engineering proceedings

MDPI

Proceeding Paper

Chemiresistive Sensor Based on Metal Organic Framework-Reduced Graphene Oxide (Cu-BTC@rGO) Nanocomposite for the Detection of Ammonia+

Mayuri S. More [1], Gajanan A. Bodkhe [2], Fouran Singh [3], Babasaheb. N. Dole [1], Tibor Hianik [4] and Mahendra D. Shirsat [1,4*]

[1] RUSA Center for Advanced Sensor Technology, Department of Physics, Dr Babasaheb Ambedkar Marathwada University, Aurangabad (MS) - 431 004, India; mayurimore098@gmail.com (MSM); drbndole.phy@gmail.com (BND); mdshirsat.phy@bamu.ac.in (MSD)
[2] Department of Food Science and Technology, Yeungnam University, Gyeongsangbuk-do, Gyeongsan, 38541, South Korea; gabodkhe@gmail.com (GAB)
[3] Inter University Accelerator Centre (IUAC), New Delhi 110 067, India; fouran@gmail.com (FS)
[4] Department of Nuclear Physics and Biophysics, Faculty of Mathematics, Physics and Informatics, Comenius University, 842 48 Bratislava, Slovak Republic ; tibor.hianik@fmph.uniba.sk (T.H)
* Correspondence: mdshirsat.phy@bamu.ac.in (M.D.S)
+Presented at the 2nd E-Conference on Chemical Sensors and Analytical Chemistry (CSAC2023), 16-30 September 2023; Available online: https//CSAC2023.sciforum.net/.

Abstract: The detection of ammonia is very crucial for the welfare of modern society because of its hazardous effect on the environment and human beings. High response time is one of the serious concerns of most of the ammonia detector reported so far in the literature. This issue has been comprehensively addressed in the present investigation. Herein, the solvothermally synthesized Cu-BTC was combined with the 5 wt%, 10 wt% and 20 wt% of partially reduced graphene oxide (rGO). The structural, spectroscopic, morphological and electrical studies of as-synthesized CuBTC@rGO-5wt%, CuBTC@rGO-10wt% and CuBTC@rGO-20wt% were done by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, atomic force microscopy and current-voltage (I-V) characterization. The chemiresistive sensor based on Cu-BTC@rGO was developed on a copper-coated glass electrode via the shadow mask technique. It shows excellent sensing properties for CuBTC@rGO-10wt% in a range of 10 ppm to 80 ppm with high stability up to 30 days, good linearity and excellent response/recovery time, i.e., 84 sec and 125 sec, respectively. The limit of detection has been established as 10 ppm, which is below the maximum residue limit established by OSHA (Occupational Safety and Health Administration). Keywords: Cu-BTC, Graphene, Ammonia, Chemiresistive.

Keywords: Graphene; Reduced Graphene Oxide; Metal-Organic Framework; Chemiresistive; Ammonia.

Citation: To be added by editorial staff during production.

Academic Editor: Firstname Lastname

Published: date

1. Introduction

Increasing demand for various industrial processes, technological and agricultural development of nations across the globe contributed significantly for the emission of various hazardous pollutants such as ammonia, sulphur dioxide, carbon dioxide, carbon monoxide etc. Among these gases ammonia is most frequently used and produced in many industrial processes [1, 2]. According to the Occupational Safety and Health Administration (OSHA,) exposure beyond 50 ppm of NH_3, damage the human respiratory system and cause the throat, nose and eye irritation to the most sensitive individual [3, 4]. Hence, early detection of ammonia below its maximum residue limit (50 ppm) is the great importance for the monitoring working/living environment for ensuring the occupant

safety. Many researchers have explored carbon-based materials such as graphene, carbon nanotube, graphene oxide etc for ammonia sensing because of their conducting properties and relative easiness to device fabrication. Although sensor based on these materials exhibits excellent sensitivity, they need to be functionalized to reduce cross selectivity.

The past decade has witnessed the metal organic framework (MOF) as an extensively used sensing layer because of its extraordinary properties like high surface area, porosity and chemical activity. Among the MOFs, Cu-BTC is particularly attractive because of its structural building blocks and ability to coordinative unsaturation on the metal centre [5]. Till today MOFs have been mostly explored for gas sensing using various modalities like quartz crystal microbalance(QCM) [6], luminescence [7], work function [8] etc. However, these modalities consume high power and has complex analysis technique is required. On other hand chemiresistive sensor offers advantages like simple analysis, cost effectiveness and low power consumption. Chemiresistive sensors are most widely applied semi-conductive device because of its inherent simplicity.

Despite of advantageous properties of MOF, there are some issues which imposes limitations on their use in chemiresistive gas sensing because of its poor electrical conductivity. To address this issue, we have synthesized composite of copper-based MOF (Cu-BTC) and reduced graphene oxide (rGO) and tested it for chemiresistive ammonia sensing. The chemiresistive sensor based on Cu-BTC@rGO shows high stability up to 30 days, good linearity and excellent response/recovery time i.e., 84 sec/125sec respectively.

2. Experimental

2.1. Materials and methods

Sodium nitrate, graphite flakes, hydrogen peroxide (H_2O_2), sulphuric acid (H_2SO_4), hydrochloric acid (HCl) were procured from Moly-chem, Mumbai, India, 1,4-benzene dicarboxylate.. N, N-dimethylformamide (DMF), copper nitrate trihydrate and potassium per magnet were purchased from Sigma Aldrich (Darmstadt, Germany).

2.2. Synthesis of graphene oxide (GO) and Reduced graphene oxide (rGO)

Graphene oxide was prepared by oxidation of graphite using hummers method [9] and its reduction was done by treating as synthesized GO at 300 ºC for 10 min.

2.3. Synthesis of Cu-BTC and Cu-BTC@rGO

Cu-BTC was synthesized by hydrothermal method as reported elsewhere [10]. Briefly 2.252 g of copper nitrate trihydrate and 0.982 g of trimesic acid were added in 50 ml of DI and DMF respectively. Both solutions were then mixed and stirred for 15 min. Resultant solution then shifted to a glass flask (150 mL) kept in oil bath and heated for 4 h (105 ºC). The obtained material has been filtered and dried at room temperature.

Cu-BTC@rGO composite was synthesized by similar method by adding 5wt%, 10wt% and 20wt% of partially reduced graphene oxide at the time of solution preparation.

3. Results and discussion

3.1. X-Ray Diffraction (XRD)

The structural information of GO, rGO, Cu-BTC and Cu-BTC@rGO was obtained by using Powder X-Ray diffraction technique (D8 Advance Bruker, Germany) and depicted in Figure (a). The peaks at $2\theta = 11.9^{\circ}$ and 45° represent the (0 0 1) and (1 0 0) plane in graphene oxide respectively.

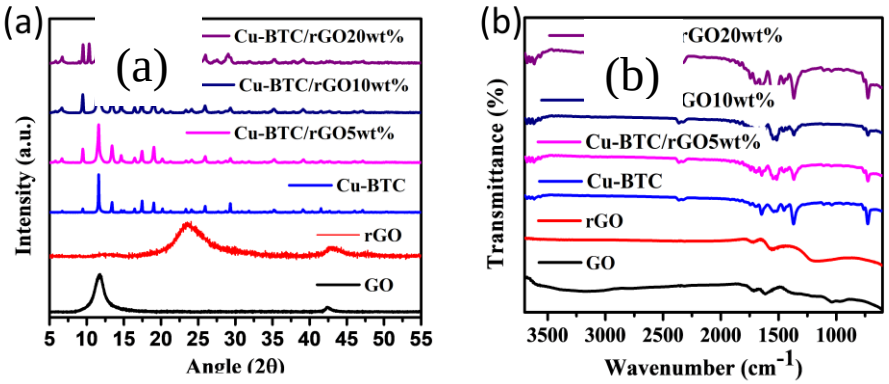

Figure 1. (a) XRD pattern of GO, rGO, Cu-BTC, Cu-BTC@rGO5wt%, Cu-BTC@rGO10wt% and Cu-TC@rGO20wt% (b) FTIR Spectra of GO, rGO, Cu-BTC, Cu-BTC@rGO5wt%, Cu-BTC@rGO10wt% and Cu-BTC@rGO20wt%Table 1.

After reduction, peak at 2θ= 11.9º reduces significantly and new hump appears between 2θ= 20º to 30º which is due to the exfoliation of graphene sheets, which confirms the successful reduction of GO[11].The XRD pattern of Cu-BTC shows the strong diffraction peaks at 2θ angle 6.7º, 9.5º, 11.6º, 14.7º, 15º, 16.5º, 17.5º, 19º, 20.2º, 21.3º, 23.4º, 24.1º, 26º, 27.7º, 28.7º and 35.7º represent the (200), (220), (222), (331), (420), (422), (333), (440), (442), (620), (444), (551), (553), (733), (660), and (951) d_{hkl} planes[10] . Cu-BTC@rGO shows the same peaks as Cu-BTC but little distortion between 2θ= 20º to 30º indicates the presence of rGO.

3.2. Fourier transform infrared spectroscopy

The coordination of metal ions with catechol unit was studied using FTIR spectroscopy in ATR mode by means of FTIR (Bruker Alpha) and FTIR spectra of GO, rGO, Cu-BTC and Cu-BTC@rGO is depicted in Figure 1(b). GO shows the absorption peaks at 1622 cm^{-1}, 1722 cm^{-1} and 3310 cm^{-1} which attributes to the stretching vibrations of C=C, C=O and O-H respectively. The peaks at 1220 cm^{-1} and 1048 cm^{-1} correspond to the stretching vibrations of the epoxy and alkoxy group [12]. After reduction, the peak at 3310 cm^{-1} and 1048 cm^{-1} completely vanishes, which confirms the successful elimination of O-H and epoxy group respectively. The peak at 730 cm^{-1} attributes to the stretching vibration of Cu-O bond. The peak at 1442^{-1} and 1649^{-1} validates the presence of C=O and C-O stretching vibration. Moreover, presence of asymmetric stretching vibration of carboxylic and C-H group can be confirmed by the presence of peaks at 1460^{-1} and 2890 cm^{-1}[13]. Absorption peaks of Cu-BTC@rGO exactly matches with the Cu-BTC which confirms the presence of rGO does not prevent the linkage between metal ion and ligand. As we increase the rGO concentration the intensity of all peaks seems to be decrease as the crystallinity decreases.

3.3. Atomic Force Microscopy

The AFM images of Cu-BTC and Cu-BTC@rGO10wt% was recorded using Park X7 system (South Korea) to evaluate the surface roughness of the sensing film as shown in Figure 2 (a,b). The result reveals that the surface area/average roughness values are increased from 12.36μm²/0.7μm to 17.9 μm² /1.08μm respectively after incorporation of rGO into the Cu-BTC which is favourable for the gas sensing.

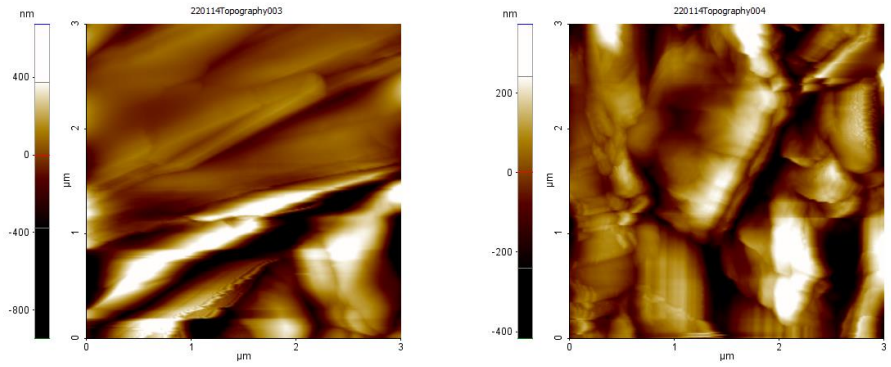

Figure 2. AFM images of (a) Cu-BTC, (b) Cu-BTC@rGO10wt%.

4. Sensing performance

The Current-Voltage characteristics of synthesized materials were studies using Keithley 4200A (Keithley, Solon, OH, USA) in the potential range -5V to 5V at room temperature and shown in figure 3(a). With increasing of rGO concentration the conductivity of Ce-BTC@rGO increases significantly. The chemiresistive sensor based on Cu-BTC@rGO composite was fabricated on copper coated glass substrate.

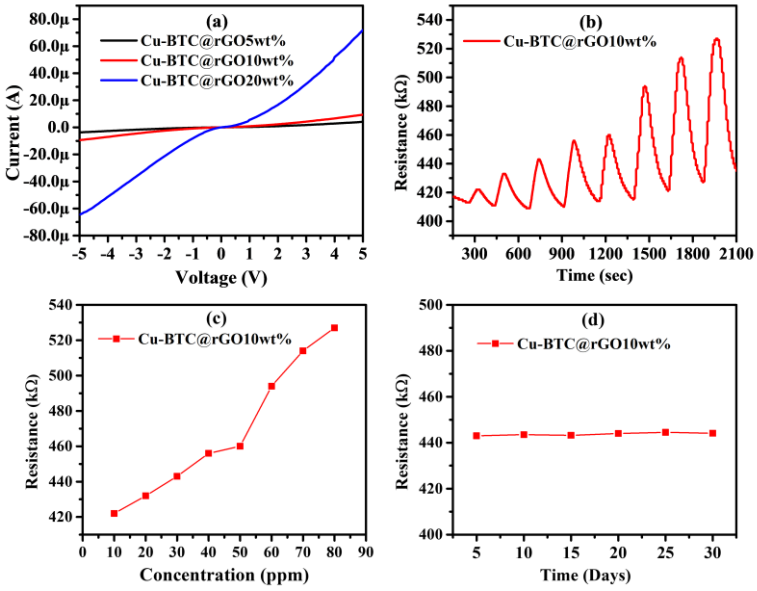

Figure 3. (a) I-V Curve of Cu-BTC@rGO5wt%, Cu-BTC@rGO10wt% and Cu-BTC@rGO20wt% (b) real time sensing curve for NH_3, (c) Linearity plot for NH_3 and (d) Stability at 30 ppm NH_3.

The gap between electrodes were prepared by simply cutting copper coated substrate using diamond cutter and Cu-BTC@rGO was drop casted to bridge the gap between two electrodes. Real time chemiresistive sensing performance was studied on indigenously fabricated dynamic gas sensing system. Results shows that the Cu-BTC@rGO5wt% and Cu-BTC@rGO20wt% does not show any sensing response because of its electrical conductivity was not suitable for the sensing performance. Whereas Cu-BTC@rGO10wt % selectively detect ammonia (NH_3) (Figure 3(b)) up to 10 ppm which is below maximum residue limit suggested by Occupational Safety and Health Administration (OSHA) with good response and recovery time i.e., 84sec/125 sec respectively. Figure 3(c) confirms that as

fabricated sensor shows good linear dependency between NH_3 concentration and sensor response. To depict the stability of the chemiresistive sensor-based Cu-BTC@rGO composite, we have repeated the sensing measurement at 30 ppm after every 5 days of interval and results (Figure 3(d)) shows that the sensor has excellent stability up to 30 days.

5. Conclusions

In summary, we have for the first time developed high performance room temperature chemiresistive sensor using Cu-BTC@rGO nanocomposite for detection of NH_3. Structural, spectroscopic and morphological studies were done using XRD, FTIR and AFM to confirm the successful synthesis of nanocomposite. The sensor was prepared on copper coated glass electrode using drop casting method. The sensor shows good linearity, good response/recovery time i.e., 84sec/125 sec with excellent stability up to 30 days below maximum residue limit suggested by OSHA

Author Contributions: Conceptualization, M.S.M. and M.D.S.; formal analysis, M.S.M., G.A.B., B.N.D., M-L.T., F.S. and T.H.; investigation, M.S.M.; writing—original draft preparation, M.S.M. and M.D.S.; writing—review and editing, M.S.M., G.A.B., B.N.D., M-L.T., F.S., T.H and M.D.S.; supervision, M.D.S.; project administration, M.D.S.; funding acquisition, M.D.S.

Funding: This research was funded by Inter-University Accelerator Center (IUAC), New Delhi, India (UFR no. 69330), University Grants Commission – Department of Atomic Energy (UGC—DAE) CSR, Indore (Project No. CRS/2021-22/ 01/456 dated March 30, 2022), Department of Science and Technology, Govt of India (DST—SERB), New Delhi (Project No. EEQ/2017/000645), University Grants Commission (UGC-SAP Programme) (F.530/16/DRS-I/2016 (SAP-II) Dt.16-04-2016), Department of Science and Technology, Govt of India (DST-FIST) (Project No. SR/FST/PSI-210/2016(c) dtd. 16/12/2016), and Rashtriya Uchachatar Shiksha Abhiyan (RUSA), Government of Maharashtra

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not Applicable

Acknowledgments: Mahendra D, Shirsat gratefully acknowledges the Slovak Academic Information Agency (SAIA) and Department of Nuclear Physics and Biophysics, Faculty of Mathematics, Physics and Informatics, Comenius University, Bratislava, Slovak Republic, for the sanction of scholarship under the framework of National Scholarship Program (NSP) of Slovak Republic

Conflicts of Interest: The authors declare no conflicts of interests.

References

1. Tabrizi, L.; Chiniforoshan, H., High-performance room temperature gas sensor based on gold (III) pincer complex with high sensitivity for NH3. *Sensors and Actuators B: Chemical* **2017,** 245, 815-820.

2. Kaushik, A.; Kumar, R.; Arya, S. K.; Nair, M.; Malhotra, B.; Bhansali, S., Organic–inorganic hybrid nanocomposite-based gas sensors for environmental monitoring. *Chemical reviews* **2015,** 115, (11), 4571-4606.

3. Singh, S.; Deb, J.; Sarkar, U.; Sharma, S., MoSe2 crystalline nanosheets for room-temperature ammonia sensing. *ACS Applied Nano Materials* **2020,** 3, (9), 9375-9384.

4. Jin, L.; Wu, C.; Wei, K.; He, L.; Gao, H.; Zhang, H.; Zhang, K.; Asiri, A. M.; Alamry, K. A.; Yang, L., Polymeric Ti3C2T x MXene composites for room temperature ammonia sensing. *ACS Applied Nano Materials* **2020,** 3, (12), 12071-12079.

5. Zeinali, S.; Homayoonnia, S.; Homayoonnia, G., Comparative investigation of interdigitated and parallel-plate capacitive gas sensors based on Cu-BTC nanoparticles for selective detection of polar and apolar VOCs indoors. *Sensors and Actuators B: Chemical* **2019,** 278, 153-164.

6. Wang, L., Metal-organic frameworks for QCM-based gas sensors: A review. *Sensors and Actuators A: Physical* **2020,** 307, 111984.

7. Moscoso, F. G.; Almeida, J.; Sousaraei, A.; Lopes-Costa, T.; Silva, A. M.; Cabanillas-Gonzalez, J.; Cunha-Silva, L.; Pedrosa, J. M., Luminescent MOF crystals embedded in PMMA/PDMS transparent films as effective NO 2 gas sensors. *Molecular Systems Design & Engineering* **2020,** 5, (6), 1048-1056.

8. Davydovskaya, P.; Pohle, R.; Tawil, A.; Fleischer, M., Work function-based gas sensing with Cu-BTC metal-organic framework for selective aldehyde detection. *Sensors and Actuators B: Chemical* **2013,** 187, 142-146.

9. Shahriary, L.; Athawale, A. A., Graphene oxide synthesized by using modified hummers approach. *Int. J. Renew. Energy Environ. Eng* **2014,** 2, (01), 58-63.

10. Bodkhe, G. A.; Khandagale, D. D.; More, M. S.; Deshmukh, M. A.; Ingle, N. N.; Sayyad, P. W.; Mahadik, M. M.; Shirsat, S. M.; Al-Buriahi, M.; Tsai, M.-L., Ag@ MOF-199 metal organic framework for selective detection of nickel ions in aqueous media. *Ceramics International* **2023,** 49, (4), 6772-6779.

11. More, M. S.; Bodkhe, G. A.; Ingle, N. N.; Singh, F.; Tsai, M.-L.; Kim, M.; Shirsat, M. D., Metal-organic framework (MOF)/reduced graphene oxide (rGO) composite for high performance CO sensor. *Solid-State Electronics* **2023,** 204, 108638.

12. Noor, T.; Zaman, N.; Nasir, H.; Iqbal, N.; Hussain, Z., Electro catalytic study of NiO-MOF/rGO composites for methanol oxidation reaction. *Electrochimica Acta* **2019,** 307, 1-12.

13. Bodkhe, G. A.; Hedau, B. S.; Deshmukh, M. A.; Patil, H. K.; Shirsat, S. M.; Phase, D. M.; Pandey, K. K.; Shirsat, M. D., Selective and sensitive detection of lead Pb (II) ions: Au/SWNT nanocomposite-embedded MOF-199. *Journal of Materials Science* **2021,** 56, 474-487.