

# Exploring the Physiosorption Mechanism of Pristine Onion-like Carbons (OLCs) as Gas Sensitive Element

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**Abstract** –Although the response mechanism of carbon nanotubes (CNTs) based sensors exposed to a variety of gases has been extensively discussed and studied, pristine onion-like carbon (OLCs), part from the same class of fullerenes, have not been fully investigated as sensing application. A room-temperature working chemiresistor based on onion-like carbons (OLCs) as sensing element with good sensitivity has been developed and tested with the main purpose of being implemented within the next generation of gas sensors. Many industries require a room temperature working gas sensor without an external heating source: leakage detections of explosive gases (such as hydrogen), detection of flammable gases and explosives in plants, biomedicine and pharmaceuticals, monitor combustibles, early detection of fires, real-time detections of toxic or pathogenic gases in industries, ambient environmental monitoring and control. One industry that would also benefit from development of such a sensor is the food industry which requires a smart label that warns the consumer on the presence of toxic substances to avoid ingestion of contaminated food. Ingestion of food contaminated with different chemicals due to a malfunctioned manufacturing process or due to food spoilage from an improper storage could trigger severe trauma within human body.

**Keywords** –sensing mechanism, spoilage marker, chemiresistor sensor, onion-like carbons.

## I. INTRODUCTION

Warning signs of food spoilage from an earlier phase would help the consumer to avoid eating unsafe spoiled food. Among other markers of food spoilage, as Dimethyl sulfide, Trimethylamine, Diacetyl, ammonia is used by researchers to precisely identify the starting point of decaying in meat-products since ammonia is a byproduct of microorganism infestation.

Besides, accidental contamination with ammonia during production could lead to severe trauma since ammonia is an irritating and corrosive gas and inhalation of high quantities of ammonia would immediate cause burning of respiratory tract. Ammonia solutions (ammonium hydroxide) ingestion can cause excessive salivation and extensive alkali burns of the aerodigestive tract. Ammonia is extremely soluble in water and dissolves in the mucus fluid covering the mucous lining of the respiratory system.

Under these circumstances, the next generation of food smart-label would have to offer protection of consumers against accidentally exposure to ammonia. To overcome this possible health hazard researchers have been developed chemiresistors-type sensor based on carbon nanotubes (CNT) aimed to detect ammonia down to parts-per-million (ppm) [1-6]. These CNTs based ammonia sensors can work at room temperature without the need of an external heating source, by interacting with gas molecules and, depending on reducing or oxidizing properties, inject or either extract electrons from CNTs providing an electrical signal that can be measured between the electrodes' terminals [7-8].

The OLCs have been chosen as an alternative to classical CNTs to develop the sensitive element of the sensor due to their:

- smaller dimensions in comparison to CNTs as the distances between the carbon layers are of 0.34 nm [9],
- enhanced solubility, improved dispersion in the solvent and better dispersion stability [10],
- high temperature stability [11],
- large aspect ratio,
- non-porous texture.

The sensing mechanism in the sensor studied in this paper is largely based on reactions occurring on the surface of the sensor as a result of the change in the concentration of oxygen absorbed. Oxygen ions adsorbed on the surface of the material (considering a n-type

semiconductor material) extract electrons from the material and create a potential barrier that limits electron movement and conductivity. When ammonia combines with this oxygen, the height of the potential barrier increases and thus decreases the conductivity. This change in conductivity is directly related to the amount of specific gas present in the medium, hence the possibility of determining the presence and concentration of the gas.

## II. CHARACTERISATION

Onion-like Carbons (OLCs) are quasi-spherical nanoparticles, considered as multishell fullerenes, which consists concentric shells of graphitic carbon with sizes ranging between 5 to 10 nm. These types of nanoparticles can be synthesized through electron-beam irradiation, by arc discharge between two graphite electrodes in water, by vacuum annealing of nanodiamond (ND) powder at 1800°C or through laser ablation.

The OLCs structures used in our study have been obtained through annealing of carbon nanodiamonds in vacuum or in controlled atmosphere at slightly positive pressure in the presence of Helium (He) or Argon (Ar). This process lead to a productivity of over 90% and a higher purity of the nanodiamond. Nanodiamond produced through this method had a 5-7 nm diameter, and OLCs with 6 to 8 layers. Spherical OLCs were obtained through detonation of nanodiamond at 1650°C (Fig. 1).

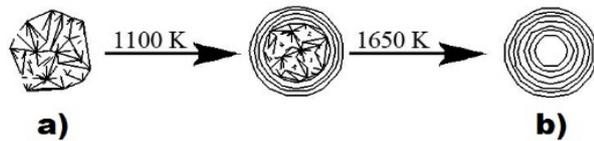


Fig. 1. Developing process of onion like carbons: (a) diamond nanoparticles, (b) spherical carbon onions.

The detailed preparation procedure of OLCs is presented in [12-13].

OLCs covers a multiple domain of applications as: energy storage devices [14-15], as electromagnetic shielding applications [16], application as catalysis, optical limiting and molecular junctions in scanning tunneling microscopy [17] and also has excellent mechanical properties so that it can sustain very high pressure [18]. An impressive list of applications in various areas of interest and an elaborated study regarding the OLCs functionalization methods is presented in [19].

As sensing element, Romanenko investigated in [20] the temperature dependences of the conductivity of onion-like carbon (OLC) and catalytic multiwalled carbon nanotubes (MWNTs) under exposure to various gas environments, and the conductivity suffered significant changes, but the curves of conductivity for the OLCs have no anomalies and are linear in the  $\ln[\sigma(T)/\sigma(300K)] - T^{-1/2}$  axis. Breczko investigated the OLCs as biosensing device within [21]. He presented the

development of carbon nano-onion (CNO) and poly(diallyldimethylammonium chloride) (PDDA) composite for detection of dopamine in the presence of ascorbic (AA) and uric (UA) acids. Joanna Luszczynand her colleges reported in [22] the first covalent functionalization of oxidized CNOs (ox-CNOs) with biomolecules, and the tests showed excellent cytocompatibility of all CNOs, so these carbon nanostructures can be safely used for biological applications. Diana M. Bobrowska et al. combines in [23] the hydrophilicity of surfactants with the robustness of carbon structures to produce carbon nano-onion/surfactant (CNO/surfactant) composites with superior and unusual physicochemical properties to assay the biological activity of well-dispersed CNO/surfactant composites against a strain of *Escherichia coli*. In [24] Juchan and coworkers studies the electrochemical performance of carbon nano-onions derived from nanodiamonds and discovers the remarkable electrochemical activities of CNOs with high sensitivity, high selectivity and stable electrode responses for the detection of biologically important molecules in comparison to the MWCNTs, graphenenanoflakes GNFs and glassy carbon (GC).

Although various researchers have developed sensing application for functionalized CNOs, a chemiresistor based on pristine nanoparticle as sensing probe for gaseous substances such as volatile compounds havenot been developed yet. To our knowledge this is the first attempt to develop a chemiresistor based on pristine OLCs.

To manufacture the chemisensors, the nanoparticles were deposited on a gold interdigitated microelecrod (IDE) via dielectrophoresis (DEP). The basis of this method of electromanipulation relies on the fact that a polarizable particles suspended in a fluid can be displaced towards or away from areas of strong electric field, generated by the IDEs fed with alternating current, when their permittivity is higher or lower than that of the suspending fluid [25].

For the particular case of a particle with spherical geometry, the dielectrophoretic (DEP) force has the following expression:

$$F_{DEP} = 2\pi r^3 \epsilon_0 \epsilon_m \text{Re}[K(\omega)] \nabla E^2, \quad (1)$$

where  $r$  is the radius of the spherical particle,  $\epsilon_0$  is the permittivity of free space,  $\epsilon_m$  is the permittivity of the fluid,  $E$  is the local electric field. The  $\text{Re}[K(\omega)]$  parameter is the real part of Clausius-Mossotti factor:

$$K(\omega) = \frac{\epsilon_p^* - \epsilon_m^*}{\epsilon_p^* + 2\epsilon_m^*}, \quad (2)$$

$\epsilon_p^*$  and  $\epsilon_m^*$  being the complex permittivities of the suspended particle and the fluid, respectively. In fact, the  $Re[K(\omega)]$  polarization dictates if the DEP force will be positive, when the particle's permittivity is higher than the fluid's permittivity or the other way around, when DEP force is negative.

To ensure the required electric field gradient for electromanipulating the OLCs, a gold IDE, manufactured by photolithographic techniques on glass substrate, was acquired from by DropSens, Spain, having 22.8 mm length and width of 7.6 mm. The IDE has a patterned comb shape composed of two interdigitated electrodes of 6760  $\mu\text{m}$  length with 250 digit each, 5- $\mu\text{m}$  digit width and 5- $\mu\text{m}$  gap between the digits.

To obtain the desired dispersion of OLCs in ethanol, a solution with 0.1  $\mu\text{g}/\text{ml}$  of OLCs/ethanol concentration was made, firstly being centrifuged for one hour to break the large agglomeration of OLCs and then the dispersion was ultrasonicated for two hours in a 130 W ultrasonic bath at 28 kHz frequency.

Particle trapping on microelectrode was accomplished by setting an arrangement setup based on a signal generator, a power amplifier to feed to the microelectrode and an acrylic chamber filled with a freshly developed dispersion of OLCs/ethanol through a peristaltic pump where the microelectrode was immersed.

Five OLCs-based chemiresistor gas sensors (CGSs) were manufactured by immersing the electrodes in the dielectrophoretic acrylic chamber, holding the signal amplitude at 20Vpp while frequencies were varied at a) 50kHz b) 100 kHz and c) 150 kHz. Another two sensors were made by holding the frequency at 100 kHz, and varying the signal amplitude to 10 and 30 Vpp, respectively.

Particle trapping were validated by optical observation via scanning electron imaging (SEM) as seen in Fig. 2.

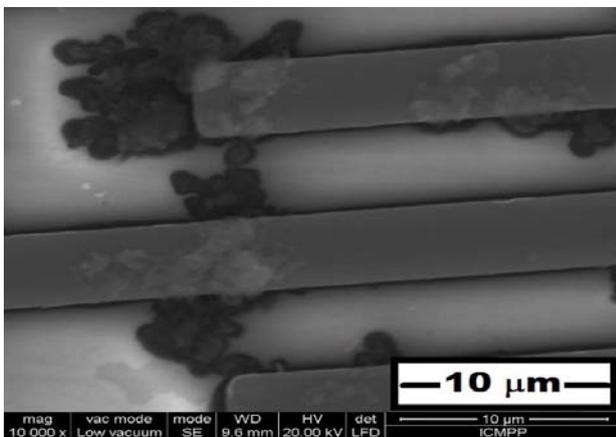


Fig. 2. SEM view of OLCs trapped between the electrode fingers.

Finally, the resistance of all the four sensors were measured with a digital multimeter (corresponding

trapping frequency): 50 kHz 20Vpp (136,05 Ohm), 100 kHz 20Vpp (36,9 Ohm), 150 kHz 20Vpp (64.36 Ohm), 100 kHz 10Vpp (46.8 Ohm), 100 kHz 30Vpp (68.3 Ohm). Also, an electrical characterization was performed through current-voltage (I-V) characteristic of all five sensors with a Keithley 2635 source meter interfaced with a personal computer (PC) by (General Purpose Interface Bus) GPIB interface, which confirms the "ohmic" contacts formed between the microelectrode's fingers.

All measurements were taken at 50% relative humidity and 25C temperature, inside a controlled environment chamber, values monitored with a thermohygrometer. The I-V characteristics were fitted with a linear function within a data analysis and graphing software Originlab OriginPro 2016 (Fig. 3).

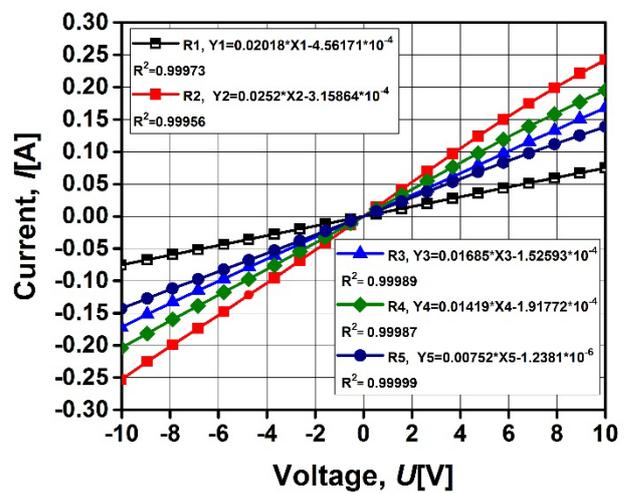


Fig. 3. I-V characteristics for all sensors: R1-50 kHz 20Vpp (120 Ohm), R2-100 kHz 20Vpp (40 Ohm), R3-150 kHz 20Vpp (60 Ohm), R4-100 kHz 10Vpp (50 Ohm), R5-100 kHz 30Vpp (60 Ohm).

### III. EXPOSURE TO AMMONIA

The measuring setup is presented through a schematic view in Fig. 4, which allows obtaining a mixture of ammonia (99.99 % purity) and dry air, while humidity is controlled through a bubbler. The gas concentration was controlled by mass flow controllers (MFC) and resistance changes of the CGS exposed to ammonia inside the acrylic chamber were acquired with a digital multimeter (DMM) connected to a personal computer (PC).

The test chamber was first purged with dry to clean up pre-absorbed moisture on the surface of the sensors. The relative humidity was controlled through a bubbler by varying the volumetric moisture content until it reaches the desired value.

All five sensors were exposed to ammonia (0-400 ppm with 50 ppm steps) and the output resistance was recorded.

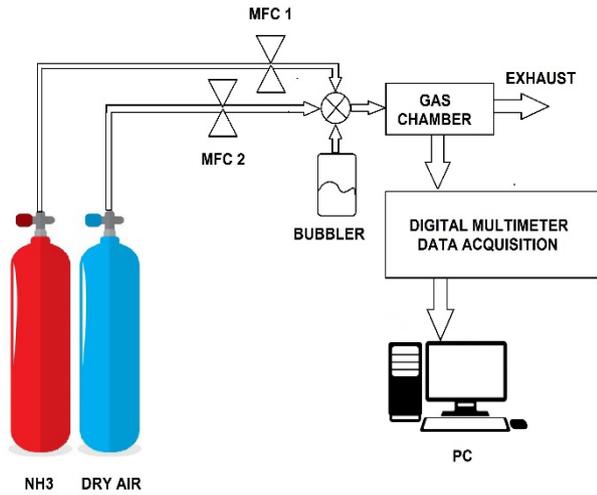


Fig. 4. Schematic setup for measuring ammonia and calibrating the CGS at ppm level.

In Fig. 5 normalized resistance  $R/R_0$  is plotted, where  $R_0$  is the initial resistance measured in clean air, while  $R$  is the change response resistance of the sensor under exposure to ammonia at different concentrations. Humidity was monitored continuously to eliminate it as parameter since its variations could influence the results.

Sensor R5 exhibits the most linear characteristic but it has a reduced sensitivity related to ammonia concentration. On the other hand, sensors R2 and R3 exhibits a very good sensitivity but also an increased pronounced non-linearity. Sensors R1 and R5 maintain a good linearity of characteristic while manifesting a good sensitivity to ammonia concentration. The plot in Fig. 6 depicts the repeated exposure of the CGS to fixed concentrations of ammonia in order to determine the recovery time and sensor's potential for other applications.

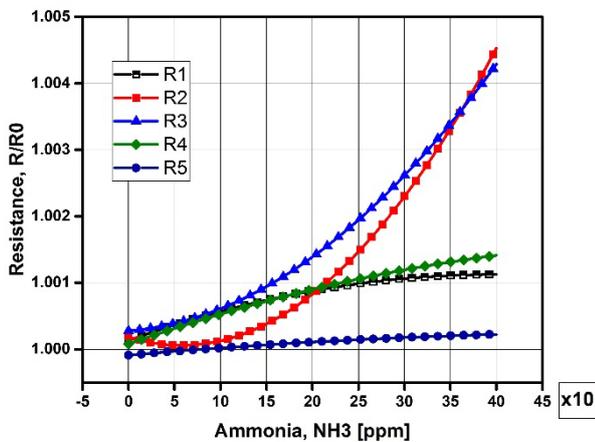


Fig. 5. Normalized resistance  $R/R_0$  of CGS exposed to 400 ppm  $NH_3$ .

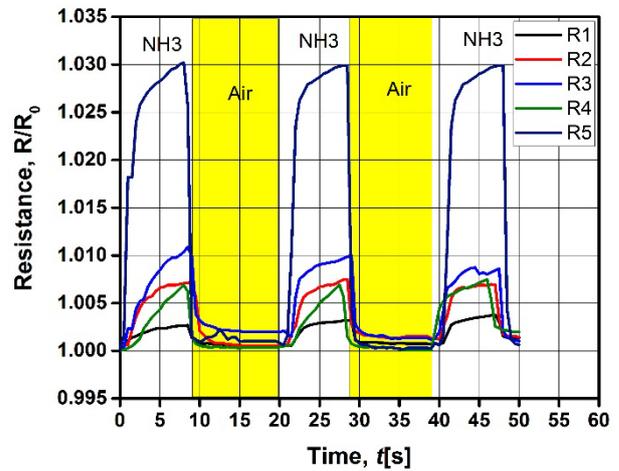


Fig. 6. Sensor's responses to repeated exposure of ammonia

Most of the ammonia molecules are released instantly after the CGS 's exposure to ammonia was stopped. This is due to the weak physisorption bond of the ammonia molecules to the OLCs. However, there are stronger bonds which are delaying the complete desorption process, as it can be noticed from Fig. 7.

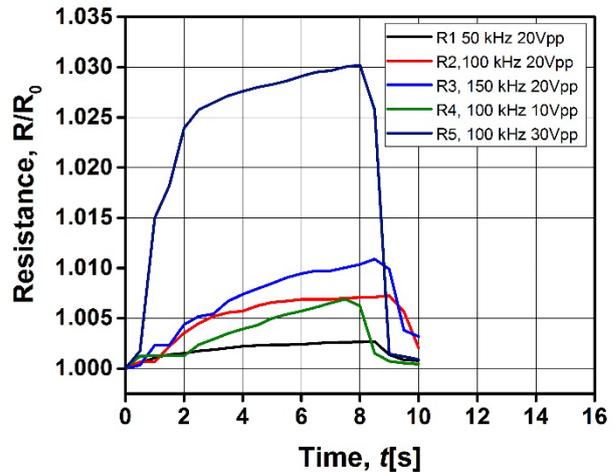


Fig. 7 Detailed view of sensors response to ammonia regarding the recovery time.

Special results on sensitivity and recovery time are obtained by sensor R5. The explanation of these results is attributed to the high voltage used in the particle electromanipulation method that has helped to produce an increased electric field and thus has led to the homogeneous distribution of carbon nanoparticles on the surface of the microelectrode. Sensor R5 manifests a sensitivity which is 10 times higher than sensor R1 and 3 times greater than that of sensor R3. Since a linear output of a sensor is desirable for interfacing a sensor with a microcontroller, and also an increased response time to be

inserted into a measurement setup, CGS sensor R5 proved to be the most suitable candidate for future gas sensing application.

Also the influence of an important parameter-humidity-was studied based on data acquired from sensors inserted inside a climatic chamber model KBF 115 (Binder), normalized resistance  $R/R_0$  being plotted in Fig. 8.

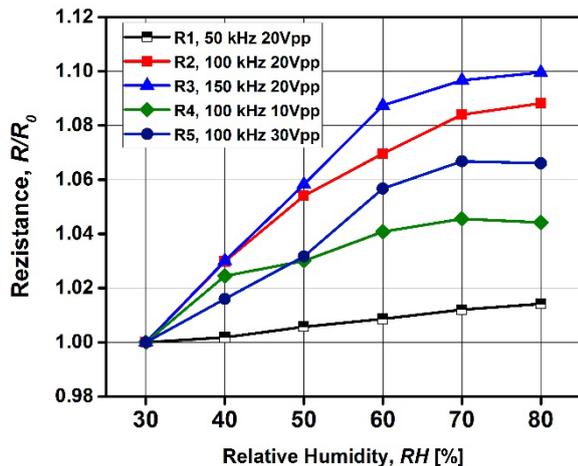


Fig. 8. Normalized resistance  $R/R_0$  of CGS regarding the influence of humidity.

Sensor R1, with a quasi-linear characteristic, is the less sensitive to humidity, while all other sensors manifest a very strong reaction to humidity and a pronounced curve of the resistance characteristic, sensor R5 having the highest sensitivity. All sensors exhibit n-type semiconducting behavior with gradual increase in relative humidity.

#### IV. CONCLUSIONS

Accidentally exposure of food to high concentration of ammonia during a malfunctioned fabrication process or contamination with ammonia generated as a result of decaying process as a result of improper storage of food could lead to severe trauma when ingested or inhaled. A smart food label for alerting the presence of this possible health hazard is an imperative requirement for the food industry concerning the safety of the consumer.

Within this paper a novel chemiresistor sensor, working at room temperature, based on onion-like carbon has been investigated as gas sensitive element. The sensing mechanism has been tested by measuring the resistance change between the sensors's terminal under exposure to ammonia.

The sensor developed in this paper is based on the use of pristine carbon nanoparticles of the OLCs type without any chemical treatment. The sensing mechanism in the sensor studied in this paper is largely based on reactions occurring on the surface of the sensor as a result of the

change in the concentration of oxygen absorbed. Oxygen ions adsorbed on the surface of the material (considering a n-type semiconductor material) extract electrons from the material and create a potential barrier that limits electron movement and conductivity. When ammonia combines with this oxygen, the height of the potential barrier increases and thus decreases the conductivity. This change in conductivity is directly related to the amount of specific gas present in the medium, hence the possibility of determining the presence and concentration of the gas. Carbon-based nanomaterials have the advantage associated with the particular volume-to-contact ratio and also the non-porous structure that allows the absorption of ions.

The sensor's low profile offers a facile integration into a smart label with a flexible substrate. Being a chemiresistor-type sensor, allows easy interfacing with microcontroller to be integrated into a wireless smart label. Also this type of sensor works without requiring a preheating, thus having very low energy consumption.

Special results on sensitivity and recovery time are obtained by sensor R5. The explanation of these results is attributed to the high voltage used in the particle electromanipulation method that has helped to produce an increased electric field and has led to the homogeneous distribution of carbon nanoparticles on the surface of the microelectrod. Sensor R5 has sensitivity 10 times higher than sensor R1 and 3 times greater than sensor R3. High sensitivity and low recovery time support the integration of this resistive sensor for ethanol detection into various mobile devices that allow the implementation of some warning algorithms.

#### V. ACKNOWLEDGMENT

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