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

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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 detectors 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 a high stability of up to 30 days, good linearity, and excellent response/recovery time, i.e., 84 s and 125 s, respectively. The limit of detection has been established as 10 ppm, which is below the maximum residue limit established by the OSHA (Occupational Safety and Health Administration).

Keywords: graphene; reduced graphene oxide; metal-organic framework; chemiresistive; ammonia

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1. Introduction

Increasing demand for various industrial processes and the technological and agricultural development of nations across the globe contributes significantly to the emission of various hazardous pollutants such as ammonia, sulfur dioxide, carbon dioxide, carbon monoxide, etc. Among these gases, ammonia is the 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 damages the human respiratory system and causes 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 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 ease of use in device fabrication. Although sensors based on these materials exhibit 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 center [5]. Until 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 require complex analysis techniques. On the other hand, chemiresistive sensors offer advantages like simple analysis, cost effectiveness, and low power consumption. Chemiresistive sensors are the most widely applied semiconductive device because of their inherent simplicity.

Despite the advantageous properties of MOF, there are some issues which impose limitations on their use in chemiresistive gas sensing because of their poor electrical conductivity. To address this issue, we have synthesized a 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 a high stability of up to 30 days, good linearity, and excellent response/recovery time, i.e., 84 s/125 s, respectively.

2. Experimental Methods

2.1. Materials and Methods

Sodium nitrate, graphite flakes, hydrogen peroxide (H_2O_2), sulfuric acid (H_2SO_4), and hydrochloric acid (HCl) were procured from Moly-chem, Mumbai, India. Then, 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 the oxidation of graphite using the hummers method [9] and its reduction was completed by treating with synthesized GO at 300 °C for 10 min.

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

Cu-BTC was synthesized with the 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. The resultant solution was then shifted to a glass flask (150 mL) and kept in oil bath and heated for 4 h (105 °C). The obtained material was filtered and dried at room temperature.

Cu-BTC@rGO composite was synthesized with a similar method by adding 5 wt%, 10 wt% and 20 wt% 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 the powder X-ray diffraction technique (D8 Advance Bruker, Germany) and depicted in Figure 1a. The peaks at $2\theta = 11.9^\circ$ and 45° represent the (0 0 1) and (1 0 0) plane in the graphene oxide, respectively.

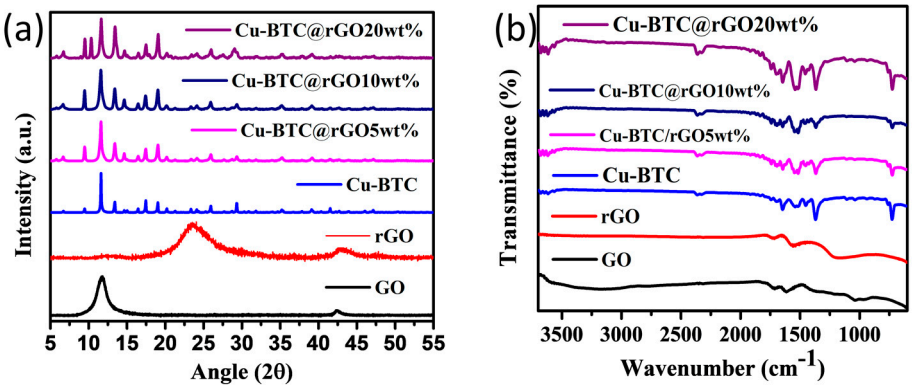


Figure 1. (**a**) XRD pattern of GO, rGO, Cu-BTC, Cu-BTC@rGO5wt%, Cu-BTC@rGO10wt%, and Cu-BTC@rGO20wt% (**b**) FTIR Spectra of GO, rGO, Cu-BTC, Cu-BTC@rGO5wt%, Cu-BTC@rGO10wt%, and Cu-BTC@rGO20wt%.

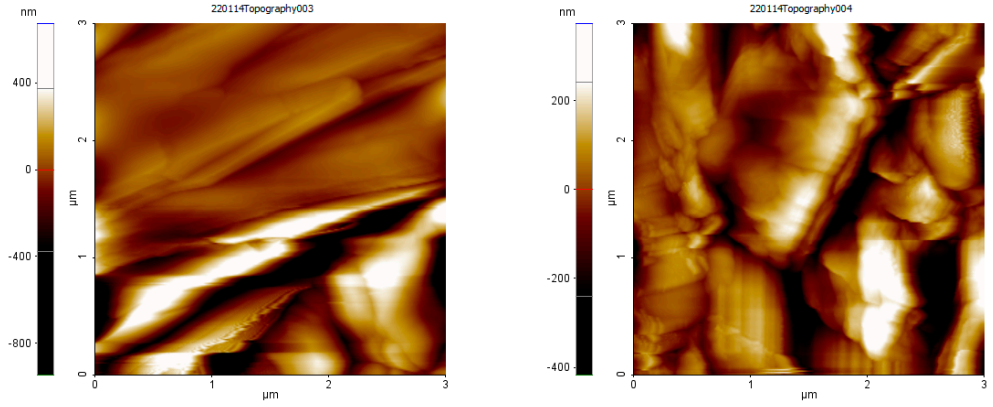
After reduction, the peak at 2θ = 11.9° reduces significantly and new hump appears between 2θ = 20° to 30° which is due to the exfoliation of graphene sheets, which confirms the successful reduction of GO [11]. The XRD pattern of Cu-BTC shows the strong diffraction peaks at the 2θ angles 6.7°, 9.5°, 11.6°, 14.7°, 15°, 16.5°, 17.5°, 19°, 20.2°, 21.3°, 23.4°, 24.1°, 26°, 27.7°, 28.7°, and 35.7° 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 = 20° to 30° 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 the ATR mode by means of the FTIR (Bruker Alpha) and FTIR spectra of GO, rGO, Cu-BTC, and Cu-BTC@rGO is depicted in Figure 1b. GO shows absorption peaks at 1622 cm^{-1}, 1722 cm^{-1}, and 3310 cm^{-1}, which are attributed 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 the O-H and epoxy groups, respectively. The peak at 730 cm^{-1} is attributed 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, the presence of the asymmetric stretching vibration of the carboxylic and C-H group can be confirmed by the presence of the peaks at 1460^{-1} and 2890 cm^{-1} [13]. The absorption peaks of Cu-BTC@rGO exactly matches with the Cu-BTC, which confirms that the presence of rGO does not prevent the linkage between metal ion and ligand. As we increased the rGO concentration, the intensity of all peaks seemed to decrease as the crystallinity decreased.

3.3. Atomic Force Microscopy

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



(**a**) (**b**)

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

4. Sensing Performance

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

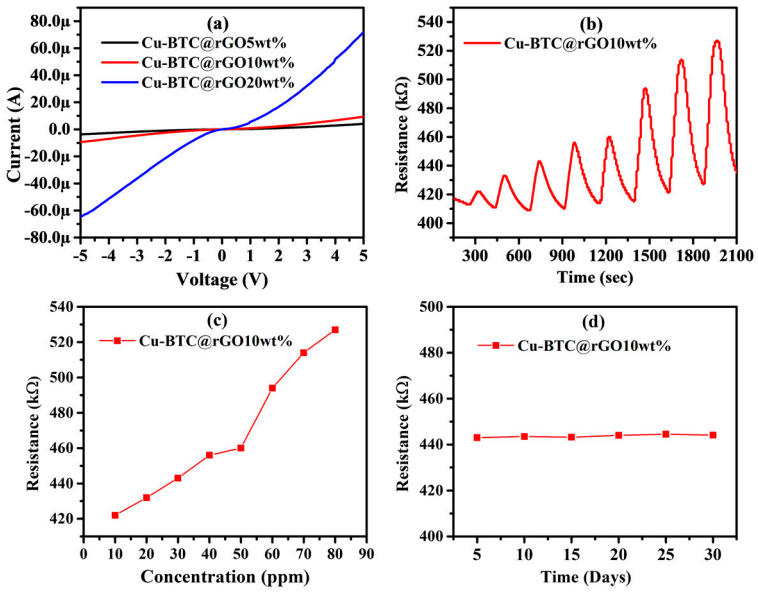


Figure 3. (**a**) I-V Curve of Cu-BTC@rGO5wt%, Cu-BTC@rGO10wt%, and Cu-BTC@rGO20wt% (**b**) real time sensing curve for NH_3, (**c**) Linearity plot for NH_3 and (**d**) Stability at 30 ppm NH_3.

The gaps between the electrodes were prepared by simply cutting copper coated substrate using diamond cutter and Cu-BTC@rGO was drop cast to bridge the gap between two electrodes. Real time chemiresistive sensing performance was studied on an indigenously fabricated dynamic gas sensing system. The results show that the Cu-BTC@rGO5wt% and Cu-BTC@rGO20wt% do not show any sensing response because their electrical conductivity was not suitable for the sensing performance. Whereas Cu-BTC@rGO10wt% selectively detected ammonia (NH_3) (Figure 3b) 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., 84 s/125 s, respectively. Figure 3c 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 3d) 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 a copper-coated glass electrode using the drop casting method. The sensor shows good linearity, and a good response/recovery time, i.e., 84 s/125 s, with an excellent stability of up to 30 days below the maximum residue limit suggested by OSHA.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Tabrizi, L.; Chiniforoshan, H. High-performance room temperature gas sensor based on gold (III) pincer complex with high sensitivity for NH_3. *Sens. Actuators B Chem.* **2017**, *245*, 815–820. [CrossRef]
2. Kaushik, A.; Kumar, R.; Arya, S.K.; Nair, M.; Malhotra, B.; Bhansali, S. Organic–inorganic hybrid nanocomposite-based gas sensors for environmental monitoring. *Chem. Rev.* **2015**, *115*, 4571–4606. [CrossRef] [PubMed]
3. Singh, S.; Deb, J.; Sarkar, U.; Sharma, S. $MoSe_2$ crystalline nanosheets for room-temperature ammonia sensing. *ACS Appl. Nano Mater.* **2020**, *3*, 9375–9384. [CrossRef]
4. Jin, L.; Wu, C.; Wei, K.; He, L.; Gao, H.; Zhang, H.; Zhang, K.; Asiri, A.M.; Alamry, K.A.; Yang, L. Polymeric $Ti_3C_2T_x$ MXene composites for room temperature ammonia sensing. *ACS Appl. Nano Mater.* **2020**, *3*, 12071–12079. [CrossRef]
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. *Sens. Actuators B Chem.* **2019**, *278*, 153–164. [CrossRef]
6. Wang, L. Metal-organic frameworks for QCM-based gas sensors: A review. *Sens. Actuators A Phys.* **2020**, *307*, 111984. [CrossRef]
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. *Mol. Syst. Des. Eng.* **2020**, *5*, 1048–1056. [CrossRef]
8. Davydovskaya, P.; Pohle, R.; Tawil, A.; Fleischer, M. Work function-based gas sensing with Cu-BTC metal-organic framework for selective aldehyde detection. *Sens. Actuators B Chem.* **2013**, *187*, 142–146. [CrossRef]
9. Shahriary, L.; Athawale, A.A. Graphene oxide synthesized by using modified hummers approach. *Int. J. Renew. Energy Environ. Eng.* **2014**, *2*, 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. *Ceram. Int.* **2023**, *49*, 6772–6779. [CrossRef]
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 Electron.* **2023**, *204*, 108638. [CrossRef]
12. Noor, T.; Zaman, N.; Nasir, H.; Iqbal, N.; Hussain, Z. Electro catalytic study of NiO-MOF/rGO composites for methanol oxidation reaction. *Electrochim. Acta* **2019**, *307*, 1–12. [CrossRef]
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. *J. Mater. Sci.* **2021**, *56*, 474–487. [CrossRef]