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Carbon-dots conductometric sensor for high performance gas sensing

Shadi Sawalha[a,b,1], Kaveh Moulaee[c,1], Giuseppe Nocito[d], Alessandro Silvestri[e], Salvatore Petralia[f], Maurizio Prato[e,g,h,i], Simona Bettini[b], Ludovico Valli[j], Sabrina Conoci[d,k,l,**], Giovanni Neri[c,*]

[a] Department of Chemical Engineering, An-Najah National University, Nablus, Palestine
[b] Dipartimento di Ingegneria dell'Innovazione, Università del Salento, Lecce, Via Monteroni 73100, Italy
[c] Dipartimento di Ingegneria, Università di Messina, Contrada Di Dio, Messina 98186, Italy
[d] Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali (ChiBioFarAm), Università di Messina, Viale F. Stagno d'Alcontres 31, Messina 98186, Italy
[e] Center for Cooperative Research in Biomaterials (CIC biomaGUNE), Basque Research and Technology Alliance (BRTA), Paseo de Miramon 182, Donostia San Sebastián 20014, Spain
[f] Dipartimento di Scienze del Farmaco e della Salute, Università di Catania, Viale Andrea Doria 6, Catania 95125, Italy
[g] Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM), Via G. Giusti 9, Firenze 50121, Italy
[h] Center of Excellence for Nanostructured Materials (CENMAT), Dip. Di Scienze Chimiche e Farmaceutiche, Università di Trieste, Via Giorgieri 1, Trieste 34127, Italy
[i] Ikerbasque, Basque Foundation for Science, Plaza Euskadi 5, Bilbao 48009, Spain
[j] Dipartimento di Scienze e Tecnologie Biologiche e Ambientali, Università del Salento, Via Monteroni, Lecce 73100, Italy
[k] STMicroelectronics, Stradale Primosole 50, Catania 95121, Italy
[l] Istituto per la Microelettronica e Microsistemi, Consiglio Nazionale delle Ricerche (CNR-IMM), Ottava strada n. 5, I-95121 Catania, Italy

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ABSTRACT

In this paper the first example of using C-dots (CDs) as sensing nanomaterial for monitoring low concentrations of NO_2 in ambient air is reported. In the logic to support a green circular economy, CDs were prepared from a natural low cost precursor consisting in olive solid waste (OSW) by a simple pyrolysis process combined with chemical oxidation. Characterization data showed the formation of spherical CDs with dimensions in the narrow size range from 0.5 to 5 nm and charged with functional groups (COO- (carboxylate), C-O-C (epoxide) and C-OH (hydroxyl) imprinting excellent water colloidal dispersion. The nanomaterial was used to fabricate and test a conductometric gas sensor (CDs-sensor) that was found to exhibit excellent performances in terms of high and selective response to sub-ppm concentration of NO_2 at low temperature (150 °C), low limit of detection (LOD) of 50 ppb, good reproducibility and stability over use and aging. To the best of our knowledge, this is the first example reported in the literature of CDs high performances gas sensing material. Results here presented pave the way for a new class of a carbon nanomaterial for gas sensing to be applied in the field of environmental monitoring.

1. Introduction

Carbon dots (CDs) represent one of the most promising nanomaterial for many advanced applications due to their multifunctional properties deriving from their unique quantum confinement and edge effects [1,2]. They also exhibit high chemical stability and good conductivity which, coupled with the very high surface area, can address effectively the use of CDs for sensing applications. In a recent review paper, the use of CDs for sensing towards several class of both organic and inorganic analytes has been extensively described [3]. However, most of the studies address sensing applications focusing on both CDs fluorescence and electrochemical properties as transduction detection method. Target analytes were mostly metal ions (Fe^{+3}, Cu^{2+}, Hg^{2+}, etc.) and electroactive (bio)molecules (H_2O_2, dopamine, glucose, etc.) [3].

Surprisingly, no particular attention has been given to CDs as material for gas sensing that is one of the most important ap-

* Corresponding author.
** Corresponding author at: Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali (ChiBioFarAm), Università di Messina, Viale F. Stagno d'Alcontres 31, Messina 98186, Italy.
E-mail addresses: sconoci@unime.it (S. Conoci), gneri@unime.it (G. Neri).
[1] These authors contributed equally to this work.

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plicative sector for environmental sustainability. Limited study appeared only very recently. In one paper, a CDs-based quartz crystal microbalance sensor was used for the detection of gaseous formaldehyde [4]. In another work, Shauloff et al. fabricated an artificial nose based on CDs as the principle capacitance sensing determinant [5]. However, conductometric (resistive) sensors, which represents the most suitable, practical and cheaper gas sensing technology for monitoring a wide variety of gases [6], based on CDs are not reported so far.

In the environmental pollution, one of the most dangerous gas is nitrogen dioxide (NO_2) representing a relevant source of atmospheric pollution being a product of burning fossil fuel in industry, power plants, houses heating, and car engines. It relevantly contributes to particulate matter, photochemical smog and acid rain and it is very toxic for human health even at very low concentrations [7–10]. Therefore, sensitive, selective and easy to use sensors for NO_2 monitoring in both industrial and urban areas are strongly required and today no satisfactory solutions are present [11]. In this respect, only one study has been reported for optical detection (fluorescence) of NO_2 gas using a hybrid carbon nanodot functionalized aerogel (CDs/SiO_2,) tested in a pure nitrogen atmosphere [12]. Also for the electrical detection, a single example describing a conductometric sensors uses a hybrid reduced graphene oxide-carbon dots (rGO–CD) sensing material has been described so far [13,14]. However, both above mentioned studies have practical limitations. Actually, CDs/SiO_2 fluorescence material has been demonstrated to work only in N_2 atmosphere, displaying a detection of limit of 250 ppb, which rule out its use for the low concentrations of NO_2 to be monitored in ambient air. In this respect, the Environmental Protection Agency (EPA) has settled one-hour exposure to NO_2 at the level of 100 ppb. Further, these work are based on sensing layer obtained by complex and multi-step synthetic procedures for the preparation.

In this work we present the first example of pure CDs sensing nanomaterial exhibiting excellent performances towards NO_2 monitoring in conductometric sensor architecture with selective and sensitive response up to sub-ppm concentrations of NO_2 in air.

The CDs here used were obtained from olive solid wastes (OSWs) raw material, an agricultural waste from the olive oil industry, highly appealing from an economical point of view due to its abundance and low cost [15]. Actually, OSWs are produced in massive quantities during olive oil production and represent a waste with high pollution potential. Therefore, providing to its reuse is within the logic of the circular economy. The transformation of OSWs in CDs here described leads to carbon nanoparticles having very small particle size, which implies an extremely large surface-to-volume ratio and hence an elevated proportion of highly reactive sites. These features make these materials very appealing candidates for gas sensors material with high performance. Further, the easy processability of CDs enables the use of a facile integration on a variety of sensing platforms made in plastics, ceramics, or silicon, so offering different possibility for various practical applications. Finally, due the lack of investigation on CDs for gas sensing, this study can also represent a stimulus for further investigations on these nanomaterials in the environmental sensor field.

2. Experimental section

2.1. Synthesis of carbon dots (CDs)

The CDs were prepared according to the method reported in [15]. Briefly, olive solid wastes (OSWs) (collected from Puglia – Italy) were purified from impurities by means of Soxhlet extractor using water as a solvent. The purified OSWs then were pyrolyzed for 1 h at 600 °C to obtain a carbon-based material named as carbonized olive solid wastes (COSWs). 0.1 g of COSWs was dispersed in 10 mL of 0.45 wt% H_2O_2 aqueous solution and sonicated for 10 min. The mixture was then refluxed for 90 min. When cooled down to room temperature, the brownish supernatant obtained after centrifugation (9900 rcf for 20 min) was filtered through 0.2 μm microfilter and then dialyzed against MilliQ-water through a dialysis membrane (500–1000 Da cutoff). When required the CDs solution was lyophilized to obtain a dry brown powder.

2.2. Morphological and surface charge characterizations

Transmission Electron microscopy (TEM) analysis was performed by JEOL JEM 1400-Plus microscope operated at an accelerating voltage of 120 kV, equipped with GATAN US1000 CCD Camera. Samples were prepared by drop casting of CDs solution on Lacey carbon film coated copper TEM grids.

AFM images and profiles were acquired by multimode V AFM from Bruker microscope on drop casted diluted CDs solution on silicon substrates.

ζ-potential measurements were conducted using a Malvern Nano ZS90 Zetasizer at room temperature.

Raman measurements were carried out using a Horiba Raman XploRA coupled with Olympus BX 41 with a laser excitation source at 532 nm (power 0.125 mW cm^{-2}).

2.3. Cyclic voltammetry

Cyclic voltammetry (CV) was carried to estimate the HOMO and LUMO energy levels of the CDs and the band gap. The electrochemical measurement was performed by the electrochemical workstation Autolab MSTAT204 Potentiostat/Galvanostat using a three-electrode electrochemical cell with a glassy carbon (3 mm Dia.) working electrode, an Ag/AgCl reference electrode, and a platinum counter electrode (Pt wire) in a 20 mL acetonitrile solution containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte and 1 mL of 1 mg/mL CDs solution. Cyclic voltammetry of the sample was run at a scan rate of 50 mV/s at room temperature.

2.4. Sensing tests

Devices for the sensing tests were fabricated by printing thick films of the C-dots powders dispersed in water on alumina substrates (6 mm × 3 mm) and provided by Pt interdigitated electrodes and a Pt heater located on the backside [8]. For the sensing tests, the sensors were introduced in a stainless-steel test chamber and after an initial time of stabilization at the fixed working temperature in flowing synthetic dry air (20% O_2 in nitrogen), exposed to pulses of gas mixtures of selected composition.

Electrical measurements were collected through a data acquisition unit Agilent 34970A, while a dual channel power supplier instrument Agilent E3632A was employed to bias the built-in heater of the sensor. The concentration of NO_2 was varied from 140 ppb to 2.8 ppm. The gas response, S, is defined as $S = R/R_0$ for NO_2, where R is the electrical resistance of the sensor at different NO_2 concentrations and R_0 is the baseline resistance in dry synthetic air. Dynamic characteristics, such as response time, τ_{res}, defined as the time required for the sensor resistance to reach 90% of the equilibrium value after the target gas is injected and recovery time, τ_{rec}, taken as the time necessary for the sensor resistance to reach 90% of the baseline value in air, were also evaluated.

3. . Results and discussion

CDs was produced by using OSWs as starting material (see Scheme 1). First, the pyrolysis of OSWs at 600 °C for one hour has been carried to produce carbonized olive solid wastes (COSWs).

Scheme 1. . Schematization of the synthesis process of CDs.

The chemical oxidation of this intermediate material was employed to obtain CDs using H_2O_2 as an oxidizing agent. Optimization of H_2O_2 concentration (0.45 wt%) led to CDs of low diameter with a production yield of 10%. H_2O_2 is beneficial for breaking down the carbonaceous particles and extracting CDs with surfaces rich of oxygenated groups [15].

The morphology of the CDs obtained from OSWs has been investigated by TEM and AFM

The HR-TEM micrographs show well dispersed nanoparticles with good contrast and narrow size dispersion ranging from 1 to 4.5 nm as shown by the size distribution histogram drawn from TEM images and an average size of 2.8 ± 0.6 nm (Fig. 1a and b). Similar dimensions have been obtained by AFM for the height of the CDs with a range of 0.5 to 5 nm having an average of 2.8 ± 0.9 nm, demonstrating that the particles have quasi-spherical morphology (Fig. 1c,d)

The functional surface groups were investigated using FTIR spectroscopy (Fig. 2). The peaks shown at 3424, 3236, 2923/2850, 1656, 1412, 1320 and 1116 and 1096 cm^{-1} are assigned to –OH, N-H, C-H, C=O (carbonyl), COO- (carboxylate), C-OH (hydroxyl) and C-O-C (epoxide) [16,17] groups, respectively. The presence of such functional groups implies that the synthesized CDs have excellent water-soluble colloidal dispersion [18]. It was also found that these dots are negatively charged with ξ-potential = 32 mV in 10 mM PBS, the negative charge could be ascribed to the existence of oxygenated functional groups [19–21].

Raman spectrum of the CDs sample is provided in the Fig. S1 in the Supplementary Information. Weak D and G bands, at about 1370 and 1590 cm^{-1}, respectively, can been recognized in the Raman pattern. Further, a very high photoluminescence background is also presents, covering the Raman signals and hindering a deeper investigation. The photoluminescence background is likely due to the existence of chemical groups on the surface of carbon dots, such as C=O and -NH_2, and the presence of amorphous carbon.

In terms of conduction properties, the synthesized CDs evidence a semiconductor behavior with a band gap of 1.55 eV, estimated from the difference between LUMO (-4.24 eV) and HOMO (-5.79 eV) energy levels [22]. The HOMO – LUMO levels were calculated from oxidation and reduction onset resulted from the cyclic voltammogram (see Fig. 3a) using the Eqs. (1) and (2):

$$HOME = -[E_{onset,ox} + 4.66\,eV] \quad (1)$$

$$LUMO = -\left[E_{onset,red} + 4.66\,eV\right] \quad (2)$$

where $\boldsymbol{E_{onset,ox}}$ and $\boldsymbol{E_{onset,red}}$ are the onset of the oxidation and reduction potentials respectively [23,24].

The semiconductor behavior has been confirmed by analyzing the electrical resistance of thick films (around 10 μm) at different temperatures. The electrical measurements have been performed on the same platform used for the conductometric sensing tests (Fig. 3b), with the aim to acquire also direct information on the behavior of CDs as a sensing layer in the practical device. In the inset of this Fig. 3b is noted CDs deposited as thick films by printing on the conductometric transduction device having a pair of interdigitated Pt electrodes on the ceramic substrate.

The range of temperature investigated was between 50 °C and 200 °C due to both the restrictions imposed by the very high resistance registered below 50 °C and the unstable and large baseline drift observed at temperatures higher than 200 °C. The trend of baseline resistance in this temperature range is reported in Fig. 3c. At near room temperature, the resistance is out of the range of

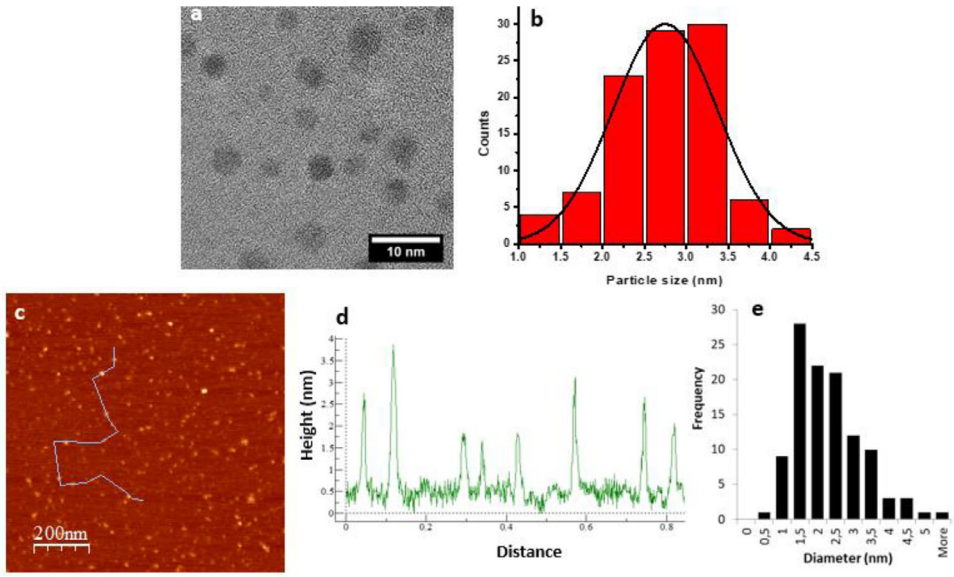

Fig. 1. Morphological characterization of CDs: (a) HR-TEM micrograph, (b) TEM size distribution histogram, (c) AFM height micrograph, (d) AFM height profile, (e) AFM height distribution histogram.

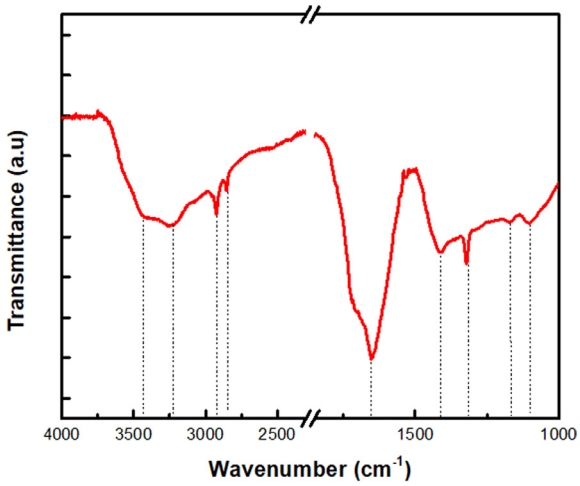

Fig. 2. FTIR spectrum of synthesized CDs.

measurement with our instrumentation. Increasing the temperature, the resistance decreases, as expected by a semiconductor material. This behavior can be explained as follows: at low temperature, free electrons are trapped by O_2 molecules as ionized species (O^- or O^{-2}), generating a depletion layer (Schottky potential barrier); further, the grain boundaries at the contact between the very small CDs might create additional potential barriers, increasing the electrical resistance. Increasing the operating temperature, thermally generated electrons give the main contribution to the resistance decrease. However, as an additional process due to the adsorbed O_2 molecules desorption from the CDTs surface upon increasing of the temperature, releases the trapped electrons and decreases the resistance.

On the basis of above described electrical characteristics that make CDs to be full compatibles for their use in conductometric platform for gas sensing, we have tested its performances in the monitoring of low NO_2 concentration in air. First, we evaluated the effect of operating temperature on the sensor response. Fig. 4a reports the variation of resistance for the CDs sensor subjected to pulses of NO_2 at the concentration of 2 ppm in dry air.

From the above reported data, it clearly appears that the CDs-based sensor is very sensitive to NO_2 gas exposure exhibiting a tendency to a response enhancement with the temperature decrease. However, by reducing the temperature, the recovery time becomes longer (see Fig. 4b) and this limits the practical application of the sensor. Therefore, the best balance between high response and faster dynamics can be settled at 150 °C. Fig. 5a reports the resistance variation for the CDs sensor, at the optimal temperature of 150 °C, subjected to pulses of NO_2 at different concentration (from 140 ppb to 2 ppm) in dry air. The interaction among NO_2 molecules and CDs leads to a linear variation of the resistance with the nitrogen dioxide in the investigated concentration range, as highlighted in the calibration curve graph reported in Fig. 5b. It is noteworthy the good reproducibility of the two reported calibration curves, registered by two diverse sensors fabricated by using the same CDs. The resistance variations observed are well reversible; the response and recovery times are in the order of about 150 s and 315 s, respectively.

The interaction between the NO_2 molecule and CDs leads to a decrease of the resistance at all temperatures and NO_2 concentrations investigated, indicating that the CDs sensor has a p-type behaviour. This finding can be attributed to presence of electron withdrawing oxygen functional groups on the surface of CDs, as also suggested by some authors for other colloidal quantum dots [25].

The sensing mechanism can be described into the framework of general theory of p-type semiconducting gas sensors functioning [26]. However, the true sensing mechanism of NO_2 on carbon materials is still not fully understood and only hypotheses could be formulated taking into account examples coming from CNTs and graphene as previous carbon nanostructures-based sensing material for NO_2 [27–29]. Here, we can suppose that the resistance of sensing layer decreases after adsorption of NO_2 gas molecule due to the direct adsorption/chemisorption of NO_2 on the CDs surface, which is covered of adsorbed O^- oxygen ions, the main surface oxygen species present at the operating temperature of 150 °C. NO_2 interacts with the chemisorbed oxygen ions on the surface and extracts electrons. Indeed, NO_2 as an electron acceptor consume electrons, resulting in the increase of hole concentration.

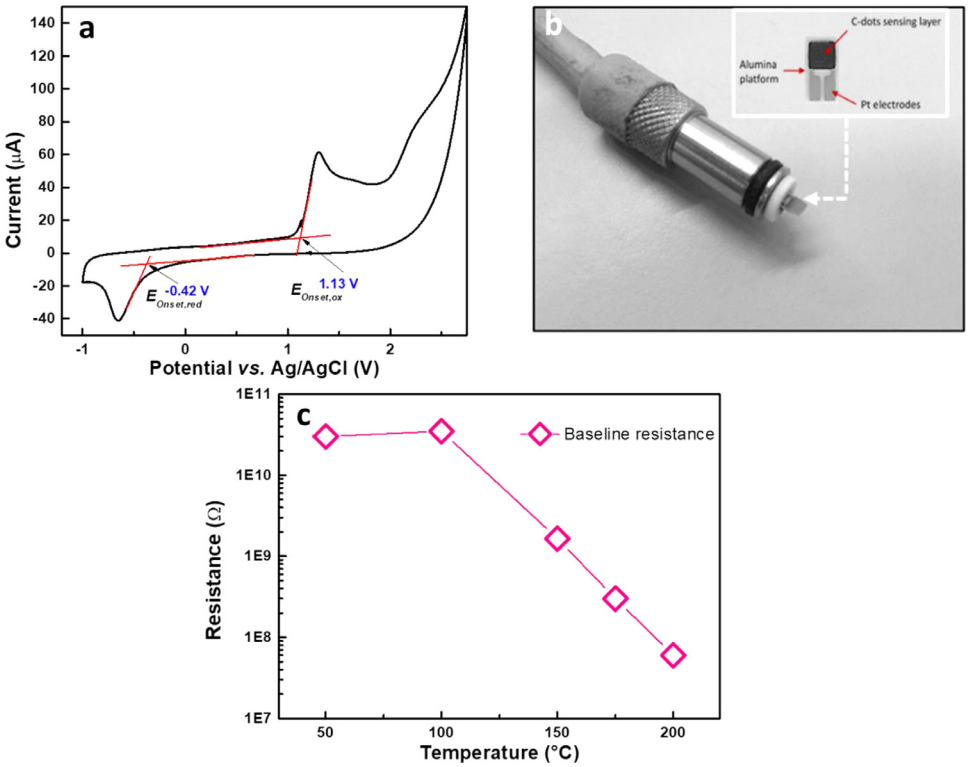

Fig. 3. (a) Cyclic voltammogram versus Ag/AgCl reference electrode of synthesized CDs; (b) picture of the conductometric sensor probe; in the inset is shown the sensor head; (c) Baseline resistance vs. operating temperature trend.

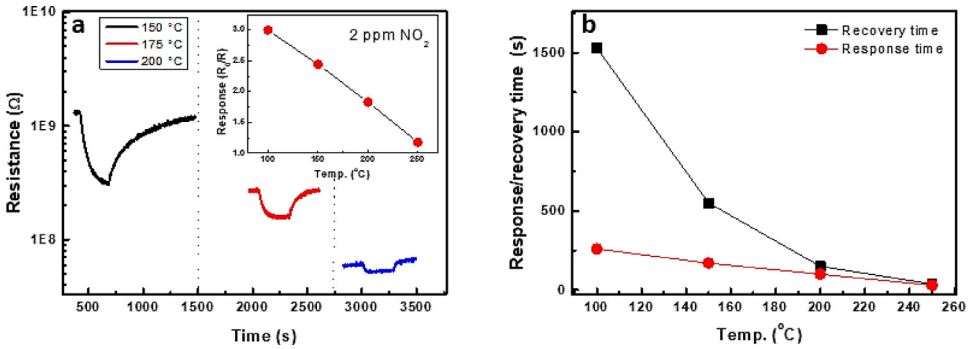

Fig. 4. (a) Resistance variation at different temperatures of CDs sensor subjected to pulses NO_2 at the concentration of 2 ppm. Inset shows the trend of sensor response with temperature; (b) Response/recovery time at different temperatures of the CDs sensor.

The depletion layer becomes thinner (low electrical resistance, see Fig. 5c) and therefore, electrical resistance decreases, as experimentally observed.

Above explanation is in according with data reported for other carbon nanostuctures, such as CNTs, were Schottky barrier modulation is the main detection mechanism postulated for gas sensing [30]. However, other sensing mechanisms cannot be excluded and can be concurrently present, depending on many factors linked mainly to size of carbon nanostructures. Indeed, carrier transport through the electrode-carbon particles is influenced by the particle size and the width of the depletion region. In air, oxygen is adsorbed at the active carbon sites, accepting electrons from the conduction band and causing, depending on the size, a partial to fully depleted region devoided of mobile charge carriers. The conduction mechanism is then governed by Schottky barriers at the grain boundaries, and grain control mechanism, respectively.

For our CDs-based conductometric sensor, the sensing mechanism can be supposed to be related to limited charge transport across Schottky barriers. The conduction across Schottky barriers is regulated by thermoionic emission carrier transport, or less usually, by tunnelling. Relevant to gas sensing is however that the activation energy for conductance is a function of the barrier height, which is directly affected by the charge and fractional coverage of the surface species and, hence, a function of the composition of the gas surrounding the sensor.

Selectivity to target gas, response reproducibility and stability are also important parameters of a sensor for the practical use. From inset reported in Fig. 5b is noted a very low response toward reducing gases (CO, NH_3, CO_2, CH_4), which implies that the sensor is also highly selective towards NO_2. Experimental results have also demonstrated a good signal reproducibility. Fig. 6a shows the reproducibility test when the sensor was exposed to pulses of 2 ppm of NO_2 at 175 °C. A fairly stable response was observed for a period of approximatively three months (see Fig. 6b).

The good sensing properties (sensitivity, selectivity, stability) of the sensor towards NO_2 can be then explained with the characteristics of CDs synthesized. First, the large specific surface area of the

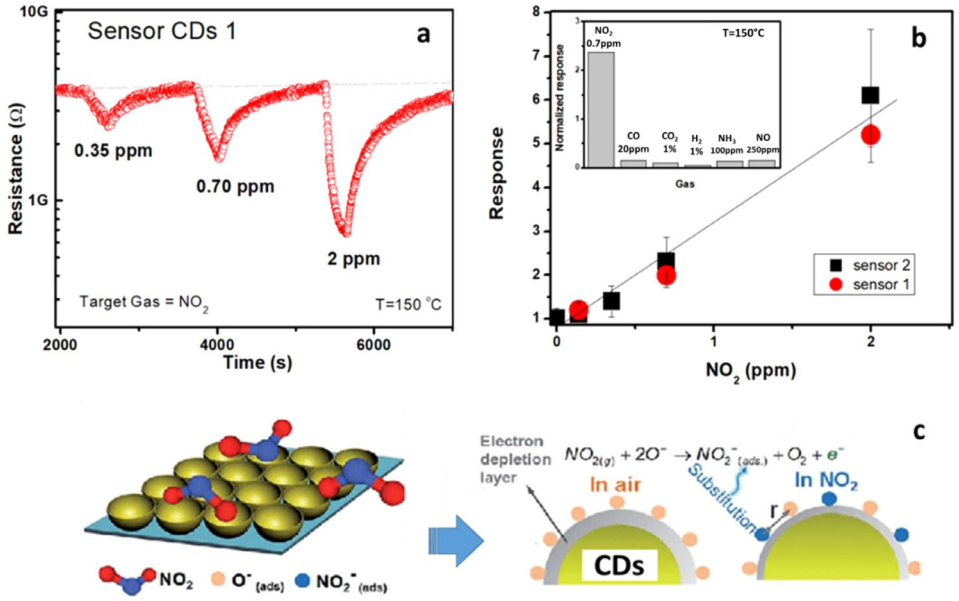

Fig. 5. (a) Transient response towards different NO_2 concentrations for the CDs sensor; (b) calibration curve towards NO_2, whereas the inset shows the response to different gases; (c) schematization of the NO_2 proposed sensing mechanism on CDs-based conductometric sensor.

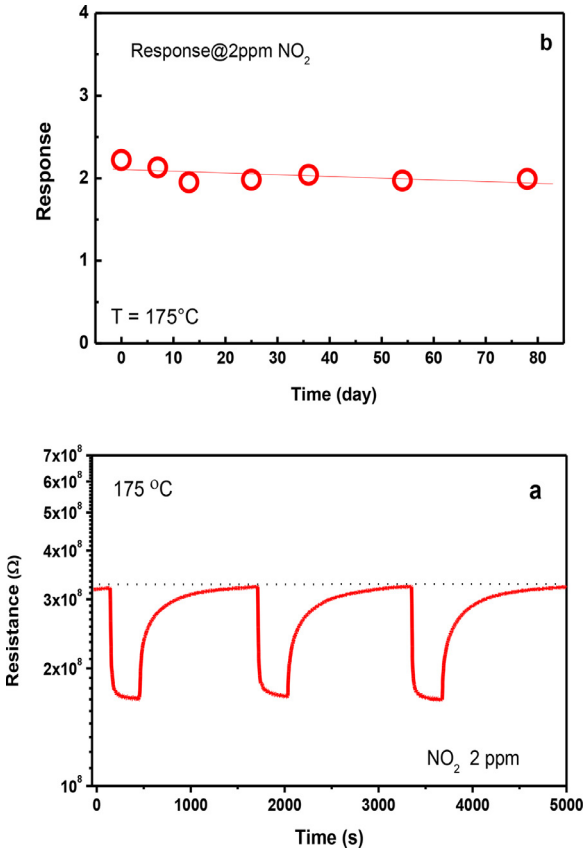

Fig. 6. (a) Response of the sensor to consecutive pulses of 2 ppm of NO_2; (b) Sensor response evaluated for a period of approximatively 3 months.

very small CDs provides many unsaturated sites with high reactivity, maximizing the interaction with the target gas. As regarding the excellent selectivity towards NO_2, it is associated to the surface state of CDs. Indeed, other than addressing the semiconducting behaviour, the chemical structure of the surface has the noticeable function to interact with the gases surrounding the sensor. In this way, depending on the chemical nature on the CDs surface and gaseous specie, the interaction will have a different strength and charge transfer. It seems then that the presence of the various organic groups on the CDs surface as indicated by FT-IR and XPS investigation can be relevant for NO_2 gas. In this perspective, it is interesting to note that it is possible to modulate the surface chemistry of the C-dots by introducing new ligands. These modifications can change the interaction of CDs with the gas molecules, modulating then the selectivity of the sensor versus different gases. At last, the long term stability of the sensor can be related to mild temperature (150 °C) chosen for sensing tests. This aspect is fundamental in order to avoid thermal stress to sensing layer in general, and in particular in the case of CDs sensing layer, this mild temperature avoids to modify/degradate the labile surface groups on the surface of CDs.

Finally, the sensing performances of the developed CDs-based sensor were also compared with previously reported conductometric sensors based on other carbon nanomaterials (see Table 1).

From this comparison, it is worthy to mention the outstanding sensitivity (3rd column in Table 1) of our nanomaterials. Further, this remarkable sensitivity and full and fast response/recovery of the signal is reached without the use of UV light. Once again, these comparative data confirm that the suitable carbon nanostructure obtained improve the performance of conductometric device for monitoring NO_2 at part-per-billion levels. However, we plan to further improve the performances of our materials by investigating in future studies both the effect of possible surface functionalization of C-dots and also the optimization of film structure and morphology.

4. Conclusion

In summary, CDs here reported were produced by a simple pyrolysis process combined with chemical oxidation from olive solid wastes, a cheap and readily available natural precursor. Morphological and microstructural characterization indicated that these nanometer CDs have a spherical shape with dimension ranging from 0.5 to 5 nm. Further, the presence of charged functional groups (COO- (carboxylate), C-O-C (epoxide) and C-OH (hydroxyl),

Table 1
Comparison of the NO_2 sensing performances of carbon conductometric sensors.

Sensing material	Limit of Detection [ppb]	Response[1]/concentration	Operating temperature	Measurement range [ppm]	UV light	Reference
SWCNTs[2]	86	100/0.1 ppm	50 °C	0.1–10	no	[30]
Graphene oxide	0.21	10/1 ppm	150 °C	1–9	no	[31]
Aligned SWCNTs	-	7/0.5 ppm	RT[3]	0.5–10	yes	[32]
S-doped graphene	-	0.2/500 ppt	RT	0.5–100	no	[33]
3D rGO[4]	186	0.1/1 ppm	22 °C	1–8	no	[34]
rGO	-	37/5 ppm	RT	5–100	no	[35]
CVD Graphene	4	3/1 ppm	RT	1–20	yes	[36]
C-dots	50	140/0.7 ppm	150 °C	0.14–2	no	This work

[1] Response (R) is defined as $R= 100*|R_g-R_a|/R_a$, where R_a and R_g are, respectively, the recorded signal in the absence and presence of NO_2 at the indicated concentration.
[2] Single-wall carbon nanotube;
[3] Room temperature.
[4] Reduced Graphene Oxide.

which imprint excellent water colloidal dispersion properties, has been also highlighted.

NO_2 sensing properties of CDs has been investigated showing excellent performances in terms of sensitivity, selectivity, full recovery after exposure and stability. Noteworthy, this study represents the first evidence of using CDs sensing material for conductometric gas sensor. Therefore, we expect that this study will pay the way for a large family of CDs produced by different natural sources to be employed as highly sensitive sensors.

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.

Acknowledgments

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cartre.2021.100105.

References

[1] S. Anwar, H. Ding, M. Xu, X. Hu, Z. Li, J. Wang, L. Liu, L. Jiang, D. Wang, C. Dong, M. Yan, Q. Wang, H. Bi, Recent advances in synthesis, optical properties, and biomedical applications of carbon dots, ACS Appl. Bio Mater. 2 (2019) 2317–2338.
[2] H. Li, Z. Kang, Y. Liu, S.T. Lee, Carbon nanodots: synthesis, properties and applications, J. Mater. Chem. 22 (2012) 24230–24253.
[3] M. Li, T. Chen, J.J. Gooding, J. Liu, Review of carbon and graphene quantum dots for sensing, ACS Sens. 4 (2019) 1732–1748.
[4] W.A. Amer, A.F Rehab, M.E. Abdelghafar, N.L. Torad, A.S. Atlam, M.M. Ayad, Green synthesis of carbon quantum dots from purslane leaves for the detection of formaldehyde using quartz crystal microbalance, Carbon 179 (2021) 159–171.
[5] N. Shauloff, A. Morag, K. Yaniv, S. Singh, R. Malishev, O. Paz-Tal, L. Rokach, R. Jelinek, Sniffing bacteria with a carbon-dot artificial nose, Nano Micro Lett. 13 (2021) 112.
[6] J. Zhang, X. Liu, G. Neri, N. Pinna, Nanostructured materials for room-temperature gas sensors, Adv. Mater. 28 (2016) 795–831.
[7] T.W. Hesterberg, W.B. Bunn, R.O. McClellan, A.K. Hamade, C.M. Long, P.A. Valberg, Critical review of the human data on short-term nitrogen dioxide (NO_2) exposures: Evidence for NO_2 no-effect levels, Crit. Rev. Toxicol. 39 (2009) 743–781.
[8] R. Rella, A. Serra, P. Siciliano, A. Tepore, L. Valli, A. Zocco, NO_2 gas detection by Langmuir-Blodgett films of copper phthalocyanine multilayer structures, Supramol. Sci. 4 (1997) 461–464.
[9] R. Rella, A. Serra, P. Siciliano, A. Tepore, L. Valli, A. Zocco, Effects of NO_2 oxidizing gas on a novel phthalocyanine Langmuir-Blodgett thin film, Thin Solid Films 286 (1996) 256–258.
[10] R. Rella, A. Rizzo, A. Licciulli, P. Siciliano, L. Troisi, L. Valli, Tests in controlled atmosphere on new optical gas sensing layers based on TiO_2/metal-phthalocyanines hybrid system, Mater. Sci.Eng. C 22 (2002) 439–443.
[11] M. Urso, S.G, Leonardi, G. Neri, S. Petralia, S. Conoci, F. Priolo, S. Mirabella, Room temperature detection and modeling of sub-ppm NO_2 by low-cost nanoporous NiO film, Sens. Actuator. B Chem. 305 (2020) 127481.
[12] R. Wang, G. Li, Y. Dong, Y. Chi, G. Chen, Carbon quantum dot-functionalized aerogels for NO_2 gas sensing, Analyt. Chem. 85 (2013) 8065–8069.
[13] J. Hu, C. Zou, Y. Su, M. Li, N. Hu, H. Ni, Z. Yang, Y. Zhang, Enhanced NO_2 sensing performance of reduced graphene oxide by in situ anchoring carbon dots, J. Mater. Chem. C 5 (2017) 6862–6871.
[14] Q.R. Liu, J.J. Zhang, H. He, G.X. Huang, B.L. Xing, J.B. Jia, C.X. Zhang, Green preparation of high yield fluorescent graphene quantum dots from coal–tar-pitch by mild oxidationx, Nanomaterials (8) (2018) 844–853.
[15] S. Sawalha, A. Silvestri, A. Criado, S. Bettini, M. Prato, L. Valli, Tailoring the sensing abilities of carbon nanodots obtained from olive solid wastes, Carbon 167 (2020) 696–708.
[16] V. Nguyen, L. Yan, J. Si, X. Hou, Femtosecond laser-induced size reduction of carbon nanodots in solution: effect of laser fluence, spot size, and irradiation time, J. Appl. Phys. 117 (2015) 084304.
[17] P. Das, M. Bose, S. Ganguly, S. Mondal, A.K. Das, S. Banerjee, N.C. Das, Green approach to photoluminescent carbon dots for imaging of gram-negative bacteria escherichia coli, Nanotechnology 28 (2017) 195501.
[18] K. Radhakrishnan, P. Panneerselvam, M. Marieeswaran, A green synthetic route for the surface-passivation of carbon dots as an effective multifunctional fluorescent sensor for the recognition and detection of toxic metal ions from aqueous solution, Anal. Methods 11 (2019) 490–506.
[19] M.Y. Xue, Z.H. Zhan, M.B. Zou, L.L. Zhang, S.L. Zhao, Green synthesis of stable and biocompatible fluorescent carbon dots from peanut shells for multicolor living cell imaging, New J. Chem. 40 (2016) 1698–1703.
[20] R. Bandi, B.R. Gangapuram, R. Dadigala, R. Eslavath, S.S. Singh, V. Guttena, Facile and green synthesis of fluorescent carbon dots from onion waste and their potential applications as sensor and multicolour imaging agents, RSC Adv. 6 (2016) 28633–28639.
[21] S. Bettini, S. Sawalha, L. Carbone, G. Giancane, M. Prato, L. Valli, Carbon nanodot-based heterostructures for improving the charge separation and the photocurrent generation, Nanoscale (11) (2019) 7414–7423.
[22] J. Chen, J. Liu, J. Li, L. Xu, Y. Qiao, One-pot synthesis of nitrogen and sulfur co-doped carbon dots and its application for sensor and multicolor cellular imaging, J. Coll. Interface Sci. 485 (2017) 167–174.
[23] J. Choi, N. Kim, J.W. Oh, F.S. Kim, Bandgap engineering of nanosized carbon dots through electron-accepting functionalization, J. Ind. Eng. Chem. 65 (2018) 104–111.
[24] Z. Zeng, W. Zhang, D.M. Arvapalli, B. Bloom, A. Sheardy, T. Mabe, Y. Liu, Z. Ji, H. Chevva, D.H. Waldeck, J. Wei, A fluorescence-electrochemical study of carbon nanodots (CNDs) in bio-and photoelectronic applications and energy gap investigation, Phys. Chem. Chem. Phys. 19 (2017) 20101–20109.
[25] P. Litvin, I.V. Martynenko, F. Purcell-Milton, A.V. Baranov, A.V. Fedorov, K Y., Gun'ko, colloidal quantum dots for optoelectronics, J. Mater. Chem. A 5 (2017) 13252–13275.
[26] H.J. Kim, J.H. Lee, Highly sensitive and selective gas sensors using p-type oxide semiconductors: overview, Sens. Actuat. B Chem. 192 (2014) 607–627.
[27] S. Mao, G. Lu, J. Chen, Nanocarbon-based gas sensors: progress and challenges, J. Mater. Chem. A 2 (2014) 5573–5579.

[28] V. Schroeder, S. Savagatrup, M. He, S. Lin, T.M. Swager, Carbon nanotube chemical sensors, Chem. Rev. 119 (2018) 599–663.
[29] L. Huang, Z. Wang, J. Zhang, J. Pu, Y. Lin, S. Xu, L. Shen, Q. Chen, W. Shi, Ultrasensitive and selective nitrogen dioxide sensor based on self-assembled graphene/polymer composite nanofibers, ACS Appl. Mater. Interfaces 6 (2014) 7426–7433.
[30] L. Sacco, S. Forel, I. Florea, C.S. Cojocaru, Ultra-sensitive NO_2 gas sensors based on single-wall carbon nanotube field effect transistors: monitoring from ppm to ppb level, Carbon 157 (2020) 631–639.
[31] J. Park, Y. Kim, S.Y. Park, S.J. Sung, H.W. Jang, C.R. Park, Band gap engineering of graphene oxide for ultrasensitive NO_2 gas sensing, Carbon 159 (2020) 175–184.
[32] S. S.Chauhan, D. Kumar, P. Chaturvedi, M.R. Rahman, Highly sensitive and stable NO_2 gas sensors based on SWNTs with exceptional recovery time, IEEE Sens. J. 19 (2019) 11775–11783.
[33] L. Guo, T. Li, Sub-ppb and ultra selective nitrogen dioxide sensor based on sulfur doped graphene, Sens. Actuat. B 255 (2018) 2258–2263.
[34] J. Wu, K. Tao, J. Miao, L.K. Norford, Carbon nanocoil-based fast-response and flexible humidity sensor for multifunctional applications, ACS App. Mater. Interfaces 7 (2015) 27502–27510.
[35] T. Han, S. Gao, Z. Wang, T. Fei, S. Liu, T. Zhang, Investigation of the effect of oxygen-containing groups on reduced graphene oxide-based room-temperature NO_2 sensor, J. Alloys Compound. 801 (2019) 142–150.
[36] X. Yan, Y. Wu, R. Li, C. Shi, R. Moro, Y. Ma, L. Ma, High-performance UV-Assisted NO_2 sensor based on chemical vapor deposition graphene at room temperature, ACS Omega 4 (2019) 14179–14187.