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Development of a novel C-dots conductometric sensor for NO sensing

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ABSTRACT

Carbon dots (CDs, C-dots) obtained from waste produced during the production of olive oil in Calabria (Italy) have been investigated as a gas sensing material for the sensitive and selective detection of nitric oxide (NO) in air. The obtained CDs were characterized by XPS, FT-IR and ATR-FTIR. CDs were deposited to yield a sensitive layer on a conductometric platform and tested for gas sensing, showing promising characteristics for the selective monitoring of NO in air. The response of CDs composite to NO was 1.5 @ 1250 ppm and the response and recovery times amounted to 90 and 200 s, respectively. The sensing behavior of C-dots prepared using olive waste from a different geographic location (Puglia, Italy) was also reported and compared. It has been found that the sensing behavior of the two different materials based sensors investigated towards nitrogen oxides (NO and NO_2) was completely different. On the one hand, the former exhibited selectivity towards NO. On the other, the latter showed prominent selectivity towards NO_2. This behavior can be ascribed to the different functional groups exposed on the C-dots surface undergoing non-covalent interactions with a marked specificity of the hydroxyl and ethers moieties for NO and NO_2, respectively.

1. Introduction

Gas detection using low-dimensional carbon nanomaterials, such as carbon nanotubes (CNTs), graphene (G) or graphene oxide (GO), has been largely pursued in the last decade [1]. Indeed, because of their highest surface-to-volume ratio, almost all their composing atoms are exposed to the environment to readily interact with gas molecules, yielding high sensitivity in the sensing process. By taking advantage of such a unique setting, conductometric sensors based on these 1-D or 2-D carbon nanomaterials revealed a significant capacity of detecting trace levels of gases [2]. In this regard, carbon dots (CDs) are 0-D carbon nanomaterials which display unique interesting electrical and optical properties, making them interesting components for a plethora of applications in energy, (bio)medical, and environmental technologies [3,4].

CDs have quasi-spherical geometry with diameters below 10 nm. Its amorphous nucleus comprises sp^2 hybridized carbon and crystalline structures given by the sp^3 hybridized carbon. CDs can be synthesized by exploiting "top-down" and "bottom-up" approaches. In the top-down approach, they are obtained from large carbon structures using characteristic methods to reduce their size with control over their morphology, and purity. Powerful strategies include laser ablation, chemical and electrochemical oxidation, and ultrasound treatment. Conversely, "bottom up" protocols enable to achieve a subtle control over their size by exploiting inexpensive procedures such as microwave synthesis, thermal decomposition, and hydrothermal treatment [5].

During the last decade, much effort has been devoted to the use organic waste materials, also defined biomass, to obtain carbon nanomaterials by exploiting simple and low-cost synthesis methods [6,7]. Particularly, carbon dots produced from biomass exhibit different

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physical and chemical properties depending on the starting biomaterial and the preparation method adopted. Within this context, carbon dots have attracted much attention due to their unique optical, chemical, and electronic properties enabling a wide range of applications. Furthermore, CDs properties can be effectively adjusted by modifying their chemical composition.

Surface groups such as -COOH, -OH and -NH_2 are characteristics of these nanomaterials, and impart them excellent optical properties, so contributing to their excellent fluorescent, photoluminescent and optoelectronic properties [8]. However, little is known about the contribution of these surface groups to the optical and electronic properties of CDs [9,10]. The unique electrochemical and optical properties of CDs were largely exploited for chemical sensing [11] by focusing on their fluorescence and electrochemical characteristics for the detection of various metal ions in water (Fe^{3+}, Cu^{2+}, Hg^{2+}, etc.) and biomolecules [12].

Given their distinct properties, they could be also used as responsive materials to develop sensors capable to detect gaseous environmental pollutants. However, only a few studies have been reported so far on the application of CDs in gas sensing. In particular, previous studies used CDs as a support for the sensing phase, typically a metal oxide, and optical detection was the preferred transduction method [13,14].

In a previous introductory work, we fabricated a CDs-based conductometric sensor for NO_2 detection in air, demonstrating for the first time the use of pristine CDs in this kind of electrical solid-state device [15]. NO_2 is one among the harmful gases, which require low-cost and reliable sensors operating at room temperature and capable of detecting sub-ppm concentrations [16].

In this work we expand our endeavor to the use of CDs obtained from olive solid waste to monitor nitrogen monoxide (NO) in air by means of a conductometric sensor. The main NO emissions in the atmosphere derive from the exhaust gases of cars, in which NO is the most common form of NO_x at around 93%, around 100–2000 ppm (parts per million). The Environmental Protection Agency (EPA) indicated that these emissions cause environmental problems, triggering an increase in the greenhouse effect as it exhibits 310 times greater impact than CO_2 ultimately threatening human health through the onset of serious diseases related to the respiratory system. The maximum exposure value amounts to 20 ppm. Because of these reasons, the development of gas sensors that can perceive NO in real time is highly sought after. However, previous CDs-based sensors were not able to detect NO [15]. The CDs used in the above study was obtained from the solid waste in oil production, coming from Puglia, a region of Italy. CDs produced from solid waste in oil production coming from different geographical origin, display different surface groups composition, thus we have tested another CDs obtained from the solid waste in oil production coming from a different region (Calabria, Italy), with the scope to monitor NO as target gas.

Here we report the fabrication and characterization of CD based conductometric sensors displaying high sensitivity and selectivity for NO present in the air. The comparison with the previous CDs-sensor comprising was also made, attempting to explain the different sensing behavior observed. We found that our CDs hold high potential for the development of inexpensive gas sensors to monitor selectively the targeted gases, by simply designing its surface composition.

2. Experimental section

2.1. Carbon dots preparation

Carbon dots were prepared by using a bottom-up approach starting from the discard of olive oil production, by following the synthetic procedure reported in [15]. The olive solid wastes were purified with Soxhlet extraction method by using water as a solvent. The obtained biomass was dried, pyrolyzed in absence of air (600 °C, 1 h) and subsequently ground. 100 mg of the product was suspended in 10 mL of deionized water and sonicated in an ultrasonic bath for 10 min followed by the addition of hydrogen peroxide solution (0.45% wt in 10 mL). The reaction mixture was refluxed for 90 min and after cooling to RT centrifuged for 20 min (9900 rcf,). The supernatant was filtered with a 0.2 μm microfilter and finally purified by dialysis against MilliQ-water (500–1000 Da) for 24 h. The final powders of CDs, which were adopted for the development of the gas sensor, were obtained through lyophilization. C-CDs were obtained via bottom-up approach by pyrolysis of the solid waste of olive oil production from Calabria (Italy). We also investigated carbon dots prepared with olive solid waste coming from the olive oil production process in Puglia (Italy), called P-CDs hereafter.

2.2. Characterization

X-ray photoelectron spectroscopy (XPS) was performed on carbon dots deposited on silicon slides using a PHI 5600 multi-technique ESCA-Auger spectrometer (Physical electronics Inc., Chanhassen, MN, USA) equipped with a monochromatic Al-K X-ray source. The XPS binding energy (BE) scale was calibrated on the C 1 s peak of adventitious carbon at 285.0 eV. Transmission Fourier Transformed Infrared (FT–IR) measurements on the silicon-deposited carbon dots were obtained using a JASCO FTIR 4600LE spectrometer (JASCO Corporation, Tokyo, Japan) in the spectral range of 560–4000 cm^{-1} (resolution 4 cm^{-1}). Attenuated Total Reflection (ATR) FTIR analyses were performed using a Spectrum Two (Perkin-Elmer) FT-IR spectrometer with a diamond ATR single reflection accessory. X-Ray powder diffraction (XRD) patterns were acquired on thin films drop-cast on silicon wafers. Measurements were carried out in air environment at room temperature by means of a Bruker D8 Advance diffractometer (Bruker Co., MA - USA) with Cu Kα radiation ($\lambda = 1.54184$ Å) and a step size of 0.05° at 40 KV and 40 mA in the range of 2θ from 2° to 60°. Thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) were performed in a Mettler-Toledo TGA/DSC 2 STARe instrument (Mettler Toledo LLC, Columbus, OH – USA). Measurements were executed on Carbon dots powder (from 1 to 2.5 mg) both in synthetic air (Air Zero X50S, Air products, Saint Quentin Fallavier, France) and in pure nitrogen environments, starting from 25 °C to 600 °C (5 °C/min). Derivative Thermogravimetry (DTG) was calculated on the first derivative of the TGA curve.

2.3. Sensing tests

Sensor devices were fabricated by printing thick films of the C-dots dispersed in an aqueous solution on alumina substrates (6 ×3 mm^2) covered with Pt interdigitated electrodes and a Pt heater located on the backside. The sensing platform used for developing the conductometric sensors based on CDs has been reported in many previous our papers (see for example ref. [15]). The sensing tests were carried out using the data acquisition instrument Agilent 34970 A to monitor the resistance and a dual-channel power supply Agilent E3632A was used to bias the built-in heater of the sensor.

Sensing tests were performed using a homemade detection setup as follows; first, the sensor was inserted in a stainless-steel test chamber and was kept at a fixed temperature while a flow of synthetic dry air (O_2 + N_2) was passing over the sensing material to order to obtain a stable baseline resistance. Afterwards, the sensor was exposed to pulses of gas mixtures supplied from certified bottles of SOL company (www.sol-group.com). The sensor response to target gas (R) is determined as the ratio of R_a (resistance of the gas sensor in dry synthetic air) to R_g (resistance of the injected gas sensor), $R = R_a/R_g$. The calculation of the response and recovery time, i.e., the variation of the sensor resistance over time until it reaches 90% of equilibrium after the start and end of NO detection, allowed to study the sensor dynamics.

3. Results and discussion

3.1. Carbon dots material characterization

Carbon dots primarily comprise a carbon core, while their surfaces expose a large amount of reactive functional groups (such as -OH, -COOH/-COO⁻, etc.). Thus, a detailed characterization has been carried out for acquiring important information on the morphological, microstructural, and surface groups composition of C-CDs.

In our previous study [7], transmission electron microscopy (TEM) measurements confirmed that C-CDs display quasi-spherical monodispersed carbon nanoparticles. Their diameter distribution ranged from 15 to 20 nm. We determined further the phase, structure, and crystallinity of C-CDs by X-Ray powder diffraction (XRD). As illustrated in Fig. 1 the XRD diffractogram exhibits several peaks. The broad peak from 20° to 24° (2θ) and the sharp one at $2\theta = 24.35°$ (3.7 Å d lattice spacing) can be attributed to the amorphous carbon phase and to graphitic C(002) plane [17]. The graphitic nature of CDs is confirmed by the peaks located at 40–45° and 53.80° (D-spacing 1.7 Å), which are ascribed to C(100) and C(004) planes of graphitic carbon [18].

To characterize the groups exposed on the surface, FT-IR and XPS analyses were performed. The FT-IR spectrum of C-CDs sample is shown in Fig. 2a. Different vibrational signatures, due to surface groups, reveal the presence of -C═O (carbonyl), -COO⁻ (carboxylate), C–OH (hydroxyl), and C–O–C (ether) groups. In particular, the wide band in the 3500–3000 cm^{-1} region can be attributed to the stretching vibration of O-H groups [19–22]. The strong feature around 1600 cm^{-1} can be ascribed to convolution to the signals due to C═O stretching of carboxylic (1660 cm^{-1}) of acids or amides, to the asymmetric stretching of carboxylate (1570 cm^{-1}) and to the bending of H_2O (1620 cm^{-1}) [19–24]. The other strong features at about 1370 cm^{-1} correspond to convolution of the symmetric stretching of carboxylate groups (1450 cm^{-1}), the C-O stretches of carboxylic acids (1250 cm^{-1}) and the bending of OH groups (1350 cm^{-1}) [19–24].

XPS spectra showed the presence of C, O, N and K. Fig. 2b shows the C 1 s, N 1 s and O 1 s regions. The complex shape of the C 1 s signal is mainly due to the presence of C-C/C-H signal at 285.0 eV and to the signal at 289.0 eV of carboxylic groups. A component around 287.3 eV is observed which can be associated to the presence of carbons in carboxylates and amides groups [22–26]. Note a small amount of K^+ is also present.

The N 1 s band mainly reveals a peak at 400.4 eV that can be due to amines and amides (C-N containing groups) [24–26]. A small shoulder at about 399.0 eV can also be attributed to the formation of imine groups (-C═N-) [24–26]. Conversely, the O1s peak position at 532.2 eV is typical of the oxygen in organic compounds.

The thermal stability study on C-CDs was performed by TGA-DSC analysis. We noticed that C-CDs, in both synthetic air and nitrogen environments, are mainly stables until 200 °C, being the weight loss in this temperature range due mainly to water desorption (Fig. 3).

According to literature, the first decomposition stage (around 21–27% of the weight loss at 175–182 °C – Air/N_2) can be attributed to the loss of water on CDs surface [27]. The second decomposition stage (around 16–22% of total weight loss at 434–450 °C – Air/N_2) may be associated with the loss of covalently linked species to CDs surface and/or to the loss of oxygen-containing groups such as -O-C═O and C═O [28–30].

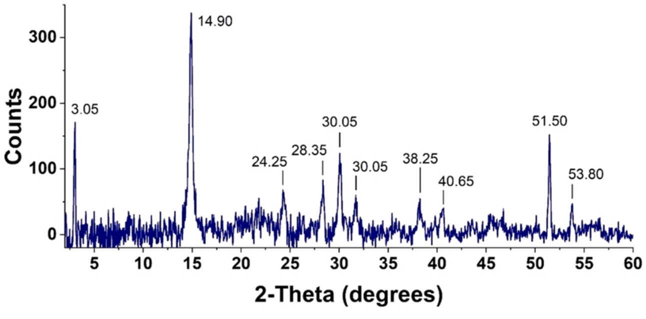

Fig. 1. XRD pattern of C-CDs.

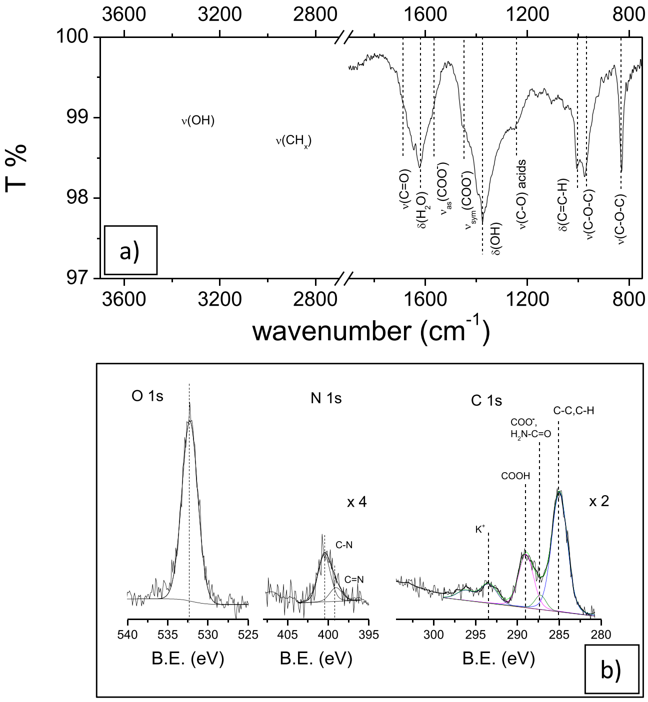

Fig. 2. a) FT-IR and b) XPS analyses.

3.2. Electrical characterization

The electrical resistance of C-CD films in dry air as a function of temperature has been investigated. The measurements were performed with the C-dots sample deposited as a layer on the conductometric platform used for the successive sensing experiments, making it possible to use the information obtained to optimize the performances. We started our measurements at room temperature and found a very high resistance of the sample layer (Fig. 4). Upon increasing the temperature there is a sharp decrease of the resistance. As CDs exhibit p-type behavior, the observed resistance decrease can be attributed to holes carriers, which are activated for the conduction upon temperature increase. In contrast to n-type sensing materials, such as metal oxides, a sharp decrease in resistance occurs by increasing the temperature, as CDs require a higher activation energy for the conduction than electrons.

Subsequently, we tested the sensing characteristics of the fabricated C-CDs sensor at operating temperatures ranging from 100 °C to 250 °C. For these measurements, NO was selected as the target gas. The choice of this target gas derived by considering that carbon nanostructures are largely used for monitoring nitrogen oxides [31].

Tests were performed by using NO at a concentration of 2500 ppm. The results displayed in Fig. 5 revealed that starting from 150 °C, the C-CDs sensor exhibits a reversible decrease of the resistance when NO pulse was injected in the sensor chamber. An increase in temperature is accompanied by an improvement in the reaction kinetics occurring on the surface of the material yielding to an increased response. The response reached a plateau at operating temperature of 200 °C.

In view of such temperature dependent response, it was concluded that C-CDs sensors operate better for a temperature set at 200 °C. The use of higher operating temperatures revealed a strong reduction in the lifetime of the sensing layer due to the occurrence of surface oxidation

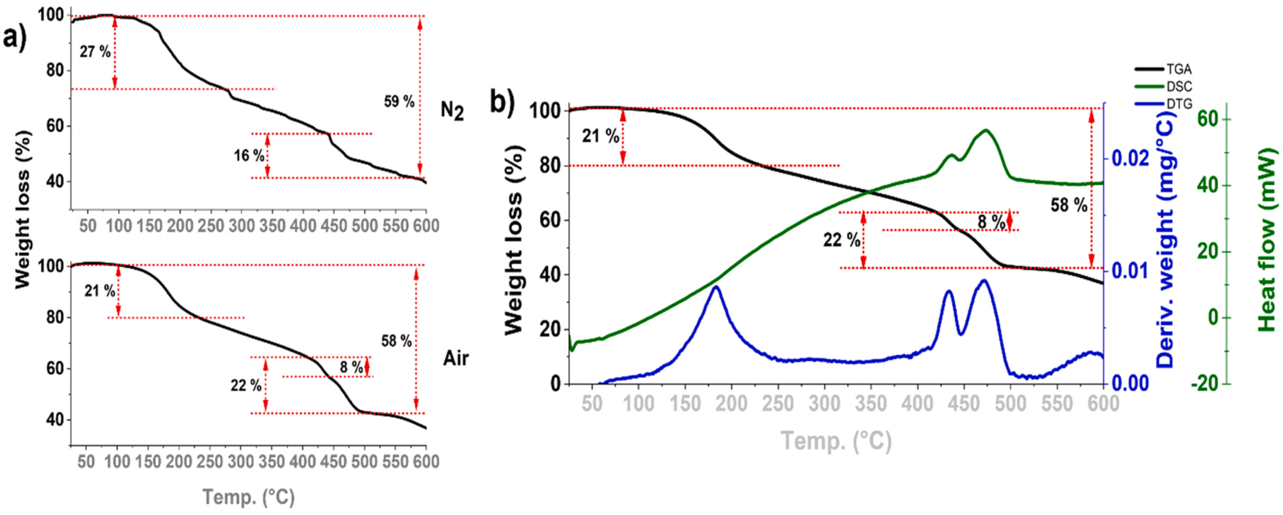

Fig. 3. a) TGA analyses in nitrogen and synthetic air of C-CDs; b) TGA/DTG/DSC graphs in synthetic air of C-CDs.

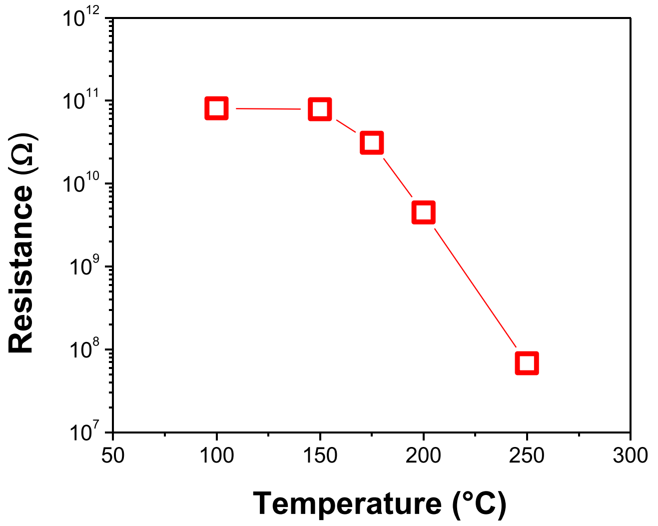

Fig. 4. Electrical resistance of C-CDs sensor as a function of the operating temperature.

[15]. As at the higher temperature tested (250 °C) surface oxidation of carbon dots may occur, the useful operating temperature "window" of the sensor was set to very narrow values, centered around 200 °C.

NO behaves as a strong π-acceptor, thus very likely yielding a strong binding between NO and the carbon dots surface The latter results in a decrease in the baseline resistance, as reported for other carbon nanomaterials [32]. We speculate that when the sensor is exposed to dry air, the oxygen molecules are adsorbed on the carbon dots surface to be ionized by electrons trapped by the semiconductor conduction band to yield oxygen ions such as O^{2-}, O^{-} or O_2^{-} depending on the operating temperature. In the presence of target gas, local doping effect occurs upon the absorption and subsequent reaction of NO with adsorbed oxygen species, ultimately leading to the observed resistance decrease.

Sensing tests were carried out to verify the performance of the C-CDs sensor towards the target gas. Therefore, the dynamics, sensitivity, reproducibility, stability over time and selectivity to the target gas in the presence of other interferent gases were also investigated. The dynamic of the C-CDs sensor was verified by testing the sensor to a concentration of 1250 ppm of NO at the operating temperature of 200 °C, as shown in Fig. 6. The quantified response and recovery time amount to approximatively 90 s and 200 s, respectively.

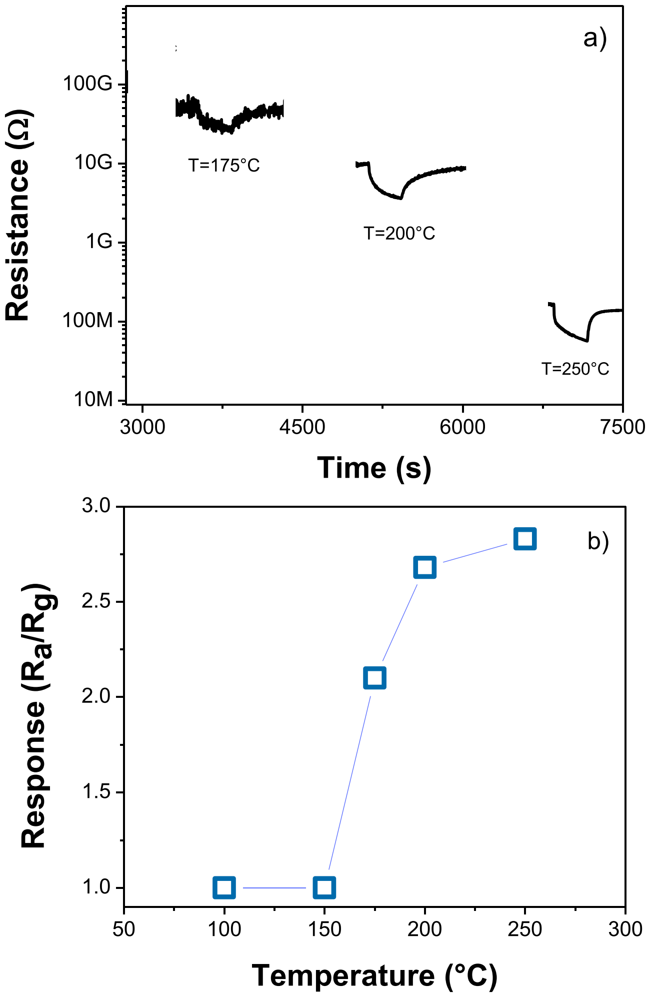

Fig. 5. a) Response at different temperature to 2500 ppm NO of the C-CDs sensor; b) trend of the sensor response vs. the temperature.

Furthermore, we have verified the response of the sensor to different concentrations of NO in the range from 125 to 4000 ppm (Fig. 7a). Moreover, to verify the presence of a memory effect, the sensor was tested at decreasing NO concentration (Fig. 7b). The response of the

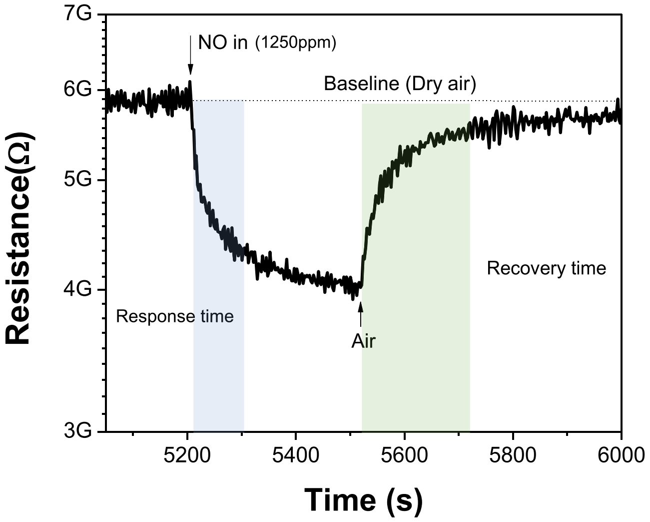

Fig. 6. Transient response of the C-CDs sensor.

sensor is reproducible over time for different concentrations, and the presence of any memory effect could be excluded (Fig. 7c). Further, the signal revealed a good reproducibilty (Fig. 7d).

The long-term stability is a fundamental characteristic for sensor applications. Temperature is the first factor affecting this characteristic because it can accelerate the degradation/oxidation of the most labile surface groups on the surface of CDs. From TGA/DCS study above reported, we demonstrated that C-CDs, in both dry synthetic air and nitrogen environments, are mainly stables until 200 °C, so CDs-sensors operating temperature is maintained in the range 150–200 °C. The sensor's long-term stability (as regarding both the electrical baseline in dry air and response to NO) has been tested for two months. Data (see Fig. 8) reveal that the baseline resistance increases a little bit, likely as a results of the slow surface oxidation of the sensing layer, but this do not appears to influence the long-term stability of C-CDs sensor response to NO in the operating conditions adopted.

Currently, we also are performing tests for acquiring information about the stability of the sensor in humid air. The effect of humidity (at rh = 50%) has been preliminary investigated. In the Fig. 9, is reported the effect of humidity (at rh = 50%) on pulses of NO, compared to the same in dry air. In particular, humidity increases a bit the baseline resistance and appears also to increase the noise. However, this does not influence so much the signal to NO pulses, indicating that little variations in both baseline resistance and signal response were caused by humidity.

Quantitatively, the change of 1% humidity has the same effect of less 25 ppm of NO. However,even if these preliminary results inferred that humidity do not influence remarkably the sensor performances, further investigations are necessary for assessing the effect of humidity on the long period and take the necessary action for limiting its adverse effects, if any.

The selectivity of the sensor was verified by evaluating the response to different interferent gases, i.e. CO_2. NH_3, NO_2 and CO. As displayed in Fig. 10, the high selectivity of the C-CDs sensor for NO over other species is confirmed.

Table 1 shows the comparison of our CDs sensor material with some

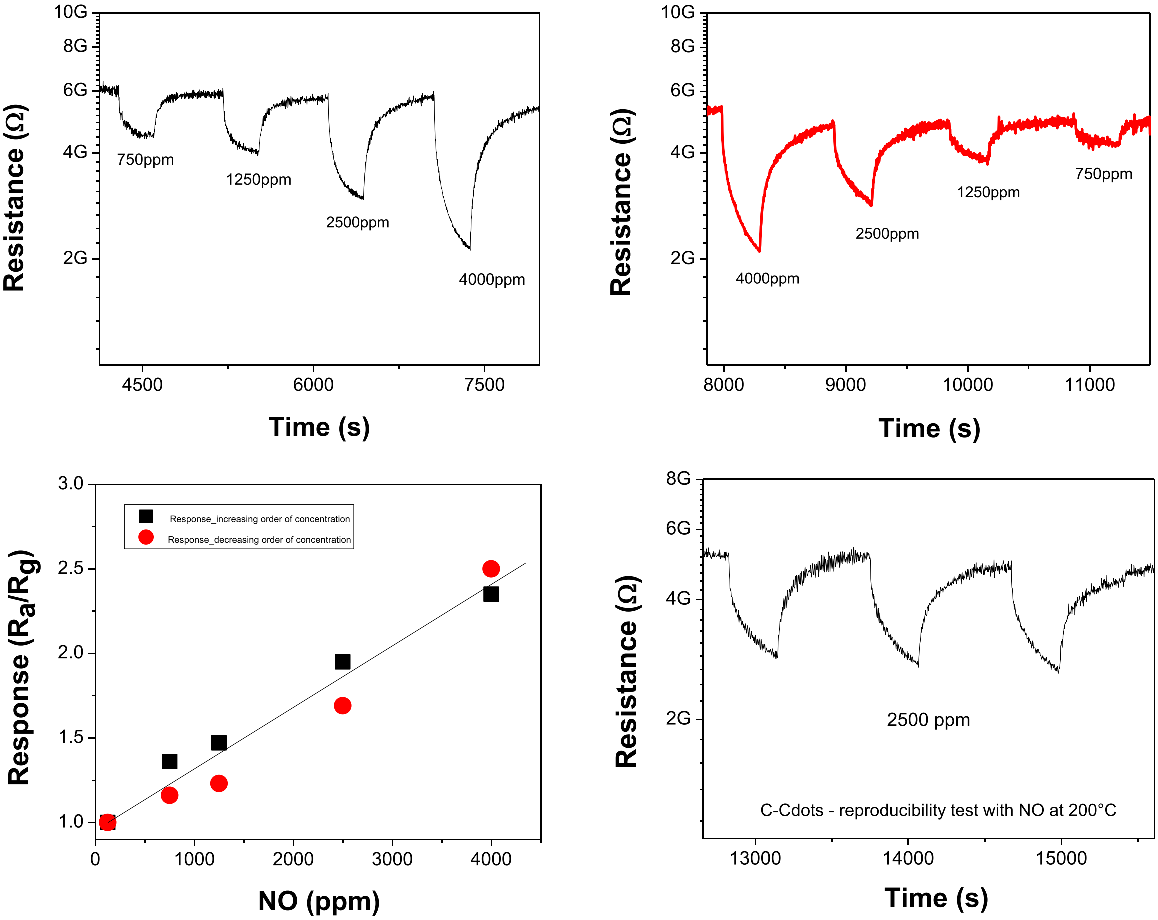

Fig. 7. Response of the C-CDs sensor at a) increasing and b) decreasing concentrations of NO; c) Calibration curve; d) Reproducibility of the signal over time at 2500 ppm of NO.

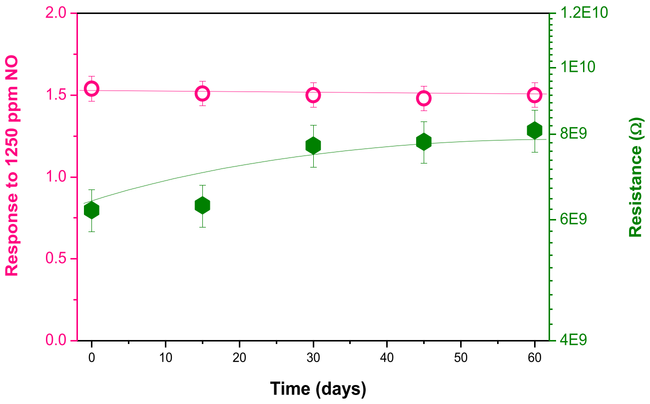

Fig. 8. Response of the C-CDs sensor registered at various times.

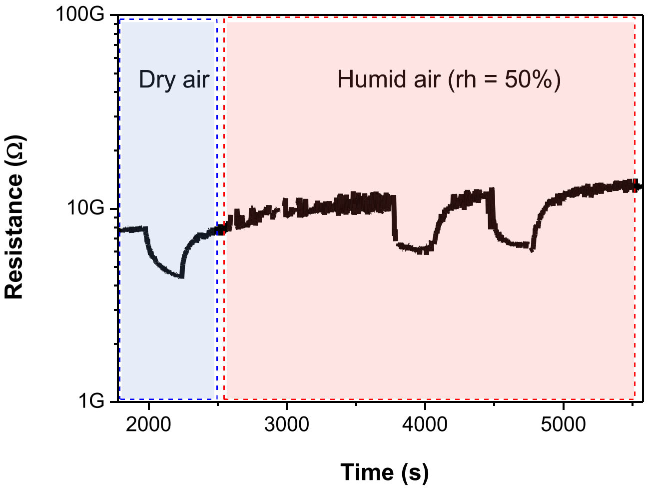

Fig. 9. Response of the C-CDs sensor registered at different humidity levels.

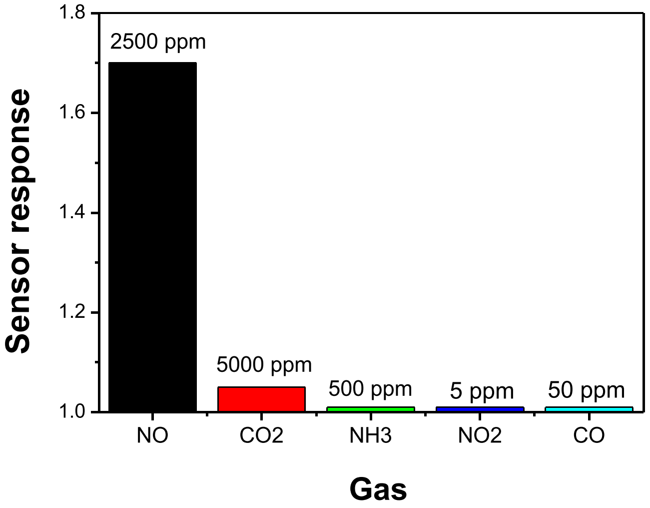

Fig. 10. Response of the C-CDs based sensor to different gases. The high response to NO, compared with the lower response to other gases, highlights the good selectivity of this sensor towards NO.

others found in the literature. Our material exhibits performances, in terms of operating temperature, sensitivity, selectivity, and response/ recovery time, that are comparable with the state-of-the-art, being a promising alternative.

Table 1

Comparison of NO sensing properties of different sensor materials.

Sensor material	Temp. (°C)	NO conc. (ppm)	Response time (s)	Recovery time (s)	Response	Ref.
C-dots	200	1250	30	200	1.50$^{\#}$	This work
GaN	35	100	280	2300	115%*	[33]
Bi-SnO_2	75	5	100	120	90	[34]
MoO_3	200	250	600	120	80	[35]
WO_3	300	500	63	88	37$^{\#}$	[36]
ZnO	28	10	135	130	1.7$^{\#}$	[37]

$^{\#}$ Ra/Rg or Rg/Ra;

* Ra-Rg/Ra or Rg-Ra/Ra where Ra and Rg represent the values of sensor resistance in presence of air and target gas, respectively.

3.3. Comparison between different CDs-based sensors and sensing mechanism

The above data unambiguously demonstrated that C-CDs sensors can detect selectively NO. In a previous paper [15] we reported a study on the sensing characteristics of a conductometric sensor based on C-dots prepared from olive oil production waste coming from a different geographic origin (Puglia, Italy). The two sensors exhibit a very different sensing behavior, presenting a large and different sensitivity and selectivity towards the nitrogen oxides, NO and NO_2.

To explain this behavior, we focused our attention on the surface characteristics of the two C-dots. Surface characteristics are very important in gas sensing, because the interaction between the gas and the sensing layer surface is mediated by the surface groups. Indeed, the gas-sensing mechanism of conductometric gas sensors is well known to be primary related to the adsorption/desorption and surface reaction of gases on surface groups [38–40].

FT-IR investigation provided information on the surface groups. Indeed, FT-IR analysis showed that C-CDs have a large signature attributed to presence hydroxyl groups, while the ether one prevails on P-CDs. Obviously, the band intensity is expected to change with the temperature, which is related to the different thermal stability of the surface groups. Then, to investigate the sensor surface in the same conditions under which operate the sensor, we carried out an in situ ATR-FTIR investigation on the sensor platform (see Fig. 11).

By comparing the ATR-FTIR results collected at different temperatures (from room temperature to 200 °C), we could confirm that the two C-dots samples investigated show different functional groups. Interestingly, the differences noted at room temperature are retained at high temperatures (max. 200 °C). Another interesting aspect was highlighted by ATR-FTIR carried on the sensor devices after about months of functioning. Indeed, the ATR-FTIR patterns reported in Fig. 12 show clearly that the surface groups on CDs have undergone small changes, confirming the good stability of the sensing material in the operative conditions adopted.

For a quantitative comparison about the sensing characteristics of the two sensors, we used the $S = R_{NO}/R_{NO2}$ ratio, where R_{NO} and R_{NO2} is the response to NO and NO_2, respectively, at the concentration of 2500 ppm for NO and 5 ppm for NO_2. For the C-CDs sensor, the above ratio is very high ($S > 23$), while for sample P-CDs is around 0.1. These values clearly indicate that C-CDs sensor is selective to NO, while P-CDs is selective to NO_2.

Our data reported above indicate that ether and hydroxyl are the main functional groups presents on C-CDs and P-CDs surface, respectively. The presence of these functional groups in other carbon nanomaterials such as CNT, graphene or GO provides the active defect sites for the adsorption of nitrogen oxides, which has been related to the improvement of the binding and charge-transfer properties [41]. In a computational study, Salih et al. [42], explored the interaction of nitrogen oxides with graphene nanoribbons differently functionalized on

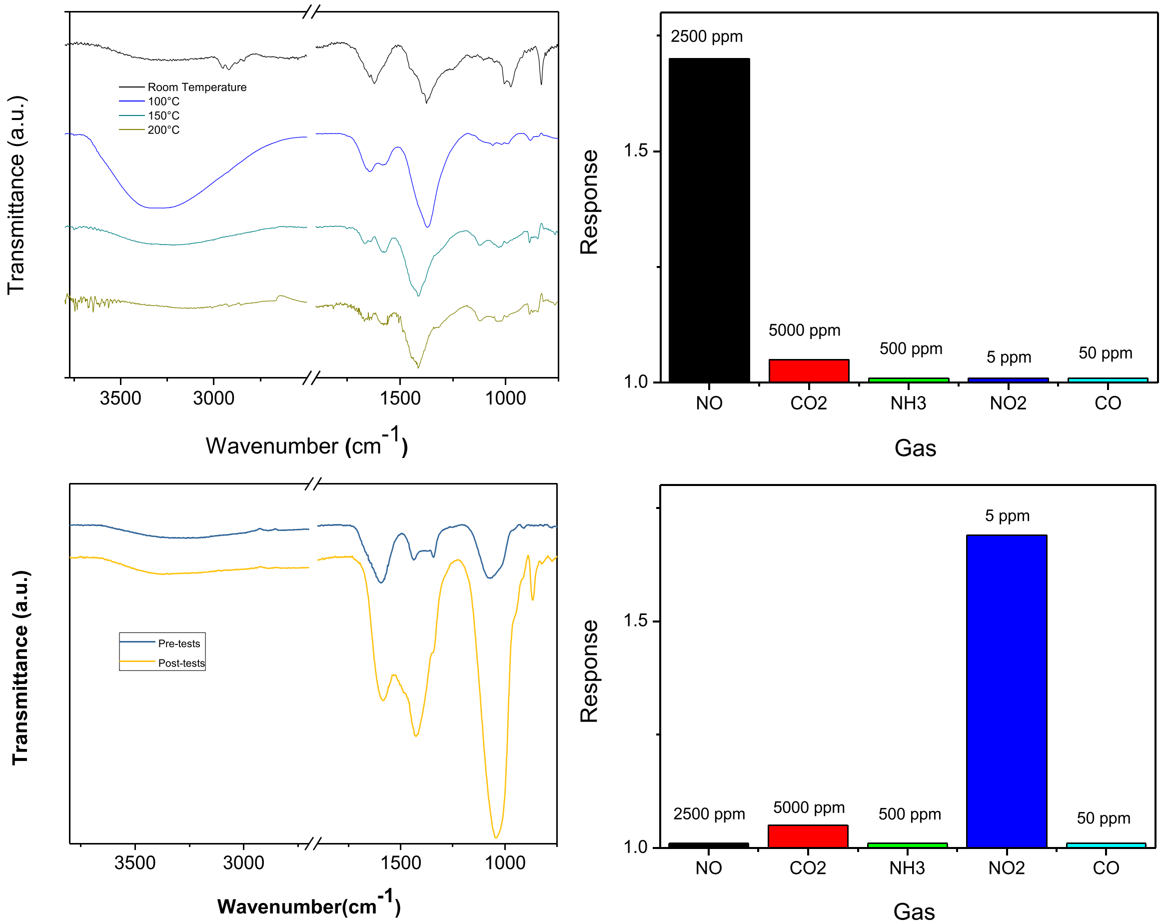

Fig. 11. a) ATR-FTIR spectra and b) selectivity plot for the C-CDs sensor; c)ATR-FTIR spectra and d) selectivity plot for the P-CDs sensor.

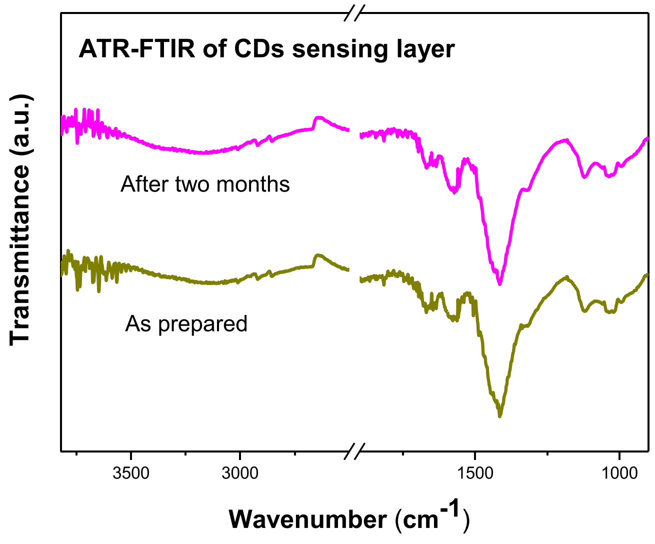

Fig. 12. a) ATR-FTIR spectra for the C-CDs sensor as prepared and after a functioning period of about two months.

the surface. The results of this study indicate that ZGNR-OH is the most selective to NO gas. Instead, ZGNR-O-OH can be considered as promising gas sensors for NO_2. Tang et al. reported a density functional calculations study on the adsorption of nitrogen oxides on graphene and graphene oxides [41]. These predictions are in accordance with experimental data here reported. In addition, Arunragsa et al. reported computational calculations which confirmed the hypothesis that the OH functional group was a major contributing factor to the NH_3 sensitivity and selectivity on graphene quantum dots (GQDs) modified via edge functionalization [43]. Another example illustrating the structure-activity relationship of surface OH groups during NO_2 reaction on TiO_2 and the generation of nitrogen-containing species has been reported by Liu et al. [44].

Based on the above literature reports and our gas sensing results, a schematic representation of the gas sensing mechanism in these CDs sensors is illustrated in Fig. 13.

The main pathway to be highlighted is the chemisorption of target gaseous molecules (NO, NO_2) on CDs and the subsequent interaction with the surface groups. Indeed, the interaction of nitrogen oxides with these functional groups results in the formation of different chemisorbed species. These intermediates can further react with the adsorbed oxygen species, explicating the transduction function. Based on the previous computational studies, the charge transfer per NO_2 increases as the number of hydroxyl group decrease, suggesting that the P-CDs sensor will increase the sensor response to this gas, as observed experimentally. The opposite behavior observed on C-CDs sensor, leading to prominent NO selectivity, agree with this view.

4. Conclusion and final remarks

In this work, we focused our attention on the sensing properties of conductometric platforms based on C-dots, acting as sensing layer for common gas pollutants, such as NO and NO_2. Comparing the sensing properties of C-dots coming from olive waste of different geographic origins, we observed opposite sensitivity and selectivity towards these gases, which has been explained by the presence of different functional

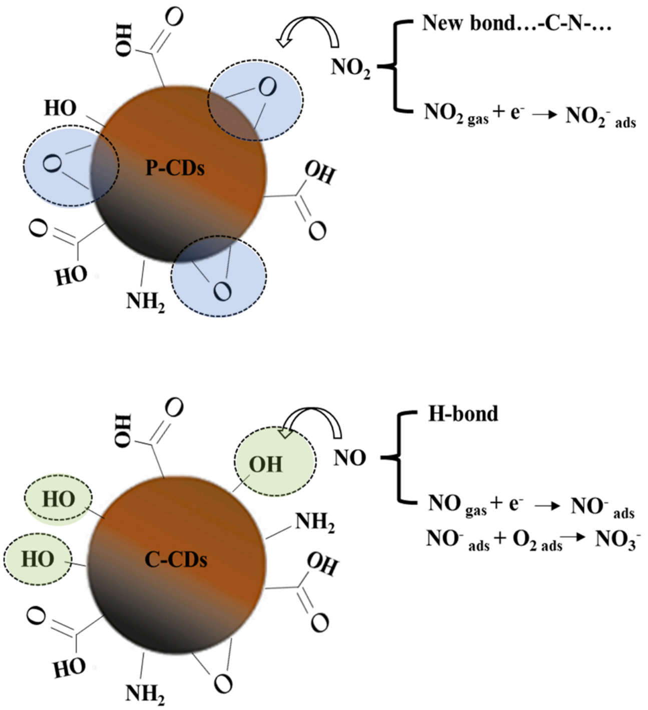

Fig. 13. Schematic representation of the NO and NO_2 sensing mechanism on C-dots sensors.

groups on the surface of these CDs. We believe that developing controllable synthetic and production methods, will greatly extend the application of CDs-sensors for other target gases. Establishing structure-to-property relationships in CDs will enhance understanding the gas sensing mechanism of CDs-based materials. For the practical application of these sensors, however, some issues need to be still addressed, such as the effect of humidity on the long-term affordability and stability.

CRediT authorship contribution statement

S. Crispi, **G. Nocito**, **F. Nastasi**, **G. Condorelli**: Investigation. **G. Condorelli**, **A. G. Ricciardulli**, **P. Samorì**, **S. Conoci**, **G. Neri**:: Supervision. **S. Conoci**, **G. Neri**: Writing- Reviewing and Editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

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