published by Ural Federal University
eISSN 2411-1414; chimicatechnoacta.ru

ARTICLE
2022, vol. 9(3), No. 20229311
DOI: 10.15826/chimtech.2022.9.3.11

Solvent effect on the NO_2 sensing properties of multi-walled carbon nanotubes

Nikita I. Lapekin [a], Tatyana V. Anufrieva [a], Arina V. Ukhina [b], Artem A. Shestakov [a], Alexander G. Bannov [a*]

a: Department of Chemistry and Chemical Technology, Novosibirsk State Technical University, Novosibirsk 630073, Russia
b: Institute of Solid State Chemistry SB RAS, Novosibirsk 630090, Russia
* Corresponding author: Bannov.alexander@gmail.com

This paper belongs to the CTFM'22 Special Issue: https://www.kaznu.kz/en/25415/page.
Guest Editors: Prof. N. Uvarov and Prof. E. Aubakirov.

Abstract

This article is devoted to the investigation of the influence of the solvent on sensing properties, such as response and recovery rate, of chemiresistive gas sensors. Multi-walled carbon nanotubes were used as an active material for the sensors. The initial material was investigated by scanning electron spectroscopy and transmission electron microscopy, low-temperature nitrogen adsorption, Raman spectroscopy, and X-ray diffraction. The active material was produced by drop casting. Different polar solvents (acetone and ethanol) were used for suspension preparation. Textolite with copper contacts on the edges of one side was used as a sensor substrate. The gas sensing properties (the response and the recovery time) were investigated in the range of 100–500 ppm NO_2 at room temperature. The films made using different solvent suspensions showed high sensitivity and rapid recovery rate to nitrogen dioxide. It was found that the method of film preparation has an effect on the measured sensing properties. The films prepared using different suspensions possessed different properties: the film made from the acetone suspension had the response values from 8.49% to 20.26%, and the recovery values from 0.06%/min to 0.16%/min. The response of the film made from the ethanol suspension increased , being from 12.25% to 23.63%; the recovery rate were also increased (from 0.19%/min to 0.39%/min).

Keywords

carbon nanomaterials
MWNTs
films
gas sensors
NO_2 detection
ultrasonic dispersion
polar solvent

Received:25.06.22
Revised: 22.07.22
Accepted: 22.07.22
Available online: 08.08.22

1. Introduction

The detection of hazardous and toxic gases in industry and everyday life is of interest from environmental and occupational health and safety points of view. This is because exposure to such gases, even at low concentrations, can cause visual disturbances, respiratory diseases and even death [1–4]. That is why the development of effective techniques with rapid, sensitive and selective real-time monitoring capabilities is an urgent task.

There are several ways of detecting gases in the air. One of the most commonly used methods of analysis is gas chromatography-mass spectrometry due to its reliability and accuracy [5, 6]. However, this method has a number of disadvantages, such as high cost and complex equipment, as well as time-consuming preconcentration of samples [7–9], which prevents real-time monitoring and analysis of gas content in the air. Because of the problems described above, this method of analysis is not suitable for the real-time detection of hazardous gases. Chemiresistive gas sensors are preferable for gas detection due to the obvious advantages. In addition, with the development of MEMS (microelectromechanical systems), chemiresistive gas sensors can be integrated into smart devices such as smartphones, smartwatches, and hand-held medical instruments [10, 11]. Thus, the use of chemiresistive gas sensors will enable reliable real-time monitoring of hazardous gases.

Compared to traditional semiconductor-based sensors which consume high power and operate at high temperatures, sensors operating at room temperature have many challenges to overcome: improving sensor response, increasing sensor recovery rate, and finding ways to improve sensitivity. Typically, gas sensors are implemented

in the form of metal oxide semiconductor sensors, but they operate at relatively high temperatures (200–350 °C), which requires high energy input [12]. This is another problem that can be solved by using new active materials. In view of this, the development of sensors operating at room temperature (25±2 °C) is an urgent task that needs to be done.

A wide range of nanomaterials, including materials based on carbon, noble metals, metal oxides or sulphides, and organic semiconductors, opens up opportunities for the development of functional gas sensors. Recently, carbon nanomaterials (CNMs) have received much attention in this field and have found wide application as the materials of catalysts, biosensors and chemoresistive gas sensors [13, 14]. This is due to their unique physical structure and excellent electronic properties. Multi-walled carbon nanotubes (MWNTs) are a special type of material that can be used for hazardous gas detection [15–17]. The use of MWNTs as an active material for chemiresistive gas sensors is preferable due to the low cost, high sensitivity, and the possibility of incorporation into portable devices. Carbon nanomaterials can be implemented in sensors both in the form of films and compacts (pellets). The method of implementation has a significant impact on the properties of the sensors.

Despite of the traditional method of sensors preparations, called drop casting, is well investigated, there are no data on the ultrasonic parameters influencing the sensory properties of films. The choice of a solvent used for the ultrasonic suspension preparation is necessary to drop casting method. It is well known [18, 19], that the nature of a solvent affects the dispersion, stability and electrical properties of MWNTs. So, it is important to evaluate the solvents' effect on the sensing properties of MWNTs.

This work is devoted to the study of the solvent's effect on the sensing properties of multi-walled carbon nanotubes for chemiresistive gas sensors of nitrogen dioxide.

2. Experimental

Commercial multi-walled carbon nanotubes (MWNTs) were used as an active material for chemoresistive gas sensors for NO_2 detection. The MWNTs were manufactured by Shenzhen Nanotech Port Co. (China).

The MWNTs were studied by transmission electron microscopy (TEM) on a JEM-2010 electron microscope (Jeol, Japan) with a resolution of 0.14 nm at an accelerating voltage of 200 kV. The morphology of the MWNT surface was investigated by a S-3400N scanning electron microscope (SEM) (Hitachi, Japan).

The structure characteristics of MWNTs were determined by Raman spectroscopy (Raman spectroscopy) on a Horiba Jobin Yvon T64000 (λ = 514 nm). The degree of degree was estimated by the ratio of intensities of peaks D and G.

The surface area of MWNTs was investigated by low-temperature nitrogen adsorption at 77 K on a Quanto-Chrome Nova 1000 e.

In addition to Raman spectroscopy, the structural features of MWNTs were also determined by X-ray diffraction (XRD). The degree of graphitization was calculated from the interlayer spacing using the following equation:

$$y = \frac{0{,}688 - 2d_{002}}{0{,}688 - 0{,}6708} \cdot 100\ \%, \quad (1)$$

where d_{002} is the interlayer spacing, nm.

The chemiresistive gas sensor was made in the form of a film of active material deposited by drop casting onto a textolite substrate. MWNT films were obtained from acetone and ethanol suspensions. The mass of MWNTs, the duration of ultrasonication and the volume of polar solvent are presented in Table 1.

The preparation of films included dispersion of an initial sample of polar solvent in an ultrasonic bath (150 W, 22 kHz) for 20 min followed by the deposition of suspension on a heated substrate. Slurry deposition was carried out on the substrate heated to 70 °C.

The sample formed a square film that partially covered the copper contacts. A scheme of the sensor is shown in Figure 1.

The sensing properties were studied in a custom dynamic type station shown in Figure 2.

The station consists of the lines of analytes and carrier gas. In the study synthetic air (79% N_2, 21% O_2, a verified gas mixture) was used as a carrier gas, nitrogen dioxide mixture in the air (5000 ppm NO_2 in air, calibrated mixture) of constant composition was used as the analyte.

Table 1 Parameters for the preparation of MWNT films.

Sample	Solvent	Mass, g	Duration of ultrasonication, min	Volume of solvent, mL
MWNTs	Acetone / Ethanol	0.01	20	5

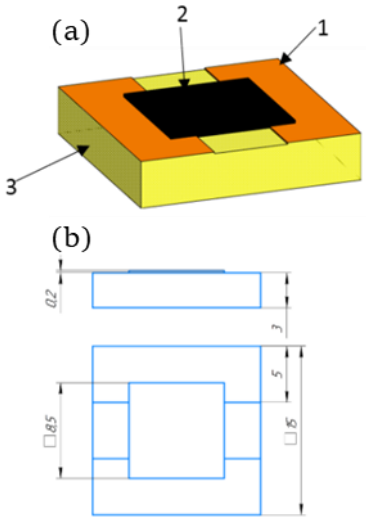

Figure 1 Obtained sensor (a): copper contacts (1), film of CNMs (2), dielectric substrate (3) and its scheme (b).

The response and recovery time of the sensors were studied. The response (%) of chemoresistive gas sensors was calculated according to equation 2:

$$\frac{\Delta R}{R_0} = \frac{R - R_0}{R_0} \cdot 100\ \%, \qquad (2)$$

where R is the sensor resistance during the contact with the analyte, Ω; R_0 is the sensor resistance during the carrier gas flowing, Ω.

The rate of recovery of sensors (%/min) was calculated according to equation 3:

$$U = \frac{R_r - R}{R_0(t_r - t)} \cdot 100\ \%. \qquad (3)$$

where R_r – the sensor resistance after regeneration in air flow, Ω; t_r – the time of measurement when the sensor resistance was R_r, min; t – the time of measurement when the sensor resistance was R, min.

The sensors were placed in a measurement cell (Figure 3) on a heater. The sensor resistance was measured using the two-point method between the two electrodes using a Keithley 2401 Source Meter at a bias voltage of 0.1 V at room temperature (25±2 °C).

The total flow rate of the gas mixture fed into the measuring chamber for contact with the sensor was 100 mL/min. The concentration of the analyzed gas in the system was controlled by the flow of the air-analyte mixture coming from the cylinder. The carrier gas flow was varied so that the resulting mixture had a certain gas concentration.

All sensor measurements were taken according to the following procedure: firstly, before the experiment, empty cell was blown by 100 mL/min of synthetic air for 10 min to clean the system after the last measurement. After cleaning, the sample was placed in the cell and was heated by 70 °C by the same carrier gas flow for the same time for desorption of moisture and adsorbed compounds. The last preparation part included the cooling of the cell and the sensor inside by the same flow rate for 10 min. After the preparation, the humidity inside the cell was 18–19% and the temperature of the sensor was 25±2 °C.

The measurement was started with baseline recording for 60 min in the 100 mL/min of carrier gas flow followed by three 10 min cycles of analyte flow (for 100 ppm, 250 ppm, 500 ppm of NO_2) alternated with three 10 min cycles in synthetic air flow.

3. Results and discussion

The SEM and TEM microphotographs are shown in Figure 4. The MWNTs sample consisted of relatively thick carbon nanotubes and chain like carbon nanofibers with a diameter of 60–80 nm and a narrow hollow channel of 10–20 nm.

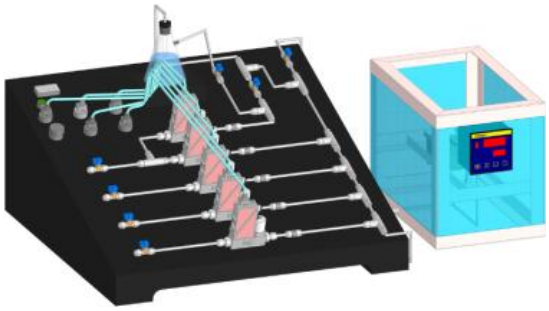

Figure 2 Scheme of a station for gas sensor testing.

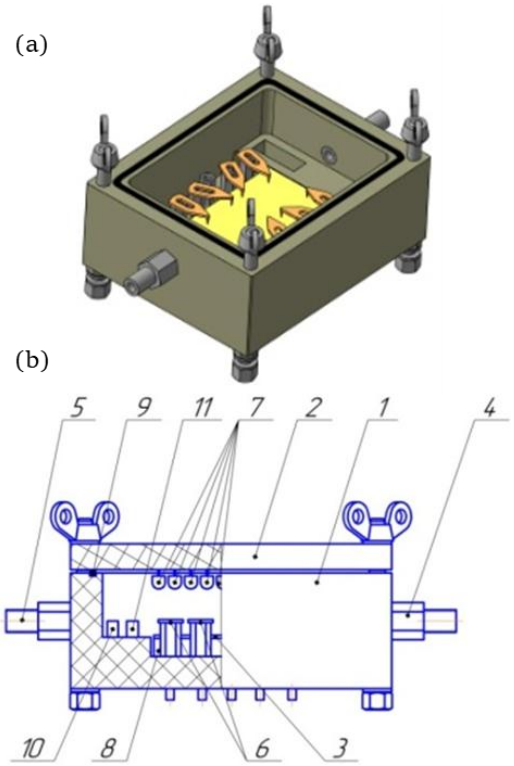

Figure 3 Model of measurement cell for the characterization of gas sensors (a) and its scheme (b): housing (1), cover (2), common contact (3), gas inlet connection (4), gas outlet connection (5), clamping contacts (6), LEDs (7), heater (8), sealing (9), humidity-temperature sensor (10), pressure sensor (11).

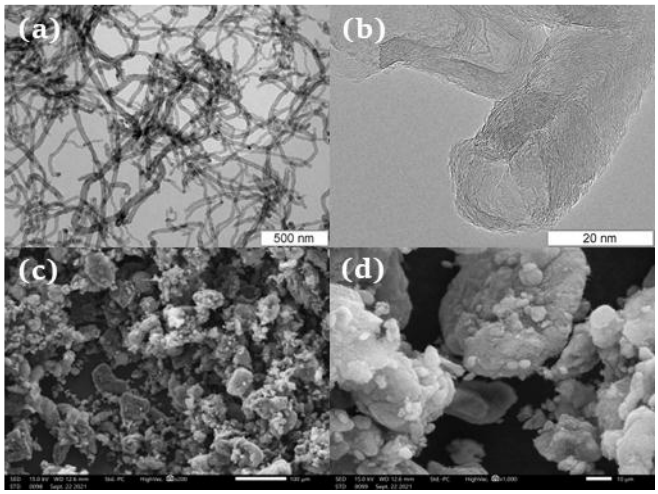

Figure 4 TEM-micrographs (a, b) and SEM-micrographs (c, d) of MWNTs.

The MWNTs were relatively defective, which was confirmed by Raman spectroscopy, namely, by a high value of the $I(D)/I(G)$ peaks ratio ($I(D)/I(G) = 0.99$), which, in turn, corresponds to the disordered structure of the carbon material and the ordered structure of carbon in the sp_2-hybridized state, respectively (Figure 5).

MWNTs had a 128 m^2/g surface area, as measured by low-temperature nitrogen adsorption. The data of Raman spectroscopy is consistent with the graphitization degree data obtained from XRD (Figure 6).

Table 2 summarizes the data obtained for the MWNTs.

The MWNT samples showed a high response to NO_2 in the concentration range of 100–500 ppm at room temperature (Figure 7). For both sensors an increase in the response value with increasing analyte concentration was observed.

However, the sample obtained in ethanol showed outstanding results of response and recovery, more than 1.5–2 times compared to that synthesized from the acetone dispersion.

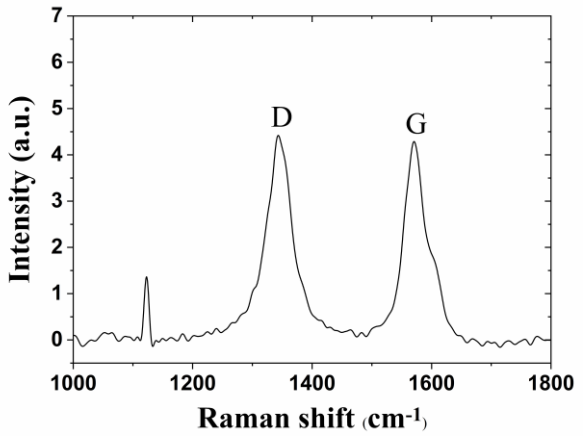

Figure 5 Raman spectrum of MWNTs.

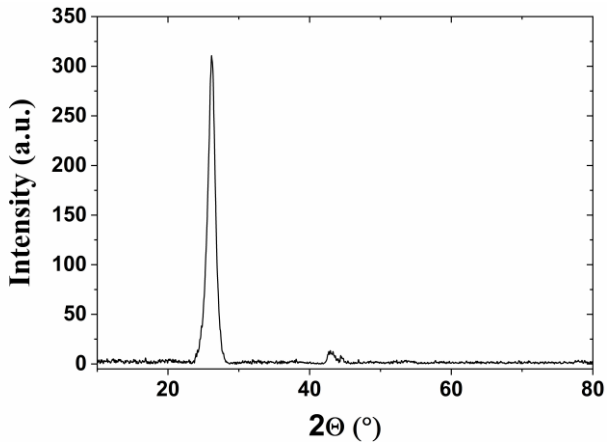

Figure 6 X-ray diffraction pattern of MWNTs.

Table 2 Properties of the pristine MWNTs.

Sample	MWNTs
Diameter, nm	60–80
$I(D)/I(G)$	0.99
Surface area, m^2/g	128
Interlayer spacing, nm	0.34
Degree of graphitization, %	46.51

The response values of the MWNTs obtained in acetone ranged from 8.49% to 20.26%; the recovery rate values ranged from 0.06%/min to 0.16%/min. The response values of the MWNTs obtained in ethanol increased from 12.25% to 23.63%, the recovery values also increased (from 0.19%/min to 0.39%/min). For clarity, the response values and recovery rates are shown in Table 3.

The differences in sensing properties are based on the nature of the solvent or, to be more precise, on the value of dielectric permittivity. For ethanol, the permittivity is higher than for acetone: 25 and 21, respectively [20]. Probably, the higher the permittivity of a polar solvent, the better the dispersion during ultrasonication, the better the adsorption of NO_2 on a surface of an MWNT.

Due to the high degree of disorder (according to the Raman spectroscopy), good recovery without heating and UV irradiation, it can be concluded that the physisorption is a dominate mechanism of the gas detection.

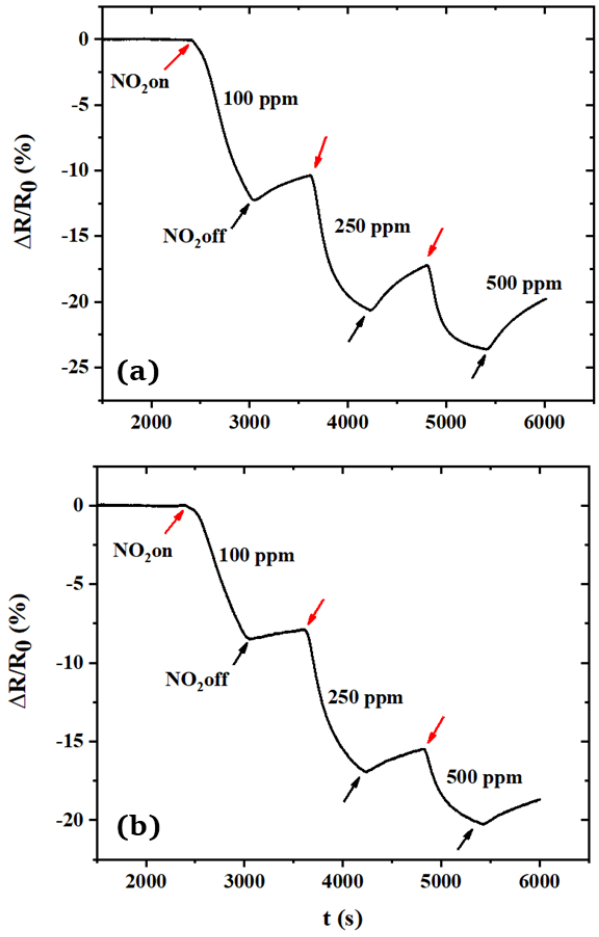

Figure 7 Response of MWNT films obtained in ethanol (a) and in acetone (b) to 100–500 ppm NO_2 at room temperature.

Table 3 Response and recovery rate (values module) of MWNTs obtained in ethanol and acetone.

Solvent	R, Ω	Response, %			Recovery rate, %/min		
		100 ppm	250 ppm	500 ppm	After 100 ppm	After 250 ppm	After 500 ppm
Acetone	329	8.49	16.93	20.26	0.06	0.15	0.16
Ethanol	979	12.25	20.65	23.63	0.19	0.34	0.39

It should be noted that sensing properties of the prepared sensors are better compared to the other sensors [21–23]. The detailed comparison is shown in Table 4.

Also, the sensing properties of the MWNT films were compared with the sensing properties of the MWNT pellets. In work [24] the pellets were made of the same MWNTs under the pressure of 9–13 MPa. The graphs of the response of the MWNT pellets compacted under 9 MPa and 13 MPa are shown in Figure 8.

Table 4 Comparison of sensing properties of proposed NO_2 sensor with other published NO_2 sensors.

Material	Concentration, ppm	Operating temperature, °C	Response, %	Reference
rGO-CNTs-SnO_2	100	RT	5,3	[21]
SnO_2-rGO	100	45	1,08	[22]
ZnO-SWCNT	500	150	9	[23]
MWNT obtained in ethanol	100	RT	12,25	This work

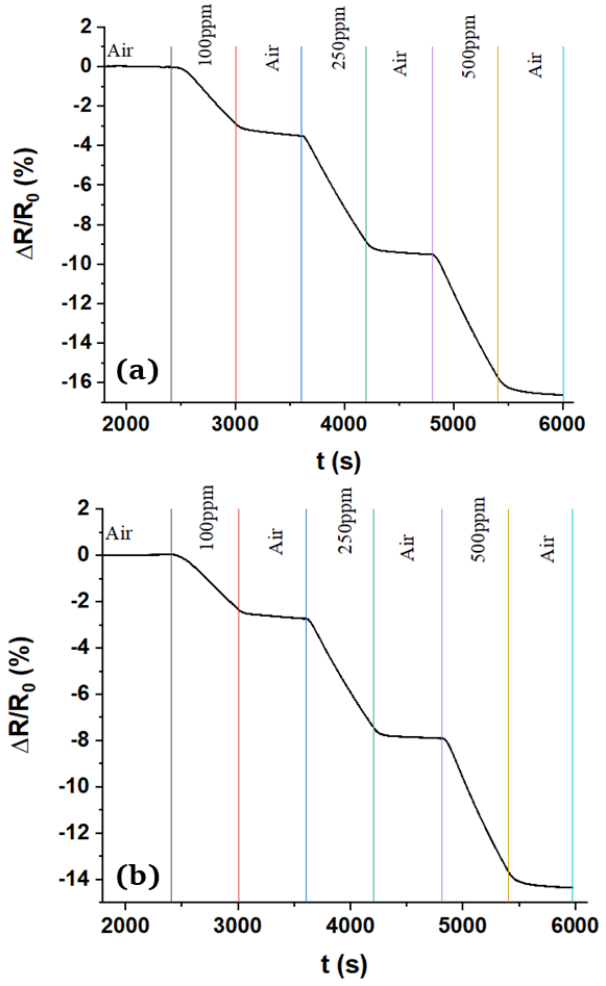

Figure 8 Response of MWNT pellets compacted under 9 MPa (a) and 13 MPa (b) pressure to 100–500 ppm NO_2 at room temperature.

According to the data shown in Figure 7 and Figure 8, it was established that the films are better as active materials for chemoresistive gas sensors as compared to the-pellets, made of compacted powder of MWNTs. For the pellets of MWNTs the recovery was not observed, because of the pores blocked and the plastic deformation of MWNTs during pressure. Also, according to the XRD, the degree of graphitization of the initial MWNTs was 46.51%, and the degree of graphitization of the MWNT compacts pressed under 11 MPa was only 26.82%.

The response of the MWNT compacts, pressed under 9 MPa and 13 MPa, increased in range of 2.94–16.65 % and 2.35–14.33%, respectively. A comparison of films and compacts of MWNTs showed the better response of the former. The differences in gas-sensing properties between films and pellets are in the thickness. For gas sensors based on carbon nanomaterials, the thinner the active layer, the better the properties. Because of the bigger response and the better recovery rate, films are more appropriate for active materials of gas sensors despite their higher cost.

4. Conclusions

Chemoresistive gas sensors based on MWNT films have a relatively high response toward NO_2 and a rapid recovery rate compared to MWNT pellets.

The method of film preparation also has an effect on the sensing properties. The films made using different suspensions have different properties. The film made using the acetone suspension has the response values from 8.5% to 20.3%, and the recovery values from 0.06%/min to 0.16%/min. The response of the film made from the ethanol suspension increased, being from 12.3% to 23.6%; the recovery values also increased (from 0.19%/min to 0.39%/min).

Because of the lack of the data on the solvent influence on sensing properties reported in the literature, we suppose that the differences in sensing properties are based on the nature of the solvent, namely, the value of permittivity, the surface tension, the dipole moment, etc.

Supplementary materials

No supplementary materials are available.

Funding

The work was carried out within the scope of the State task of the Ministry of Science and Higher Education of Russia (project no. FSUN-2020-0008).

Acknowledgments

None.

Author contributions

Data curation: N.I.L., A.G.B.
Resources: A.V.U.
Supervision: A.G.B.
Validation: A.A.S., T.V.A.
Writing – original draft: N.I.L., A.G.B.

Conflict of interest

The authors declare no conflict of interest.

Additional information

Author IDs:
Nikita Lapekin, Scopus ID 57220028358;
Arina Ukhina, Scopus ID 54382315900;
Artem Shestakov, Scopus ID 57220033659;
Alexander Bannov, Scopus ID 54788777600.

Websites:
Novosibirsk State Technical University, https://en.nstu.ru;
Institute of Solid State Chemistry SB RAS, http://www.solid.nsc.ru/en.

References

1. Li H-Y, Zhao S-N, Zang S-Q, Li J. Functional metal–organic frameworks as effective sensors of gases and volatile compounds. Chem Soc Rev. 2020;49:6364–6401. doi:10.1039/C9CS00778D
2. McGinn CK, Lamport ZA, Kymissis I. Review of gravimetric sensing of volatile organic compounds. ACS Sensors. 2020;5:1514–1534. doi:10.1021/acssensors.0c00333
3. Freddi S, Emelianov AV, Bobrinetskiy II, Drera G, Pagliara S, Kopylova DS, Chiesa M, Santini G, Mores N, Moscato U, et al. Development of a sensing array for human breath analysis based on swcnt layers functionalized with semiconductor organic molecules. Adv Health Mater. 2020;9:2000377. doi:10.1002/adhm.202000377
4. Lin T, Lv X, Hu Z, Xu A, Feng C. Semiconductor metal oxides as chemoresistive sensors for detecting volatile organic compounds. Sensors. 2019;19. doi:10.3390/s19020233
5. Peng G, Tisch U, Adams O, Hakim M, Shehada N, Broza YY, Billan S, Abdah-Bortnyak R, Kuten A, Haick H. Diagnosing lung cancer in exhaled breath using gold nanoparticles. Nat Nanotechnol. 2009;4:669–673. doi:10.1038/nnano.2009.235
6. Kumar V, Kim K-H, Kumar P, Jeon B-H, Kim J-C. Functional hybrid nanostructure materials: advanced strategies for sensing applications toward volatile organic compounds. Coord Chem Rev. 2017;342:80–105. doi:10.1016/j.ccr.2017.04.006
7. Lee J, Jung M, Barthwal S, Lee S, Lim S-H. MEMS gas preconcentrator filled with CNT foam for exhaled VOC Gas detection. Biochip J. 2014;9. doi:10.1007/s13206-014-9106-y
8. Bruderer T, Gaisl T, Gaugg MT, Nowak N, Streckenbach B, Müller S, Moeller A, Kohler M, Zenobi R. On-line analysis of exhaled breath. Chem Rev. 2019;119:10803–10828. doi:10.1021/acs.chemrev.9b00005
9. Zhou X, Xue Z, Chen X, Huang C, Bai W, Lu Z, Wang T. Nanomaterial-based gas sensors used for breath diagnosis. J Mater Chem B. 2020;8:3231–3248. doi:10.1039/C9TB02518A
10. Zhang L, Khan K, Zou J, Zhang H, Li Y. Recent advances in emerging 2d material-based gas sensors: potential in disease diagnosis. Adv Mater Interfaces. 2019;6:1901329. doi:10.1002/admi.201901329
11. Wang T, Qi D, Yang H, Liu Z, Wang M, Leow WR, Chen G, Yu J, He K, Cheng H, et al. Tactile chemomechanical transduction based on an elastic microstructured array to enhance the sensitivity of portable biosensors. Adv Mater. 2019;31:1803883. doi:10.1002/adma.201803883
12. Bannov AG, Jasek O, Manakhov A, Marik M, Necas D, Zajickova L. High-performance ammonia gas sensors based on plasma treated carbon nanostructures. IEEE Sens J. 2017;17:1964–1970. doi:10.1109/JSEN.2017.2656122
13. Wang M, Wei Y, Zou Q, Zhang W, Xu A, Li X. Tuning manganese (iii) species in manganese oxide octahedral molecular sieve by interaction with carbon nanofibers for enhanced pollutant degradation in the presence of peroxymonosulfate. J Colloid Interface Sci. 2019;536:271–280. doi:10.1016/j.jcis.2018.10.055
14. Bannov AG, Prášek J, Jašek O, Zajíčková L. Investigation of pristine graphite oxide as room-temperature chemiresistive ammonia gas sensing material. Sensors. 2017;17. doi:10.3390/s17020320
15. Ahmad Z, Naseem Manzoor S, Talib M, Islam SS, Mishra P. Self-standing MWCNTs based gas sensor for detection of environmental limit of CO_2. Mater Sci Eng B. 2020;255:114528. doi:10.1016/j.mseb.2020.114528
16. Sharma S, Hussain S, Singh S, Islam SS. MWCNT-conducting polymer composite based ammonia gas sensors: a new approach for complete recovery process. Sensors Actuators B Chem. 2014;194:213–219. doi:10.1016/j.snb.2013.12.050
17. Ionescu R, Espinosa EH, Sotter E, Llobet E, Vilanova X, Correig X, Felten A, Bittencourt C, Lier G. Van Charlier J-C, et al. Oxygen functionalisation of MWNT and their use as gas sensitive thick-film layers. Sensors Actuators B Chem. 2006;113:36–46. doi:10.1016/j.snb.2005.02.020
18. Sabri FNAM, Zakaria MR, Akil HM. Dispersion and stability of multiwalled carbon nanotubes (MWCNTs) in different solvents. AIP Conf Proc. 2020;2267. doi:10.1063/5.0024711
19. Santiago EV, López MAC, Marcelino JEM, López SH. Dispersion of MWNT under different solvents and its effect on the electrical properties of cured-epoxidized linseed oil composites. Int J Compos Mater. 2018;8:10–17. doi:10.5923/j.cmaterials.20180801.02
20. Bokach NA, Bolotin DS, Boyarsky VP, Kinzhalov MA, Tolstoy PM, Chulkova TG. Reference Tables on the theoretical foundations of organic chemistry and organometallic chemistry of transition elements; 2020; ISBN 9785965105380.
21. Liu S, Wang Z, Zhang Y, Zhang C, Zhang T. High performance room temperature NO_2 sensors based on reduced graphene oxide-multiwalled carbon nanotubes-tin oxide nanoparticles hybrids. Sensors Actuators B Chem. 2015;211:318–324, doi:10.1016/j.snb.2015.01.127
22. Li L, He S, Liu M, Zhang C, Chen W. Three-dimensional mesoporous graphene aerogel-supported SnO_2 nanocrystals for high-performance NO_2 gas sensing at low temperature. Anal Chem. 2015;87:1638–1645. doi:10.1021/ac503234e
23. Barthwal S, Singh B, Singh NB. ZnO-SWCNT nanocomposite as NO_2 gas sensor. Mater Today Proc. 2018;5:15439–15444. doi:10.1016/j.matpr.2018.05.030
24. Lapekin NI, et al. Vliyanie davleniya pressovaniya na gazochuvstvitel'nye svojstva mnogostennyh uglerodnyh nanotrubok. NSTU: Novosibirsk; 2021;51–55. Russian.