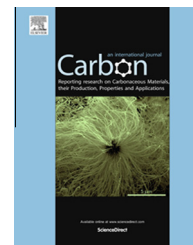


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# Nanoporous carbons as gas sensors: Exploring the surface sensitivity

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## ABSTRACT

Ammonia sensing properties of a poly(sodium 4-styrene sulfonate) derived carbon and its air oxidized counterpart were studied. The carbons were used to fabricate chips-like devices that were further used for electrical resistance measurements when exposed to various concentrations of dry ammonia. The sulfur-containing carbon after oxidation had a nine times greater response to ammonia than before oxidation. This response was evaluated from the point of view of reactive adsorption and physisorption. The initial reactions of ammonia with the sulfonic groups on the non-oxidized carbon led to an irreversible increase in resistance, while on the oxidized carbon, deprived of sulfonic groups, physisorption caused an opposite effect. After equilibration and reactive adsorption, a reversible decrease in resistance upon exposure to ammonia was found on both samples. The extensive characterization of the carbons' surfaces, and their performance as ammonia adsorbents, suggest that the sensing mechanism is governed by the physical adsorption of ammonia inside the micropores. Higher concentration of ammonia in air results in more pores being filled and thus, in the stronger response of the sensor.

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## 1. Introduction

Ammonia is a toxic gas, which is a byproduct of farming and various industrial activities [1,2]. Exposure to low ammonia concentrations for a short term irritates the respiratory tract and longer exposure times can lead to the serious ailments. Therefore, it is important to measure the ammonia levels at low concentrations. Furthermore, being able to precisely detect ammonia concentrations, will lead to the improvements in monitoring environmental air quality, and to the diagnosis of diseases where ammonia is given off [3,4].

Recently, extensive studies have been carried out on using carbon-based materials, such as carbon nanotubes, graphene and graphite oxide as gas sensors [4–12]. These materials have high conductivity with holes as their current carriers. Their sensing mechanism is based on the changes in the electrical properties that takes place via charge transfer when the material is exposed to target gases. At room temperature, these p-type materials adsorb reducing gases, such as ammonia, by collecting electrons from the gases. The electrons decrease the amount of holes in the materials, and consequently increase the materials' resistance [5,6,8–12]. However, these carbonaceous materials are not capable to distinguish

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between different reducing gases. Therefore, they are functionalized, as for instance with metals [7,8], to adjust their electrical properties, and to hereby increase the selectivity for specific gases.

Based on the working principles of graphene- and carbon nanotube-based sensors, described in the literature [4–12], we decided to evaluate the performance of nanoporous carbons for this application. Even though their electrical conductivity is limited compared to CNT, graphene, and graphite oxide, they can provide a developed surface area and a richness of surface chemistry, allowing for the better selectivity without the metal doping. For initial testing, adsorbents derived from a sulfur-containing polymer, on which the adsorption of ammonia has been investigated previously [13,14], were chosen. Since both sulfur-containing polymer-based carbon and its air oxidized counterpart have been proven as effective adsorbents for ammonia [13], coupling their adsorption capacity with an electrical signal will allow them to operate as “smart” materials for air quality measurements, and simultaneously as components of a safety equipment. For example in safety devices, these materials can detect the presence of ammonia and determine its concentration, while at the same time adsorb the gas, and limit the users’ exposure. The objective of this study is to demonstrate the electrical sensitivity of the nanoporous carbons to ammonia during the adsorption process, and to indicate its dependence on the properties of the carbon surface.

## 2. Experimental

### 2.1. Materials

Poly (sodium 4-styrene sulfonate) was used as a carbon precursor. The polymer was carbonized at 800 °C for 40 min under nitrogen, in a horizontal furnace. The flow of nitrogen was 300 mL/min and the heating rate was 50 °C/min. The sample was subsequently washed in a Soxhlet extractor with deionized water to remove an excess of water soluble species. Finally the sample was dried in air at 120 °C for 24 h. This material is referred to as C-1. The C-1 carbon was then subjected to an oxidation treatment. It was heated in a horizontal furnace for 3 h in air at 350 °C; the heating rate was 50 °C/min. The resulting material is referred to as C-2. For the carbon samples exposed to ammonia in dry air, suffix “-E” (exhausted) is added to their names.

### 2.2. Sensing procedure

To make the sensor chip, each carbon was finely grounded and then made into a slurry using N-methyl-2-pyrrolidinone. An 8 mm × 8 mm thin-film gold interdigitated electrode, with 50 μm lines/spaces on an alumina substrate, was coated with the slurry, and then dried at 120 °C for 24 h.

Testing of the chips was done in a 20 cm<sup>3</sup> gas chamber, with a total flow rate 500 mL/min of ammonia mixed with air, with an ammonia concentration of 100, 250 and 500 ppm. Electrical measurements were carried out using a VersaSTAT MC (AMETEK, Princeton Applied Research) via four-wire sensing at 1 V.

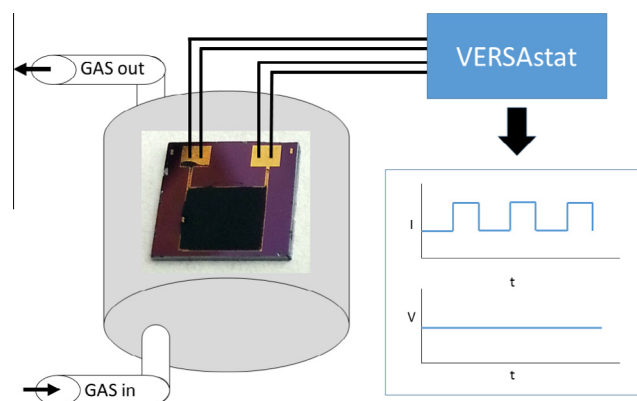
All chips were initially purged with dry air (flow rate 500 mL/min) until the electrical signal stabilized. Then they were exposed to 100, 250 or 500 ppm ammonia, flowing at 500 mL/min, until the signal reached a steady state. As a next step, the chips were purged with dry air to determine the effect of chemisorption (irreversible processes) on the sensing process. Such treated chips were then tested for sensing via reversible processes, by exposing them to ammonia for 2 min, and then purging with air for 10 min. The normalized resistance ( $R_t/R_0$ ) of the chips was calculated as the ratio of the resistance at any time  $t$  ( $R_t$ ) to the resistance of the material upon initial exposure ( $R_0$ ). The sensing set-up is presented in Fig. 1.

### 2.3. Methods

The elements present in the materials 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 a constant-pass-energy mode at 29.35 eV, with a 720 μm diameter analysis area. Further details of the procedure are described elsewhere [15].

Potentiometric titration measurements were performed with a DMS Titrimo 716 automatic titrator (Metrohm). The instrument was set at the mode where the equilibrium pH was collected. The carbon samples were stirred with sodium nitrate NaNO<sub>3</sub> (50 ml, 0.01 M) in a container maintained at 25 °C, purged with nitrogen, and equilibrated overnight. Volumetric standard NaOH (0.1 M) was used as a titrant. The experiments were conducted in a pH range of 4–11. To evaluate the surface properties, it was assumed that the population sites can be described by a continuous pK<sub>a</sub> distribution,  $f(pK_a)$ . The experimental data was transformed into a proton binding isotherm,  $Q$ , representing the total amount of protonated sites, which is related to the pK<sub>a</sub> distribution by the following integral equation:

$$Q(\text{pH}) = \int_{-\infty}^{\infty} q(\text{pH}, \text{pK}_a) f(\text{pK}_a) d\text{pK}_a$$



**Fig. 1 – Ammonia sensing set-up with the carbon chip. (A color version of this figure can be viewed online.)**

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