± 2°C) and 200°C (±2°C). The heating temperature was controlled by the DC power supply Agilent U3606A (Agilent, Santa Clara, California, USA) using temperature calibration curves. The resistance was measured by two electrodes that were placed to Au pads. Electrodes were plugged to a high voltage source meter Keithley 2410 (Keithley, Cleveland, OH, USA) using 1 V bias voltage. In the present work, no efforts were made to dope or treat NFCs for response enhancement. Solely, the correlations between the NFC deposition conditions, influencing the structure and composition of the deposit, and the gas sensor properties were investigated. Relative humidity (RH) in the chamber was controlled by the SHT25 sensor (Sensirion, Staefa, Switzerland). Also, the measurements of humidity influence on sensing properties were carried out. The level of RH during measuring the response in dry gases from cylinders was 2.5–3%. The measurements in different RH conditions were carried out by feeding the wet air to the chamber additionally with dry air and analyte.

Before each response measurement, the sensor was conditioned and recovered for 30 min at 200°C in the synthetic air flow of 1000 sccm. The baseline of the sensor resistance was stabilized at desired temperature in 500 sccm synthetic air flow for 60 min before the first measurement of each sample. After the baseline stabilization, the sensor response to \(\text{NH}_3\) was measured using alternating cycles, 10 min in synthetic air and 10 min in the mixture of the \(\text{NH}_3\) with synthetic air. This cycle was repeated for several tested concentrations, 100 ppm, 250 ppm, and 500 ppm of \(\text{NH}_3\).
The baseline resistance, \( R_0 \), was linearly extrapolated along the measurement time, and the sensor response was determined by subtracting the baseline resistance signal from the sample resistance under ammonia exposure, \( R \). The measurement of baseline and extrapolation has been done for each measurement of all samples. The sensor response was defined as follows:

\[
\Delta R = \frac{R - R_0}{R_0} \cdot 100\%.
\]

The instrumental detection limit of the sensor response was 10 ppm, the value was limited by the flow controller characteristics (low accuracy of flow rate control at the value up to 1 sccm) for the sensor measurement. To estimate the sensor selectivity, they were also tested for detection of H\(_2\) and iC\(_4\)H\(_10\). These gases were also fed diluted in N\(_2\) (5000 ppm of NH\(_3\)). The resolution of scanning of sensor resistance was 0.5 s (one experimental point per 0.5 s).

3. Results and Discussion

3.1. Characterization of Catalytic Nanoparticles and Carbon Nanostructures. The typical SEM and TEM micrographs of catalytic nanoparticles are shown in Figure 2. The catalyst formed aggregates consisting of nanoparticles with the size of 5–25 nm. It was difficult to determine the phase composition of the catalyst by X-ray diffraction or Raman spectroscopy because of the low amount of nanoparticles on the substrate. Therefore, the phase composition was studied by electron diffraction in TEM. The analyses revealed that the catalyst consisted of iron oxides, predominantly maghemite (\( \gamma\)-Fe\(_2\)O\(_3\)). Maghemite (\( \gamma\)-Fe\(_2\)O\(_3\)) phase was detected (Figure S1 Supplementary Materials) by selected area electron diffraction (SAED) by TEM. It is in agreement with the data obtained by Synek et al. [34].

The SEM and TEM micrographs of the NFC samples prepared at different temperatures and times are presented in Figure S2 (Supplementary Materials). At 600°C, the increased deposition times, 40 and 60 min, led to the growth of longer nanotubes and a formation of more dense nanotube aggregates compared to 10 min. According to EDX analysis of the CNF600-10 sample, the C/Fe weight ratio was 26.5 and it increased to 85 and 107 with increasing deposition time for CNF600-40 and CNF600-60 samples, respectively. At higher temperatures (650, 700°C), the yield of CNT increased and a denser MWCNT network was formed.

Raman spectroscopy of all the NFC samples was carried out for assessing the overall structure of the deposits. Raman spectra for the CNF600-10, CNF650-10, and CNF700-10 samples are shown in Figure 4(a). The spectra were dominated by two peaks corresponding to disordered \( D \) and graphitic \( G \) bands [38]. The positions of the \( D \) and \( G \) peaks ranged from 1349 to 1352 cm\(^{-1}\) and from 1581 to 1594 cm\(^{-1}\), respectively (Table 2).

The second-order peaks were presented above 2500 cm\(^{-1}\). The peaks of silicon at 520 cm\(^{-1}\) and 960 cm\(^{-1}\) were observed in case of sparsely coated substrates (low growth of temperature and time). The ratio of \( D \) and \( G \) peak intensities, \( I(D)/I(G) \), provided information about material’s disorder.
The dependencies of the $I(D)/I(G)$ on the NFC growth time are shown in Figure 4(b). The disorder degree increases with increasing growth time. It can be attributed to the loss of nanoparticle catalytic activity. Less defective samples, synthesized for only 10 min at 600, 650, and 700°C, had $I(D)/I(G) = 0.88$, 0.7, and 0.44, respectively. It reveals that higher temperature had a positive effect on the NFC graphitization degree, but the role of the temperature in the suppression of defects is lower for a longer growth time.

3.2. Ammonia Gas Response Measurements of NFC Films. The sensor resistances varied in a wide range from 0.87 kΩ to 38.60 kΩ (Table 3). The highest resistance for each deposition time was obtained at 600°C. The resistance dropped from 38.60 to 2.72 kΩ (for 10 min deposition time) when the deposition temperature increased from 600 to 700°C.

The resistance variations can be explained with the help of high resolution SEM images (Figure 5) that divided the sensors into three groups. The first group is represented by only one sample CNF600-10 which possesses the highest resistance. The sensing material is composed of short carbon nanofibers connected with each other by rarely dispersed MWCNTs. The second group consists of CNF650-10, CNF650-40, and CNF600-60 samples. The length of the CNFs and CNTs increases, and it creates additional connections and forms the network with a lower sensor resistance ($R \approx 6–9$ kΩ). The third group is represented by CNF650-60, CNF700-10, CNF700-40, and CNF700-60 samples. Increasing the amount of MWCNTs enhances the formation of the conductive network between nanotubes whereas the role of carbon nanofibers becomes negligible (sensor resistance $R < 3$ kΩ). The conductive network formed during longer deposition time and with the increase of the deposition temperature, and it has a certain similarity with the formation of percolating networks. The sample in the first group can be understood as a quasi-insulating state of the network (in terms of percolation theory); the second group of samples is situated in the transition region, and the third group represents a conductive network in which resistance is weakly influenced by the further increase in deposition time and temperature.

The changes of the sensor resistance could be partially explained also by a changed defectiveness of carbon structures. Indeed, a higher nanotube graphitization degree was proved by Raman spectroscopy, i.e., lower $I(D)/I(G)$ ratio,
when the temperature during the growth was increased from 600 to 650 and 700 °C (Figure 4(b)). However, the sensor resistances did not increase with increasing growth time although \( \frac{I_D}{I_G} \) was higher. The increased time resulted in the deposition of higher amount of interconnecting long MWCNTs, and it had much stronger influence on the sensor resistance that dropped significantly for 40 min of the growth, especially for 600 °C.

It is worth noting that according to chemical equipment and plasma equipment in industry, it is possible to carry out growing of CNTs on large wafers. Moreover, a CVD process is a very simple way for CNT growth, and it is appropriate for practical application. The processes with a floating catalyst for the deposition of iron nanoparticles are also successively used for plasma-enhanced CVD of nanoparticles for subsequent growth of CNTs. The possibility to control the growth time and deposition temperature is an advantage of the process used in this paper, because it is possible to obtain the defined resistance of the sensing layer that makes the process flexible and favorable for industry.

3.3. Ammonia Adsorption on Carbon Nanostructured Films. All the sensors exhibited increased resistance upon ammonia exposure. The increase of the NFC sensor resistance during an ammonia adsorption has been explained on the basis of the hole depletion in p-type MWCNTs [39, 40]. Adsorbed ammonia molecules donate electrons to CNTs inducing a decrease of charge carriers (holes). The same effect was observed for p-type SWCNTs [40]. The resistance of CNF600-10, 38.60 kΩ, was quite high for the MWCNT-based sensors [40, 41], but this sample exhibited the highest response, 2.8% to 500 ppm at room temperature (Figure 6). In addition, the sample CNF600-40 exhibited the response comparable to CNF600-10, e.g., 2.5% at 500 ppm (room temperature). Comparing results of Raman spectroscopy

![Figure 4](image-url)
Table 3: Summary of sensor properties. Sensor resistances at room temperature and 200°C are denoted \( R_{RT} \) and \( R_{200°C} \), respectively. The sensor responses, \( S_{100 \, \text{ppm}} \), \( S_{250 \, \text{ppm}} \), and \( S_{500 \, \text{ppm}} \) to 100, 250, and 500 ppm of ammonia, respectively, at room temperature (RT) and 200°C were calculated as \( \Delta R/R_0 \).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( R_{RT}, \Omega )</th>
<th>( R_{200°C}, \Omega )</th>
<th>( S_{100 , \text{ppm}} ),% at RT</th>
<th>( S_{250 , \text{ppm}} ),% at RT</th>
<th>( S_{500 , \text{ppm}} ),% at RT</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNF600-10</td>
<td>38600</td>
<td>24100</td>
<td>1.8</td>
<td>1.1</td>
<td>2.4</td>
</tr>
<tr>
<td>CNF600-40</td>
<td>8940</td>
<td>2670</td>
<td>1.8</td>
<td>0.7</td>
<td>2.3</td>
</tr>
<tr>
<td>CNF600-60</td>
<td>8610</td>
<td>2580</td>
<td>0.6</td>
<td>1.1</td>
<td>0.8</td>
</tr>
<tr>
<td>CNF650-10</td>
<td>6860</td>
<td>4380</td>
<td>1.2</td>
<td>0.5</td>
<td>1.7</td>
</tr>
<tr>
<td>CNF650-40</td>
<td>2660</td>
<td>800</td>
<td>0.4</td>
<td>0.1</td>
<td>0.7</td>
</tr>
<tr>
<td>CNF650-60</td>
<td>1680</td>
<td>670</td>
<td>0.6</td>
<td>0.1</td>
<td>0.8</td>
</tr>
<tr>
<td>CNF700-10</td>
<td>2720</td>
<td>1340</td>
<td>0.4</td>
<td>0.4</td>
<td>0.6</td>
</tr>
<tr>
<td>CNF700-40</td>
<td>1420</td>
<td>530</td>
<td>0.3</td>
<td>0.2</td>
<td>0.4</td>
</tr>
<tr>
<td>CNF700-60</td>
<td>870</td>
<td>440</td>
<td>0.1</td>
<td>n/a(^{1})</td>
<td>0.2</td>
</tr>
</tbody>
</table>

\(^{1}\)The sensor response was comparable with noise.

(Figure 4(b)), SEM images (Figure 5), and sensor resistance (Table 3), it can be concluded that the sensor response is mostly linked to the microstructure and high sensor resistance. The high resistance sensors possessed low charge carrier concentration, and thus, they were more sensitive to any change of \( \text{NH}_3 \) adsorption. Mishra et al. [32] supposed
that the increase of the disorder degree improved the sensor response because a higher defect density increased the number of active sites in which ammonia can be adsorbed. The $I(D)/I(G)$ of the five sensors from the third group (the resistance below 3 kΩ) was quite different, 0.44–0.92, but their response did not prove to be dependent on it.

From structural studies and ammonia adsorption characterization, one can conclude that not only properties of individual components of thin film (CNFs and CNTs) but also the amount and structural arrangement of nanostructures are important for thin film response towards ammonia.

The above discussed results suggest that the response of the sensors can be increased by the decrease of the deposition temperature below 600°C. However, the preliminary experiments carried out for the NFC active layers synthesized at 500°C and 550°C, showed that these sensors possessed extremely high resistance and were almost without response to NH₃. So much reduced temperatures had a negative effect on the reduction of catalytic NPs prior to the CNT and CNF growth. It resulted in a very low yield of NFCs, and iron oxide and Fe₃C NPs were covered by carbon. It is worth noting that no iron was detected on the surface of our samples by XPS analysis even for the deposition temperature of 600°C. In this connection, the iron nanoparticles have no direct contact with ammonia and have no influence on the response from the point of adsorption. The catalytic nanoparticles can change the conductivity of carbon nanomaterials but only for carbon nanomaterials synthesized using low deposition time, e.g., 10 min, or low temperature (600°C). Their presence in the active material increases the resistance of the active layer but only for limited samples, and we supposed that it has a little effect on the sensor response, because conductivity in such materials is mainly determined by the number of contacts formed between the nanotube and nanofiber network (this effect can be treated as percolation).

The response of the sensors at 100 ppm, 250 ppm, and 500 ppm NH₃ was in the ranges of 0.1–1.8%, 0.2–2.4%, and 0.2–2.8%, respectively. In comparison with previously published results, such as Cui et al. [29] obtained the response of 2.8% for bare MWCNTs under exposure to 1% of NH₃ (i.e., 10000 ppm). Hoa et al. [42] achieved approximately 8% response to 6% of NH₃ (60000 ppm) using CNTs on anodized alumina template; our NFC thin films exhibited the 2.8% response under much lower exposure of 0.05% (500 ppm) of NH₃. This is comparable to a more expensive SWCNT-/cellulose-based sensor [16] or chemically modified CNTs reported by Randeniya et al. [4], which showed 1–2% resistance growth of an acid-treated CNT yarn sensor under 550 ppm of ammonia. The sensors discussed in this work were not surface treated, and it is expected that some surface treatment will improve further their sensing properties. We recently reported that plasma treatment of PECVD-grown CNTs could enhance their response [43].

The adsorption on ammonia on the surface can be divided into two categories: physisorption and chemisorption. Bannov et al. [43] discussed that the response curve is a combination of both categories; the first steep part is related to physisorption of ammonia on the structure surface and later, an asymptotic part to chemisorption. In case of the recovery process, the response can quickly recover by the
desorption of physisorbed molecules but the recovery of chemisorbed molecules is slow or irrecoverable. For our films, we propose that the main response mechanism is physisorption and can be modelled by Langmuir isotherm. It is worth noting that it is not possible to separate chemisorption and physisorption. Nevertheless, we cannot exclude the partial chemisorption, since there is an incomplete recovery of sensor response without using heating. The use of thermal recovery makes it possible to fully carry out the desorption of ammonia molecules.

The Langmuir isotherm is usually used for the description of NH$_3$ adsorption on carbon materials taking into account few assumptions: each site holds each molecule, all sites are equivalent, and there is no interaction between NH$_3$ molecules on sites [44]. The adsorption equilibrium constant can be estimated by the following equation:

$$\theta = \theta_{\infty} \left( \frac{K \cdot p}{1 + (K \cdot p)} \right),$$

where $\theta$ is the fraction of active sites covered by NH$_3$ (with the assumption that the value is proportional to the change of resistance), $\theta_{\infty}$ is the total number of active sites, $K$ is the adsorption equilibrium constant, and $p$ is the partial pressure of NH$_3$. Results of the sample fitting by adsorption isotherm are shown in Figure 7(b). The fitting was presented taking into account that the concentration of active sites is proportional to the sensor resistance. According to the fitting, the adsorption constant of $K = 0.05$ Pa$^{-1}$ was different compared with the reported one for graphene-like materials [45] ($K = 0.16$ Pa$^{-1}$) and the graphene-based NH$_3$ sensor reported in [46].

The sensors studied can be used as industrial sensors for the determination of ammonia concentration in chemical engineering (apparatuses), oil refining, etc. The data on fitting the experimental data using Langmuir isotherm makes it possible to find the response for low NH$_3$ concentrations that makes it possible to predict the sensor response for 14 ppm (according to OSHA regulations) and below that is appropriate for environmental control sensors. It is worth noting that there is a necessity to control also the higher concentrations (1000–20000 ppm) for turning on the emergency ventilation in compressor rooms at the facilities used anhydrous ammonia and the sensors studied can be also used for this purpose.

3.4. Influence of the Operating Temperature on NFC Film Response and Its Recovery. NFC-based sensors possessed good response at room temperature that is an advantage as compared with semiconductor-based conventional sensors [47]. The sensors working at room temperature were also prepared using graphene-based materials. For example, Katkov et al. [45] created a fluorine-functionalized graphene sensor and reached 10.2% response to 10000 ppm of ammonia. The response 3–4% for 0.1% (1000 ppm) NH$_3$ in Ar was obtained on reduced graphene oxide-silver nanowires [48].

The sensor responses at room temperature and 200°C were quite different. The dependence of $\Delta R/R_0$ on the concentration had almost linear behaviour at 200°C, whereas it became nonlinear at room temperature (Figure 6(b)). The maximum response at 200°C was 2.5% in comparison with 2.8% at room temperature. The enhanced sensor response at the room temperature can be explained by the thermodynamics of adsorption. The adsorption is an exothermic process, and therefore, an increase of temperature enhances the desorption and higher temperatures (compared to room temperature) are favourable for this process. Additionally, it can be caused by weaker desorption at room temperature that lead to accumulation of small amount of ammonia on NFC surface. For example, the recovery percentage (measured after 10 min recovery in synthetic air) of the sensor CNF600-10 for 100 ppm at room temperature is only 23% in comparison with 62% at 200°C. The full adsorption-desorption cycle for wide range of concentrations of NH$_3$ (50–500 ppm) can be seen in Figure 7(a). We can see that although the recovery at 200°C was significantly better than at room temperature, we can observe at higher concentration saturation of the NFC thin film response an increase of background resistance.

Figure 7: CNF600-10 response curve to NH$_3$ in a wide concentration range at 200°C and data fitting by Langmuir adsorption isotherm ($R^2 = 0.984$).
It is worth noting that porosity of carbon nanomaterials (active material of sensor) can have an influence on the sensor response, but there is no possibility to obtain the information on the porosity of thin films because the volume of carbon nanomaterial is low enough to carry out the study of porosimetry by low-temperature nitrogen adsorption, or other techniques.

The response time of the CNF600-10 sample at room temperature was 456 s, 291 s, and 250 s for 100 ppm, 250 ppm, and 500 ppm, respectively. The increase of temperature increases the response time of the sensor to 240 s, 307 s, and 292 s, respectively. As can be seen, there is no strong dependence between concentration of ammonia and response time.

The adsorption-desorption history plays a significant role in the formation of sensor response. Therefore, the sensor response to a stepwise increase of the ammonia concentration without the recovery phase was studied for CNF600-40 in which response was very similar to CNF600-10 (Figure S3 in Supplementary Materials). The cumulative response of the CNF600-40 sample achieved at 500 ppm of ammonia was 3.5% instead of 2.5% measured after the third cycle (500 ppm) with 10 min recovery phases. The response curves showed good reproducibility, and a saturation state was not achieved during this measurement.

If the sensor recovery is required, it is necessary to employ some method, such as heating [4, 40], increasing of gas flow [40], irradiation by infrared light [49], and strong electric field [32] to accelerate it. Preliminary measurements showed that the sensor recovery performed by an air flow increase was insufficient for a complete sensor recovery. It was caused by the sensor saturation by NH$_3$ molecules from the previous concentration. In the previous section, the whole measurement was carried out at 200°C and it improved the sensor recovery but the response was lower in comparison to room temperature response. Since the idea of this work was to create the sensor working at room or only slightly elevated temperature, we tested temperature increase to 100°C for 3 min only during the recovery phase. The sensor recovery by this heating allowed almost a full desorption of NH$_3$ and achieved a good reproducibility of the sensor response (Figure 8). Recovery response of the CNF600-40 sample was stable on the level 1.1% at 100 ppm during the three cycles of ammonia exposure. In [41], the authors achieved good recovery (98.5%) only by using the heating to 150°C and increased DC bias current (3 mA) for 20 min recovery of the MWCNT-PANI sensor. The role of the bias current in our NFC sensor recovery is negligible because the bias current for the samples was 1.1·10$^{-4}$ A. The short-time sensor recovery provides more effective application of the sensor because achieving of constant response in time is very time-consuming.

As mentioned previously, we used 10 min time for adsorption and desorption in our measurement cycle. In this cycle, it was not possible to reach full response of the NFC thin film and the response was still increasing at 10 min. That is why we carried out measurement with longer exposure time of 60 min. The response curve of the steady state (CNF600-40) is shown in Figure 9. It is worth noting that even at 60 min of adsorption time, the response was still increasing for 100 and 250 ppm of NH$_3$ but was saturated for 500 ppm. The measurements in steady-state regime allowed achieving higher response of 3.6%, 4.1%, and 10.2% for CNF600-40 to 100 ppm, 250 ppm, and 500 ppm NH$_3$, respectively. The sensor response at higher durations of NH$_3$ exposure was several times higher than that data of 10 min exposure. Therefore, it can be concluded that longer exposure time led to higher response of the CNF thin film, but in industrial application, such time period is unpractical and short response time are required. Also in our case, much shorter exposure time, 1–2 min, was sufficient to reliably detect the presence of ammonia (Figure 9(b)).

3.5. NFC Film Response Selectivity and Influence of Humidity.

An important parameter for the application of every material as a gas sensor is its selectivity, i.e., response to other gases than the selected target gas. We investigated response of our NFC thin film to H$_2$ and iC$_4$H$_{10}$ (Figure 10(a)). These gases are frequently used in oil refining and petrochemistry. Therefore, the exhaust gases coming from apparatuses contain mainly hydrocarbons and hydrogen. The conventional process of NH$_3$ production by steam reforming includes them, and it is important to detect ammonia selectively.

The response to H$_2$ and iC$_4$H$_{10}$ was almost 10 times lower than to NH$_3$, and the recovery was negligible. The very low recovery of the NFC film was probably caused by thermodynamics of desorption.

Another important point for real world application of gas sensors is influence of air humidity (RH). In our work, the increase of RH led to the decrease in sensor response (Figure 10(b)) and resulted in weaker desorption of NH$_3$. This can be explained by two processes taking place on nanostructured carbon surface in the presence of H$_2$O: formation of NH$_3^+$ ions and partial oxidation of NH$_3$ to NO$_2$ on NFC surface [50]. These processes induce the formation of holes resulting in resistance decrease.

The phenomenon of change of response for carbon nanomaterials under different relative humidities is well known,
and this effect has been also found for some graphene-like materials [51]. According to chemical nature of these materials, we are not able to change the adsorption of moisture during operating the sensor but it is possible to create the calibration curves, sensor response vs. RH, and embed the relative humidity sensor for the correction of data coming from the NH$_3$ sensor based on nanofibrous carbon. Comparing the sensors studied with conventional TGS 826 (produced by Figaro Co.), it can be found that the detection range 30–300 ppm is almost similar to our sensors whereas it allows detecting ammonia in air at ambient temperature 20 ± 2°C and 65 ± 5%RH, while the active material has a relatively higher operating temperature compared to NFCs-based sensors studied in this article. As it was shown above, the sensors studied make it possible to operate under higher temperatures and a lower RH value that is favorable for NH$_3$ detection at the industrial facilities.

4. Conclusions

The nanofibrous carbon films were prepared by CVD on Si/SiO$_2$ substrates using iron catalytic nanoparticles and used as chemiresistor ammonia sensors. The prepared films contained different amounts of short bamboo-like hollow fibres and long MWCNTs depending on the deposition temperature and time. The MWCNTs were responsible for the carbon network interconnection, and their larger amount at higher temperature and longer deposition time decreased the sensor resistance from 38.60 to 0.87 kΩ. The NFC thin film resistances increased when exposed to ammonia in all
the cases, but their response varied. A decrease of the deposition time and temperature led to the 10-fold increase in sensor response. The sensor response was highest for thin films with high resistance, and the maximum response was achieved at room temperature, 2.5 and 2.8% for 500 ppm of ammonia, for the sensors deposited at 600°C for 40 and 10 min, respectively. The response was reproducible and high in comparison to other published results on bare multi-walled carbon nanotube sensors. Thin film analysis showed that the film structure as well as properties of individual CNFs influences sensor response to ammonia adsorption. Physisorption of ammonia on carbon nanostructures was identified as the main mechanism of thin film resistance change. Difference between room temperature and high temperature (200°C) response and the time dependence of response curve during subsequent measurement cycles can be explained by a competing adsorption and desorption process of ammonia on carbon nanostructured surface. An improvement of the sensor performance was achieved by a short thermal heating at 100°C during the recovery phase.

**Data Availability**

The sensor characteristic data used to support the findings of this study are included within the article. Also, the selective area diffraction patterns and scanning electron microscopy data used to support the findings of this study are included within the supplementary information file.

**Conflicts of Interest**

The authors declare that there is no conflict of interest regarding the publication of this paper.

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**Supplementary Materials**

Supplementary materials include selective area diffraction (SAD) patterns of catalyst used for nanofibrous carbon (NFC) synthesis which show the predominant presence of the γ-Fe₂O₃ phase among the nanoparticles (Figure S1). SEM micrographs of all the NFC samples prepared at different temperatures and deposition times are compared in Figure S2: (a) CNF600-10, (b) CNF600-40, (c) CNF600-60, (d) CNF650-10, (e) CNF650-40, (f) CNF650-60, (g) CNF700-10, (h) CNF700-40, and (i) CNF700-60. CNF600-40 response curve during stepwise increase of the NH₃ concentration in the range of 10–500 ppm (Figure S3).

**References**


