Insight into ammonia sensing on heterogeneous S- and N- co-doped nanoporous carbons

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Abstract

The design of S- and N-dual-doped carbon-based ammonia sensors is reported for the first time. The materials are exposed to NH_3 concentrations varying from 45 ppm - 500 ppm in dry air and normalized resistance changes are recorded. The response time is 40 s and the chips exhibit excellent reversibility and repeatability of the signal after continuous NH_3 /air cycles. The synergistic effect of N- and S- functional groups enhances the response. This behavior is governed by physical interactions of NH_3 with surface groups, pore-filling, and hole depletion/formation in the carbon matrix. The texture and the degree of carbon graphitization also contribute to the magnitude of the observed signal. The results show that heteroatom containing nanoporous carbons can both detect NH_3 and protect against its exposure.

1. Introduction

Nanoscale carbon-based materials such as single and multiwall carbon nanotubes, reduced graphene oxide and exfoliated graphene have been extensively studied as toxic gas sensors [1-7]. These p-type materials are generally nonporous with a rather limited surface area. They provide similar signal changes upon exposure to electron donating (such as NH_3) or withdrawing gases (such as NO_2), which are consistent with the extent of their hole depletion or formation, respectively. Since the lack of selectivity is an important drawback that needs to be surpassed, functionalization processes with metals/metal oxides or even polymer coating are usually necessary to be applied [8-11].

In our recent studies nanoporous carbons, either home-made S-doped, or commercial-wood based were examined as ammonia gas sensors [12, 13]. They demonstrated great potential for ammonia detection. The electrical sensing properties of these materials were governed by the extent of gas adsorption in their pore system and by specific interactions of ammonia with surface functional groups. Furthermore, it was shown that nanoporous carbon-based sensors can not only detect the target gas but also protect against it. The latter is linked to a specific chemical environment, large surface area and developed microporosity.

Sulfur or nitrogen doping procedures are often used to alter surface chemistry and to manipulate the electronic properties of carbonaceous materials for their applications as supercapacitors, oxygen reduction and photoelectrochemical water splitting catalysts [14-25]. It has been demonstrated that sulfur, owing to its various oxidation states, is able to affect/alter the chemistry of the carbon matrix. Electron-rich aromatic sulfides, by providing a more polarized surface, enhance the electrical performance of S- doped carbons upon the application of an electric field [26]. Moreover, sulfur in aromatic rings may also affect the charge of neighboring

carbon atoms and therefore it may contribute to an increase of charge storage in small pores via EDLC (electrical double layer capacitance) [27]. On the other hand, oxidized sulfur species such as sulfoxides and sulfones have been reported to enhance the pseudocapacitance by participating in Faradic/redox reactions [23, 27]. Nitrogen-doping, is also a widely used method for altering the surface chemistry and manipulating the electronic properties of carbonaceous materials [16-29]. The electron donating character of nitrogen atoms was found as enhancing the activity for oxygen reduction and the generation of superoxide ions [30, 31]. A strong dependence of capacitance on the presence of nitrogen functionalities incorporated to the carbon surface has been reported previously. Here, negatively charged nitrogen in pyrrolic and pyridinic groups was found to enhance pseudocapacitive interactions, while positively charged pyridine-N-oxides and quaternary-N promoted the charge transfer to small pores [15, 16]. An enhancement in the electrochemical activity was found especially for sulfur and nitrogen co-doped materials. It was linked to structural modifications and the redistribution of charge and spin densities, as a result of the synergistic effect of the heteroatoms [24, 32, 33].

To our best knowledge, even though S- and N- dual-doped carbon based materials have been used in the above mentioned electrochemical applications, no study has been reported using them as ammonia gas sensors. Villalpando-Paez and coworkers [34] tested N-containing CN_x (carbon nanotubes) as gas sensors and it was found that they exhibited a great potential for ammonia detection owing to the presence of pyridinic groups. These groups were able to interact with NH_3 and therefore alter the electrical resistance of the sensor. Bai and Zhou used a computational study to examine the capability of nitrogen- or boron-doped single-walled carbon nanotubes as NH_3 and NO_2 gas sensors [35]. It was shown that NH_3 detection was feasible only in the case of B-doped SWCNTs (single wall carbons nanotubes), while N-doped SWCNTs

detected both gases. In our recent study where sulfur-containing nanoporous carbons were used as NH_3 sensors, the electrical response was found to be governed by specific interactions between sulfur/oxygen functionalities and the target gas [12]. In another study of ours where a commercial wood-based carbon (BAX) and its oxidized counterpart (BAX-O) were tested [13], oxidation led to the functionalization of the carbon surface not only with oxygen but also with nitro-type complexes. These contributed to the hole annihilation of the carbon matrix itself and its conversion from a predominantly p- to predominantly n-type materials.

Even though nanoporous carbons functionalized with solely S or N have been previously tested as ammonia sensors [12, 34] to our best knowledge no study has focused on testing S- and N- co-doped nanoporous carbons for ammonia detection. Therefore in this study we test the sensing capability of such porous materials for the first time for NH_3 concentrations between 45-500 ppm. The initial carbons (C-A, C-B) [14] were synthesized from commodity polymers containing sulfur and nitrogen, while their oxidized counterparts (C-AO, C-BO) were derived by air oxidation of the carbonized polymers at 350 °C [14]. The role of S and N heteroatoms and the role of porosity in the extent of their electrical signal change is explored. The degree of the carbon graphitization which is known to enhance electron transport [1] is also investigated as an important factor affecting the electrical behavior. To better understand the mechanism of sensing, ammonia adsorption on the sensing materials is also evaluated.

Considering that the permissible exposure limit for ammonia according to OSHA is 50 ppm over an 8-h work day or a 40-h work week and that exposure to 300 - 500 ppm of ammonia has been reported as the maximum short exposure tolerance [36, 37], in this study, ammonia sensing is performed at concentrations varying from 45-500 ppm.

2. Experimental

2.1. Preparation of materials

Poly (4-ammonium styrene-sulfonic acid) and a 1:1 mixture of 30% solution of Poly (4-ammonium styrene-sulfonic acid) and Poly(4-styrenesulfonic acid-co-maleic acid) sodium salt were carbonized at 800 °C for 40 min. The flow of N₂ was 300 mL/min with a heating rate of 50 °C/min. The carbons are referred to as C-A and C-B, respectively [14]. These two carbons were oxidized in air at 350 °C for 3 hours and the resulting materials are referred to as C-AO and C-BO following the names of the parent carbons.

2.2. Preparation of sensor chips

To prepare chips, each carbon sample was grounded and made into a slurry using N-methyl-2-pyrrolidinone as a solvent. 8 mm × 8 mm thin-film gold interdigitated electrodes, with 50 μm lines/spaces on alumina substrate were then coated with the slurry, using a blade. The coated chips were finally dried at 120 °C for 24 hours. The film thickness was ~15 μm.

2.3. Sensing procedure

The polymer-derived carbon coated microchips were placed in a 20 cm³ home-made gas chamber which was purged with dry air till a dynamic equilibrium was established. The electrical measurements and sensing performance were monitored using a VersaSTAT MC (AMETEK, Princeton Applied Research) through four-wire sensing at room temperature, applying 1 V voltage. During the reversible sensing the chips were exposed to 45, 100, 175, 250, 375 and 500 ppm of ammonia followed by purging with dry air. The normalized resistance changes $(\Delta R / R_0) = (R_t - R_0) / R_0$ of the chips were calculated, where R_0 is the resistance of the sensor before exposure to NH₃, and R_t is the resistance at any time, t , during exposure to NH₃.

2.4. Impedance measurements.

The impedance spectroscopy was carried out in 0.5 M Na₂SO₄, in a three-electrode cell, using a Ag/AgCl (3M KCl) as the reference electrode, the active material as the working electrode, and a platinum rod as the counter electrode. The working electrode was prepared by coating a Ti foil collector of active area of 1cm² with the well-grounded slurry of the activated carbon and polyvinylidene fluoride (PVDF) (ratio 90:10) in N-methyl-2-pyrrolidinone (NMP). The electrodes were dried at 120 °C for 24 hour. Potentiostatic electrochemical impedance spectroscopy (EIS) measurements were performed using VersaSTAT MC (AMETEK, Princeton Applied Research) in the frequency range of 0.05 Hz – 100 kHz with a 10 mV AC amplitude, at various potential vs reference electrode, ranging from -0.2 V to 1.0 V.

2.5. Surface characterization

2.5.1. NH₃ breakthrough dynamic test: Ammonia breakthrough capacity was measured in dynamic conditions, at room temperature. Adsorbent samples were packed into a glass column (length 370 mm, internal diameter 9 mm). The bed volume used was about 2 cm³ (with particles having size 1 - 2 mm). The total flow rate of the inlet stream was 225 mL/min with ammonia concentration of 1000 ppm, in dry air. Ammonia breakthrough was monitored using an electrochemical sensor (Multi-Gas Monitor ITX system). The challenge gas flow was arbitrarily stopped at the breakthrough concentration of 100 ppm. At this point, desorption test was carried out by purging the columns with dry air in order to examine the strength of NH₃ adsorption. During this step, weakly retained ammonia desorbed from the surface. The exhausted samples have the suffix -E added to their names. These exhausted samples were then further characterized using adsorption of nitrogen, X-Ray Photoelectron Spectroscopy (XPS), potentiometric titration and thermal analysis.

2.5.2. Porosity characterization: Adsorption of nitrogen was carried out using ASAP 2020 Surface Area and Porosity Analyzer (Micromeritics). Before the experiments, the samples were outgassed at 120 °C to constant vacuum (10^{-4} Torr). From the isotherms, the surface areas (BET method), total pore volumes, V_t , (from the last point of isotherm at a relative pressure equal to 0.99), volumes of micropores, V_{mic} , mesopore volume, V_{mes} , along with pore size distributions were calculated from the isotherms. Non-Local Density Functional Theory (NLDFT) was used to calculate the pore size distributions (free download at www.nldft.com) [38, 39].

2.5.3. X-Ray Photoelectron Spectroscopy (XPS): The elements present on the surface of the carbons studied as well as their chemical state were identified by X-ray photoelectron spectroscopy (XPS) analysis. A Physical Electronics spectrometer (PHI 5700) was used with $MgK\alpha$ X-ray radiation (1253.6 eV) as the excitation source. High resolution spectra were recorded at a take-off angle of 45° by using a concentric hemispherical analyzer operating in constant-pass-energy mode at 29.35 eV, with a 720 μm diameter analysis area.

2.5.4. Potentiometric titration: Potentiometric titration measurements were performed on the active carbon components with a Titrand 888 automatic titrator (Metrohm). Reference [15] describes the details of the experiments. The experimental data were transformed into proton binding curves, Q , representing the total amount of protonated sites. From them the pK_a distributions and the numbers of groups represented by certain pK_a values were calculated [40-41].

2.5.5 Thermal analysis: Thermogravimetric (TG) curves and their derivative (DTG) were obtained for all samples using a TA Instrument analyzer (SDT Q 600), connected to a gas analysis system (OMNI StarTM) mass spectrometer. The carbon samples were heated up to 1000 °C under a flow of nitrogen (100 mL/min), with a heating rate of 10 °C/min. The composition of

gases was evaluated by MS and the gas evolution profiles were obtained as a function of temperature (m/z thermal profiles).

3. Results and Discussion

3.1. Sensing response and surface characterization

Figure 1 presents the normalized resistance change, $\Delta R/R_o$ [%], of the chips when initially exposed to 500 ppm of NH_3 and then purged with dry air. The initial resistances of the coated chips were found to be 20.9 Ω , 12.9 Ω , 5.44 k Ω , and 40.3 Ω for C-A, C-B, C-AO and C-BO, respectively. The differences in their electrical behavior are likely related to the nature of carbon and changes in their surface chemistry and texture upon oxidation. Even though C-AO exhibits the highest resistivity compared to the rest of the carbons tested, it provides the highest electrical signal changes during the sensing procedure. The effect of oxidation on the electrical behavior of the chips upon exposure to ammonia is shown in Figure 1C. While C-A exhibits a 1.5 % increase in its normalized resistance, this change is 23 times greater (50 % decrease in resistance) for C-AO, under the same conditions. Interestingly, C-B carbon shows a totally different trend of changes than those found for the rest of the samples tested. It exhibits a 1.17 % decrease in the normalized resistance followed by a two times larger (2.76 %) increase in this parameter upon exposure to ammonia. Its oxidized counterpart, on the other hand, exhibits a 21 % decrease in the normalized resistance.

The chips were initially exposed to NH_3 until the stabilization of the electrical signal was recorded due to the exhaustion of all surface reactive sites and adsorption/reactive adsorption equilibrium. Then NH_3 was turned off and the chips were purged with dry air to remove the

physically adsorbed gas. Small changes in the resistance upon air purging indicate that chemisorption is the predominant mechanism for NH_3 retention at this sensor stabilization stage.

Figure 1. Normalized change in the resistance of C-A (A), C-B (B), C-AO and C-BO (C) upon the initial exposure to NH_3 and subsequent purging with dry air, after stabilization.

To examine the reversible sensing, the chips were further exposed to NH_3 concentrations varying from 45 and 500 ppm, in dry air. Figure 2 shows that both C-AO and C-BO sensing devices exhibit a good response to various NH_3 concentrations. Since repeated cycles do not change the response levels of the sensors they exhibit a good reversibility and consistency of the measurements related to the stability of carbons. Moreover, the sensors have a very short response time of only 40 seconds. The change in the response is related to interactions of NH_3 with those surface sites that participated in weak interactions during the initial exposure. Even though C-B exhibits reversible and consistent sensing upon exposure to continuous NH_3 cycles, the electrical changes are very small (Figure 2A). For C-A, on the other hand, no change in the electrical signal was measured upon exposure to NH_3 indicating its unsuitability for this application. Therefore for further testing only C-AO and C-BO will be addressed.

The reproducibility of the results on three different chips of C-AO and C-BO is illustrated in Figure 2A and 2B. Error bars represent the standard deviations upon exposure to various gas

concentrations (Figure 2C). The relative σ (% RSD) is 3.3 ± 1.4 % for C-AO and 7.2 ± 1.3 % for C-BO. The sensors respond linearly to changes in NH_3 concentration, which is an important feature of a sensor/monitor (Figure 2C).

Figure 2. Response curves for C-B (A), C-AO and C-BO (B) exposed to various ammonia concentrations. (C) Dependence of $\Delta R/R_0$ of the oxidized samples on NH_3 concentration. The error bars are similar or smaller than the size of the data points used.

In our previous study a sulfur-containing polymer-based carbon (C1) and its air oxidized counterpart (C2) were examined as ammonia gas sensors for gas concentrations ranging from 100-500 ppm [12]. It was shown that upon exposure to 500 ppm of NH_3 , C1 and C2 exhibited ~ 0.6 % and ~ 1.7 % resistance change, respectively. Comparing the response of C2 to those of C-AO (14.1 %) and C-BO (6.2 %), and the fact that C2 and C-AO have similar surface areas (756 m^2/g and 727 m^2/g , respectively), the considerably better sensing performance of the samples addressed in this study indicates the key role of surface chemical heterogeneity on the sensor's responses. A comparative graph illustrating the sensitivity and the surface areas of C-AO and C-BO and of that the previously studied S-doped nanoporous carbon (C2) is provided in Figure 3.

Figure 3. Comparative graph of the chip normalized resistance changes (%) (at 500 ppm of ammonia) and surface area of the nanoporous carbons addressed in this work and a previously studied S-doped nanoporous carbon [12]. The surface area data for C-AO and C-BO is taken from Reference [14] and the data on C2 from Reference [12]. Copyright 2014, with permission from Elsevier [14].

The surface chemistry and texture of the carbons tested here as sensors have been previously analyzed [14]. In order to derive a sensing mechanism and understand the factors governing the electrical signal changes, NH_3 breakthrough test was carried out and the exhausted samples were characterized. The amounts adsorbed are relatively high compared to other activated carbons [42]. The breakthrough capacity values along with the collected breakthrough and desorption curves are presented in Figure S1 of Supporting Information (SI).

The surface chemistry was analyzed by XPS. Figure 4 summarizes the content of elements and their surface concentrations. Detailed results of XPS analyses with an assignment of the specific functional groups are provided in Tables S1-S5 and Figure S2 of SI.

Figure 4. (A) Content of elements; (B-E) Surface concentration of the specific carbon, oxygen, nitrogen and sulfur groups.

The deconvolution of the O 1s core energy level spectra shows that the exposure of C-AO, C-BO and C-B samples to ammonia (electron donating gas) led to the formation of superoxide ions (O_2^-). These are generated on the surface of heteroatom containing carbons [30, 43]. They are able to partially oxidize NH_3 to NO_2 (N-4), which was detected on the surface, based on the deconvolution of N 1s core energy level spectra. Formed NO_2 oxidizes the carbon surface and specifically S and N containing groups in the reduced forms [44]. During the oxidation of NH_3 to NO_2 , water molecules are most likely formed. In their presence some sulfones can be converted to sulfoxides [14], which is an additional pathway for the generation of superoxide ions.

The deconvolution of S 2p core energy levels reveals that while the relative content of sulfur in sulfonic acids decreased slightly for C-BOE, the same species exhibited a 100% decrease in the case of C-AOE. Moreover, based on the deconvolution of C 1s, the contribution of carboxylic groups showed an about 38% decrease for the C-BOE sample while C-AOE exhibited a 14% increase. These findings indicate that in the case of C-AO sulfonic groups are reactive towards ammonia and in the case of C-BO carboxylic functionalities are rather involved.

The analysis of the S 2p core energy level spectra shows that the decreased contribution of reduced S-species and the increase of sulfoxides and sulfones for C-BE, C-BOE and C-AOE are likely related to the oxidation of thiols and bisulfides by O_2^- and NO_2 [44, 45]. The latter oxidant is also active towards the N-containing functional groups. Here, owing to the variety of species existing at each one of the four distinguished energies in the N 1s core energy level spectra the species at 398.7 eV, 400.1 eV, 401.3 eV and 402.5 eV are referred to as N1, N2, N3 and N4, respectively. In N1 category we include pyridines, in N2-pyrroles/pyridines, in N3-quaternary nitrogen and/or protonated amines and in N4-pyridine-N-oxides and C-N⁺O-C, NO_2

species. The N 1s deconvolution reveals that upon exposure to ammonia, the carbon samples exhibit a decrease in the contribution of NH_4^+ ions (N-3), accompanied by an increase in the contribution of oxidized nitrogen groups, such as pyridine-N-oxides and NO_2 species (N-4). This is especially the case for the C-AO and C-BO carbons and could be linked to the oxidation of some amines (N-2) during the reactive adsorption of ammonia.

The parameters of porous structure are summarized in Table 1. As seen C-A is a nonporous carbon and C-B is a carbon of very low porosity. Air oxidation at 350 °C led to a significant increase in the total pore volume (V_t) for both carbons, with micropores and ultramicropores ($V_{<1\text{nm}}$) exhibiting the largest change. In these pores physical adsorption of ammonia should be the strongest one [46]. The mesopore volumes also increased. This is caused by the removal of some carbon atoms from the wall of the small pores and of bulky groups previously existing at the entrances to these pores. Such groups include: 1) sulfonic acids removed from the surface of C-AOE and C-BOE; 2) carboxylic groups removed from C-BE/C-BOE; and 3) quaternary nitrogen species, whose contribution decreased for all carbon samples after ammonia adsorption. Finally, the conversion of sulfones to sulfoxides may also contribute to the increased mesopore volume.

For C-BE, a significant decrease in the volume of micropores and ultramicropores (42 % and 50 %, respectively) might be linked to the formation of stable surface compounds as a result of the reactive adsorption of NH_3 or the oxidation of the carbon's surface. The same is found for the non-porous C-A sample, where, due to the lack of pore structure, ammonia retention should be governed mainly by its chemical reaction with the carbon's surface functional groups. Exposure of C-AO and C-BO to ammonia didn't cause any significant changes in the volume of micropores and ultramicropores, especially for the later sample. The unaltered pore volume upon

exposure to the challenge gas generally indicates that physisorption rather than chemisorption is the predominant adsorption mechanism. However, C-BO, despite its higher porosity compared to that of C-B, has a smaller ammonia breakthrough capacity (Figure S1 of SI). This indicates that ammonia retention on C-BO is not governed solely by the physical features of this carbon.

Table 1. The parameters of porous structure calculated from nitrogen adsorption isotherms.

Sample	S_{BET} [m ² /g]	S_{NLDFT} [m ² /g]	V_t [cm ³ /g]	V_{meso} [cm ³ /g]	V_{mic} [cm ³ /g]	$V_{<0.7\text{nm}}$ [cm ³ /g]	$V_{<1\text{nm}}$ [cm ³ /g]	V_{mic}/V_t
^a C-A	38	---	0.022	---	---	---	---	---
^a C-AE	19	---	0.002	---	---	---	---	---
^b C-AO	727	995	0.363	0.024	0.339	0.215	0.281	0.93
C-AOE	554	761	0.301	0.054	0.247	0.182	0.203	0.82
^b C-B	290	385	0.157	0.023	0.134	0.072	0.104	0.85
C-BE	174	217	0.109	0.031	0.078	0.035	0.053	0.72
^b C-BO	847	1183	0.458	0.060	0.398	0.266	0.339	0.87
C-BOE	823	1143	0.453	0.075	0.378	0.273	0.320	0.83

^anon-porous cannot be fit using 2D-NLDFT model in order to get the PSD and volume of pores.

^bdata taken from Reference [14]. Copyright 2014, with permission from Elsevier [14].

The oxidation of the carbon surface and the formation of NO₂ species upon exposure to NH₃ are also supported by the thermal analysis, which is discussed in details in Supporting Information (Figure S3). Table S6 and Figure S4 of SI summarize potentiometric titration results in terms of the strength (pK_a) and the quantity of species detected on the carbon surfaces before and after NH₃ adsorption. The presence of NH₄⁺ ions at $pK_a \sim 9.5$ for C-B, C-AO and C-BO exhausted carbons indicates the acid-base reactions of NH₃ with acidic functional groups. These are sulfonic groups in the case of C-AOE and carboxylic groups in the case of C-BE and C-BOE. This is further supported by the XPS analysis where the crucial role of sulfonic acids and carboxylic groups for ammonia retention on C-AO and C-BO, respectively, was shown.

It is important to mention that upon the characterization of the exhausted samples (after ammonia breakthrough test), using XPS analysis and nitrogen adsorption, high vacuum was applied, which possibly caused the removal of ammonia molecules from very small pores. Therefore, using these two methods, we were able to examine irreversible changes in the surface chemistry that were caused from the reactive adsorption of the target gas. Especially when N_2 adsorption was used, the decrease or increase in the pore volume is indicative of the deposition of stable surface compounds on the entrances of the pores, or the removal of carbon atoms from the walls of some pores, as a result of the partial surface oxidation, respectively.

3. 2. Sensing mechanism

The conduction type of our best performing chips (C-AO and C-BO) was explored using the Mott-Schottky approach (Figure S5 of SI) based on impedance measurements [47]. The slopes of the $1C^{-2}$ vs E indicate that the carbons exhibit predominantly p-conduction type with similar trends in the concentrations of both -p and -n carriers.

The results obtained suggest that the sensing mechanism involves four processes affecting its extent to various degrees, depending on the surface features. These include specific interactions of NH_3 with surface groups, pore-filling with NH_3 , and hole-depletion or accumulation in the carbon itself upon the presence of electron donating NH_3 and/or electron withdrawing NO_2 , respectively. Moreover, the degree of graphitization is an additional factor responsible for the electrical performance of the chips.

The decrease in the resistance during the exposure of the chips to the first NH_3 /air cycle is also caused by a charge transfer as a result of the reactive adsorption of the target gas. During this reactive adsorption step, chemical reaction of ammonia with surface groups took place,

contributing to the formation of ammonium salts, and/or other compounds such as amines or amides [48]. The former species (ammonium salts) were formed as a result of acid-base interactions of NH_3 with carboxylic/sulfonic groups. This mechanism is further confirmed by the presence of the NH_4^+ ions at $pK_a \sim 9.5$ on the pK_a distribution plots. It is worth mentioning that since we are working in dry conditions, charge transfer through ionic conductivity should be limited.

After the exhaustion of all reactive surface sites, a reversible sensing follows. At this stage of the sensing, charge transfer through the chemical reaction of ammonia with surface functional groups does no longer take place. The main mechanism governing the reversible electrical behavior of the chips involves weak interactions of NH_3 with the surface and electron/hole conductivity. The former weak interactions include hydrogen bonding, dipole/dipole and dispersive interactions. The surface groups that participate in hydrogen bonding are oxidized S-species such as sulfoxides and sulfones, reduced sulfur species such as thiols, and oxygen groups such as phenols, alcohols and carboxylic groups. Also N-containing groups, including positively charged pyridine-N-oxides and negatively charged pyridines, weakly interact with NH_3 molecule. All of these allow hopping of charge carriers across the micro- and ultramicropores, therefore providing alternate paths for charge transport [49]. Such specific surface interactions seem to play an important role in the electrical behavior of the C-AO, C-BO, and C-B carbons and are reflected in the resistance decrease upon exposure to NH_3 . The changes in surface chemistry of the carbons upon exposure to NH_3 are demonstrated in Figure S6 of SI.

Another mechanism, hole-depletion, is a consequence of NH_3 physical adsorption on the carbon surface. The increase in the normalized resistance is a typical trend for most carbons of p-conduction, with holes are the charge carriers [1]. Electrons donated from NH_3 fill the holes in

the carbon matrix leading to a conductivity decrease. The electrical behavior of limited porosity carbon (C-A, C-B) chips is an example of this mechanism.

Pore-filling also plays an important role in the sensing performance. Owing to the higher conductivity of NH_3 than that of air [50], the DC conductivity increases after NH_3 adsorption in small pores. A higher pore volume leads to a greater electrical signal. This trend is seen in differences of the signal changes for the initial and oxidized carbons. Since the magnitude of the signal is not directly proportional to the pore volume, a combination of factors should play an important role in the electrical behavior.

An unexpected phenomenon responsible for the electrical behavior of our chips is the partial oxidation of NH_3 to NO_2 by the superoxide ions (O_2^-). The electron withdrawing NO_2 leads to an increased hole concentration in the carbon matrix, and therefore an increase in its conductivity. C-B, C-BO and especially C-AO exhibit this mechanism. In the latter case, the highest concentration of O_2^- is responsible for the highest degree of NH_3 oxidation and hence the marked formation of NO_2 .

The degree of carbon graphitization that affects the electron transport [14] through the carbons' matrix also influences the electrical response. Raman spectroscopy showed a decrease in the I_D/I_G ratio upon air oxidation and a narrower G- band for C-AO compared to that of C-BO. Moreover, HRTEM showed 10 nm sp^2 "dots" in these carbon matrices [14]. The high degree of graphitization in C-AO may explain the larger signal change for this carbon compared to that of C-BO.

Among all carbons, the most resistive chip, C-AO (5.44 k Ω), exhibits the optimal sensing performance. This is related to the contribution of various above-mentioned factors such as the surface chemistry, structural heterogeneity and degree of graphitization of the carbon matrix.

4. Conclusions

The application of S- and N- co-doped carbons as NH_3 sensors is reported for the first time. It was found that they exhibit excellent reversibility and repeatability upon exposure to NH_3 /air cycles. Chemical heterogeneity plays a key role in the carbons' responses. Depending on their surface features four mechanisms were proposed to govern their electrical behaviour. These include specific interactions of NH_3 with surface functional groups, pore-filling with ammonia molecules, and hole-depletion/formation in the carbon matrix itself in the presence of electron donating NH_3 and/or electron withdrawing NO_2 , respectively. Moreover, the degree of carbon graphitization is an additional factor that affects electron transport and therefore the electrical performance of the carbons. The results demonstrate a promising approach toward the fabrication of sensing materials based on nanoporous carbons, which can both detect the toxic gas and also protect against it.

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Captions to the Tables

Table 1. The parameters of porous structure calculated from nitrogen adsorption isotherms

Captions to the Figures

Figure 1. Normalized change in the resistance of C-A (A), C-B (B), C-AO and C-BO (C) upon the initial exposure to NH_3 and subsequent purging with dry air, after stabilization.

Figure 2. Response curves for C-B (A), C-AO and C-BO (B) exposed to various ammonia concentrations. (C) Dependence of $\Delta R/R_0$ of the oxidized samples on NH_3 concentration.

Figure 3. Comparative graph of the chip normalized resistance changes (%) (at 500 ppm of ammonia) and surface area of the nanoporous carbons addressed in this work and a previously studied S-doped nanoporous carbon [12]. The surface area data for C-AO and C-BO is taken from Reference [14] and the data on C2 from Reference [12]. Copyright 2014, with permission from Elsevier [14].

Figure 4. (A) Content of elements; (B-E) Surface concentration of the specific carbon, oxygen, nitrogen and sulfur groups.