



Nanoporous carbon-composites as gas sensors: Importance of the specific adsorption forces for ammonia sensing mechanism



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ABSTRACT

Wood-based/polymer-derived nanoporous carbon composites were tested as ammonia sensors for gas concentrations from 45 to 500 ppm. A synergy between the composite components affected their electrical response. Incorporation of only a 1% polymer-derived carbon phase was sufficient to convert the conduction type of the carbon matrix and to increase the sensitivity. An increase in the amount of the polymer-derived carbon phase (10 and 25%) in the composites decreased the electrical signals. This was linked to a decrease in the porosity and thus to a decrease in the contribution of physical adsorption to a sensing mechanism. The reversible sensing of the carbon-coated chips was governed by weak physical interactions of ammonia with surface functional groups and by a charge transport through ionic conductivity (NH_4^+). The results suggested that the nature of the weak interactions rather than the electronic properties of the carbon matrix is responsible for the electrical performance in gas sensing. Based on the results obtained, a priority order of the importance of various surface functional groups for the ammonia sensing capability of nanoporous carbons is proposed for the first time.

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1. Introduction

The presence of ammonia (NH_3) in the environment, its usage in various industrial processes and its toxicity create a need for high-sensitivity sensors that work at low gas concentrations [1]. According to the Occupational Safety and Health Administration (OSHA), NH_3 has a permissible exposure limit of 50 ppm and a maximum short-term exposure tolerance of 500 ppm [2]. Various polymers and metal oxides (WO_3 , ZnO , SnO_2 , Cr_2O_3 , etc.) have been used as NH_3 gas solid-state sensors [3–5]. The latter are sensitive at high temperatures (200–500 °C). However, high power consumption makes their practical application disadvantageous. In recent years, carbon-based sensors (carbon nanotubes, graphene, and reduced graphite oxide) [6–12] have been of particular importance because of their relatively low cost, semiconducting electrical properties, potential for modifications and ability to operate at room temperature. To improve their selectivity additional functionalization with metals [13,14], metal oxides [15,16] and conducting polymers [8,9,17] is usually required. For instance, modification of

MWCNT with polyaniline led to 4 times higher sensitivity (32%) when exposed to 10 ppm of NH_3 than that on pure carboxylated MWCNT (7.2%) [8]. Functionalization of CNTs with metals was also shown to increase the sensitivity. Abdelhalim and co-workers reported 92% sensitivity (100 ppm of NH_3) for CNTs functionalized with Au nanoparticles (NPs) [18]. Polypyrrole–graphene nanocomposites decorated with titania NPs were also found to be very sensitive (~100%) to 50 ppm of NH_3 [17]. Even though such functionalization processes may improve the sensors' response and selectivity, they drastically increase production costs.

Activated carbons, on the other hand, have several advantages over the above-mentioned carbon-based materials when used as toxic gas sensors. We recently showed that the performance of nanoporous carbon-coated chips is comparable to those reported in the literature for modified graphene or CNT-based chips [19–22]. This is related to their high surface areas and pore volumes. These features strongly favor the adsorption and retention of gas molecules in the carbon matrix, leading to a high sensitivity. Furthermore, a diversity of the surface chemistry of nanoporous carbons determines the degree of surface reactivity, which is an important feature that enhances the sensor selectivity towards specific species without a need for additional high-cost doping processes (metal/metal oxides).

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An introduction of heteroatoms (such as O, S or N) to a carbon matrix is an effective way to alter its chemistry and electronic properties [19,21,23–29]. An improved electrochemical performance is related to doping-induced charge redistributions around the heteroatoms (dopants) [30]. It was previously shown that by applying a specific surface chemical modification a predominant type of charge carriers (electrons or holes) can be targeted [20,21]. This enables one to control the extent of the electronic properties of nanoporous carbons and also the nature of specific interactions when electron withdrawing or donating gas molecules are the sensor's targets. It has been shown that oxidation of O-containing wood-based activated carbon with HNO₃ caused the conversion of the conduction type from predominantly *p* to predominantly *n* [20]. The former conduction type was attributed mainly to the presence of specific O-functional groups such as carboxyl, carbonyl, ether, epoxy and sp³-hydroxyl groups in the carbon matrix [31]. On the other hand, the *n*-conduction type was related to an introduction of electron acceptor defects (–NO_x groups). In other studies, polymer-derived nanoporous carbons doped with only S [22] or co-doped with both S and N [19] were tested as NH₃ gas sensors. The results showed that a surface chemical heterogeneity played a crucial role in the chips' electrical performance. A chemical synergy between S and N- heteroatoms in the form of specific groups led to an enhanced chip sensitivity compared to the carbons doped solely with S [19]. Both oxidized and reduced S-species (such as sulfoxides, sulfones and thiols, respectively) were involved in the sensing mechanism by participating in weak interactions with ammonia.

The electronic properties of carbon-based materials are known to be governed by nitrogen incorporated to the sp² carbon lattice in specific configurations [32,33]. DFT calculations indicated that N with a coordination number of 3 induces *n*-type doping, while

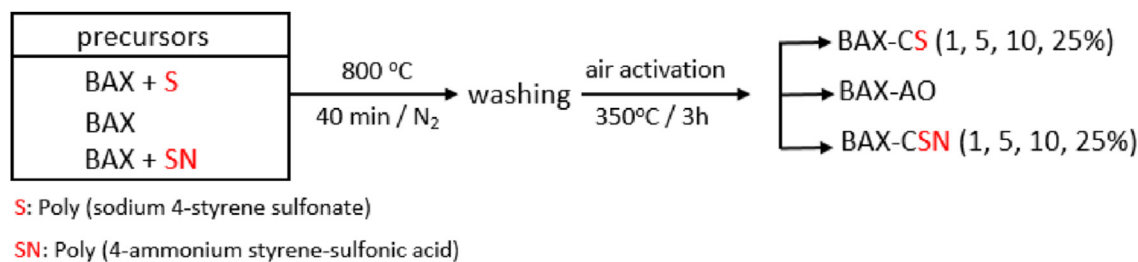
phenomenon in the pore system of carbons.

2. Experimental

2.1. Preparation of materials

Two polymers and wood-based commercial activated carbon (BAX-1500; (MeadWestvaco)) (apparent density, g/cc: 0.26–0.35, BWC, g/100 mL: 14.4 min, moisture, wt%: 10 max, pellet strength: 50 min, mean particle diameter, mm: 2.10 min) were used for the composite preparation. Poly (sodium 4-styrene sulfonate) (Sigma-Aldrich, MW~70,000, Relative density 0.801 g/mL at 25 °C) and poly (4-ammonium styrene-sulfonic acid) ammonium salt solution (Sigma-Aldrich, M_w ~200,000, 30 wt % in H₂O, solid content: 28.0–32.0%) were used as the polymer precursors. To prepare the composites with a polymer-derived carbon content of 1, 5, 10 and 20% in the final material, BAX was first mixed with the pre-determined amounts of two polymers dissolved in water. After their drying at 120 °C for 24 h, the mixtures were carbonized at 800 °C for 40 min. The flow of N₂ was 300 mL/min with a heating rate of 50 °C/min. To modify their structure and chemistry, the so-obtained carbons were oxidized in air at 350 °C for 3 h. The resulting materials are referred to as BAX-CS-X% or BAX-CSN-X% where X-represents 1, 5, 10 and 25% of the polymer-derived carbon phase. CS refers to the sulfur containing carbon that was obtained from poly (sodium 4-styrene sulfonate), and CSN refers to the sulfur and nitrogen dual-doped carbon obtained from poly (4-ammonium styrene-sulfonic acid). The same treatment (heating at 800 °C followed by air oxidation) was also applied to BAX carbon, and the resulting material is referred to as BAX-AO.

A brief description of the treatments applied is illustrated below:



pyridinic and pyrrolic-type nitrogen induces *p*-type doping [33–35]. The results of testing the NH₃ sensing capability of nanoporous carbons doped with solely N [19,21] suggested that surface acidity, by enhancing the affinity towards NH₃ adsorption, is also an important factor determining the sensitivity/selectivity of the chips.

The objective of this paper is to examine the NH₃ sensing capability of wood-based/polymer-derived nanoporous carbon composites. We investigate whether or not, and if so, to which extent, a synergistic effect of the composite formation on the carbon surface features can affect the electrical response of the sensors. Even though we have previously addressed the role of porosity and surface chemistry on sensing, the results did not lead to a clear answer which surface feature (chemistry or porosity) plays a predominant role. The relationship between the sensitivity of the chips and the volume of micro/ultramicropores was found to be either direct or indirect. The contribution of the specific configuration/arrangement of S and N heteroatoms on sensing is still hardly distinguishable and needs further attention. An additional goal of this study is to investigate effective means of increasing the sensitivity of the detection devices based on the adsorption

2.2. Characterization of the materials and electrochemical measurements

The initial and exhausted materials after NH₃ exposure were extensively characterized using XPS analysis, sorption of N₂, potentiometric titration and SEM. The suffix –ED is added to the name of the exhausted samples after NH₃ exposure in dry conditions. The reversible sensing was carried out by exposing the carbon chips to NH₃ concentrations 45–500 ppm in dry air, with a total flow rate of 500 mL/min, at room temperature, and applying the bias potential of 1 V. The changes in the resistance were monitored and are discussed in terms of a normalized resistance, $(\Delta R/R_0) = (R_t - R_0)/R_0$. For the sensing test, thin film gold interdigitated finger electrodes on 8 × 8 mm alumina substrate, with 50 micron lines/spaces, and without insulation layer were used. The electrodes were purchased from Electronic Design Center, Case Western Reserve University, Cleveland, OH. The sensing chips were coated with the active materials, and placed into a closed home-made gas chamber (20 cm³). To establish dry conditions, before ammonia dilution, the air passed through a column packed with Drierite. To establish humid

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