CO2 gas sensing properties of Na3BiO4 - Bi2O3 mixed oxide nanostructures

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Research Article

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Posted Date: February 16th, 2022

DOI: https://doi.org/10.21203/rs.3.rs-1234118/v1

CO_2 gas sensing properties of Na_3BiO_4 - Bi_2O_3 mixed oxide nanostructures

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Abstract

In this paper, we report Na_3BiO_4 - Bi_2O_3 mixed oxide nanoplates for carbon dioxide gas sensing applications. These nanoplates have been synthesized using electrochemical deposition with potentiostatic mode on ITO substrate and characterized using scanning electron microscopy (SEM) & X-ray diffraction (XRD) to analyze their surface morphology and structure. SEM study shows the presence of horizontally aligned nanoplates stacked on top of one another (thickness $\approx$ 40 nm to 75 nm). XRD pattern shows the presence of monoclinic Na_3BiO_4 and Bi_2O_3. The gas percentage response is evaluated by measuring the change in electrical resistance of the nanoplates in the presence of carbon dioxide for different pressures at 50°C, 75°C and 100°C. Percentage response of more than 100 % is seen at 30 psi gas pressure which increases to $\approx$ 277 % at 90 psi at 100°C.

Keywords: Carbon Dioxide Sensing, Nanostructured Bismuth Hexagons, Potentiostatic Electrodeposition, Nanoplates

1 Introduction

Modern industrialized society possess a great threat to our safety and well being, mainly due to the release of green house gases like carbon dioxide. These gases are responsible for the unstable environmental phenomenons like droughts and famines Dimitriou et al (2021); Shahbazi et al (2021).

A lot of environmental friendly compounds are being explored for their possible application in solid state gas sensors. Metal oxide semiconductors, carbon nanotubes based composites are few examples of materials that show good potential for sensing Barsan et al (2007); Rai et al (2014); Philip et al (2003); Rai et al (2015). Low cost, high sensitivity and quick response time makes the sensors based on metal oxide semiconductors very attractive. Bismuth oxide is environmental friendly and are known to show good sensitivity with a large number of gases like CO_2, NO_2 and NO Bhande et al (2011); Gou et al (2009); Cabot et al (2004).

Metal oxide semiconductor based sensors mainly work by adsorption and desorption of gas on the surface causing a change in their electrical resistance Fine et al (2010); Seiyama et al (1962). Thus a large surface area is highly desirable for a good sensor. Nanostructures provides an ideal way of achieving this and their morphology has a direct impact on the gas sensing behaviour of the material Gurlo (2011). In this paper, horizontally aligned nanoplates of Na_3BiO_4 - Bi_2O_3 mixed oxide have been synthesized using potentiostatic electrodeposition and their CO_2 sensing properties have been studied at different pressures.

2 Materials and methods

2.1 Materials

Bismuth nitrate pentahydrate ($Bi(NO_3)_3.5H_2O$) used in the current study was purchased from Loba. Sodium nitrate ($NaNO_3$) and nitric acid (HNO_3) were purchased from Merck and Qualigens respectively.

2.2 Synthesis

Potentiostatic electrodeposition with standard three electrode system was used for synthesis with indium tin oxide (ITO) coated glass plate as working electrode Jiang et al (2017); Rivera et al (2017). Platinum wire was used as the auxiliary electrode and Ag/AgCl (Saturated KCl) was used as the reference electrode. Electrolyte was prepared by dissolving bismuth nitrate pentahydrate ($Bi(NO_3)_3.5H_2O$), sodium nitrate ($NaNO_3$) and 69% nitric acid (HNO_3) in distilled water to obtain molarities of 0.013 M, 0.013 M and 1 M respectively. For horizontally aligned nanoplates, deposition was done at a reduction potential of - 0.07 V, 100 rpm stirring speed and 10 min deposition time. These parameters have been optimized to obtain the desired morphologies Morales et al (2005).

2.3 Sensor setup

A chemiresistor type sensor has been prepared for studying the gas sensing behavior of these nanoplates (figure 1). The nanoplates are deposited on to the ITO substrate using potentiostatic electrodeposition. After drying at room temperature, two leads of copper wire were attached using silver paste. This sensor was then installed inside a homemade stainless steel gas sensing chamber (figure 2). Keithley sourcemeter (2601B) was connected to the sample for resistance measurement at a constant current of 10 mA. Keithley power supply (2600B-250-4 360W) and a Keithley digital multimeter (2700) were used to power the heater and measure the temperature inside the chamber. Inlet and outlet valves were installed to inject and release the gas from the chamber. Chamber pressure was measured with the help of pressure meter fitted at the top of the chamber. CO_2 gas was introduced from a pressurized cylinder (100 % CO_2).

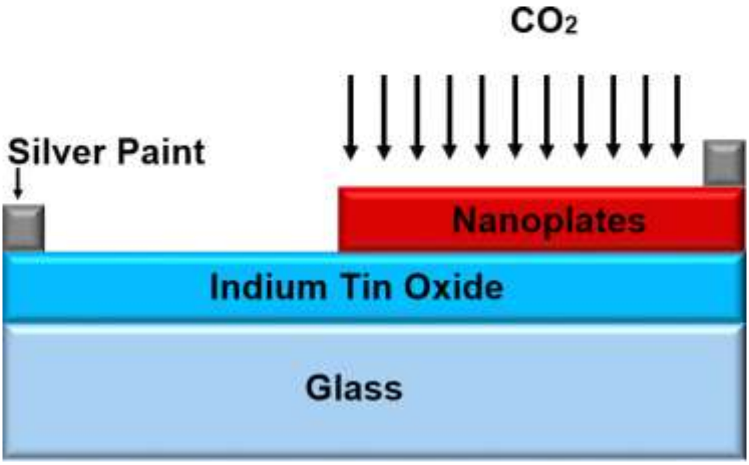

Fig. 1 Schematic device structure of the sensor

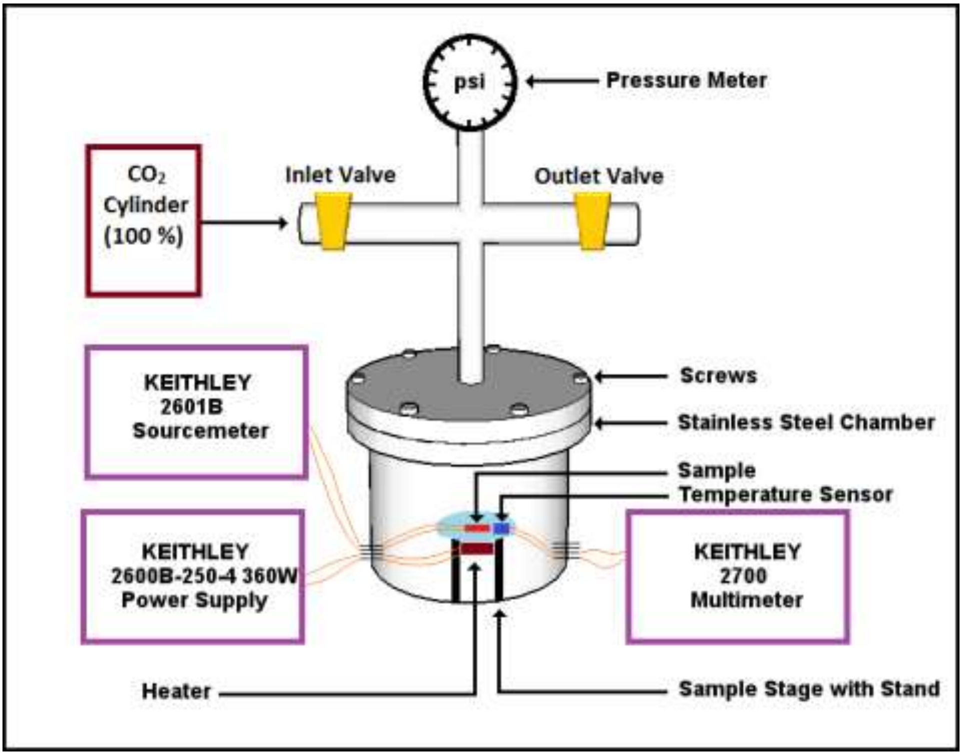

Fig. 2 Schematic diagram of gas sensing setup

3 Results and discussion

3.1 Voltammetric Studies

Figure 3 shows cyclic voltammetry studies on ITO electrode in an electrolyte containing 0.013 M Bi^{3+} ions, 0.013 M Na^{+} ions and 1 M H^{+} ions. Peaks corresponding to reduction of cations are seen at cathodic potentials. Similar results have been reported earlier on fluorine doped tin oxide gas substrate Sadale and Patil (2004). A shift in reduction peak potential is seen in successive cycles. This effect is mainly due to change in the concentrations of reactants and products near the electrode in each cycle Fried (2012).

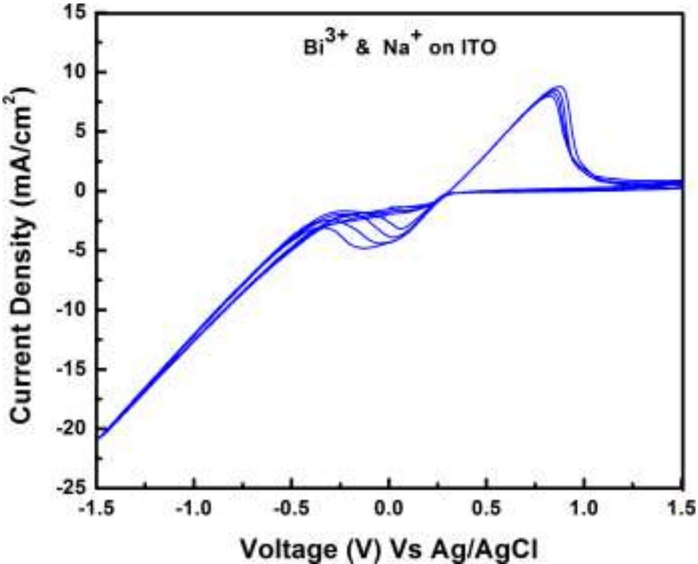

Fig. 3 Cyclic voltammetry curves on ITO in presence Bi^{3+} (0.013 M), Na^{+} (0.013 M)and H^{+} (1 M)

3.2 Morphological studies

SEM image shows the presence of horizontally aligned nanoplates with thickness ranging from 40 nm to 75 nm (figure 4). Edge length varies from 4 μm to 12 μm. These nanoplates appear to be stacked on top of one another with smooth surfaces.

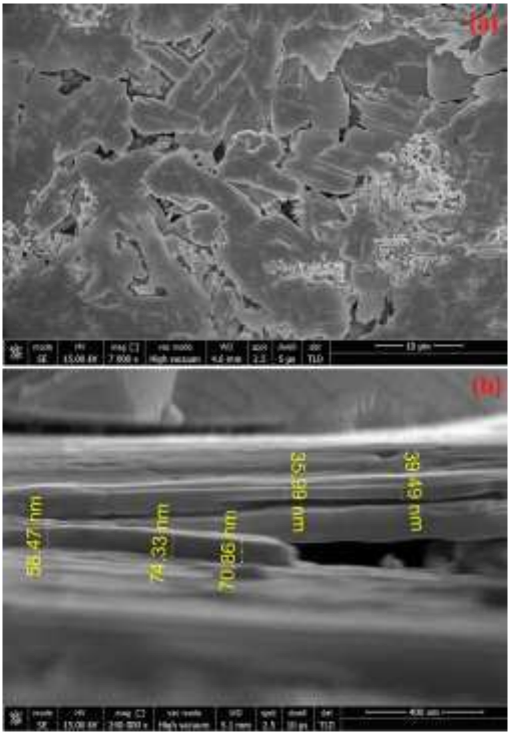

Fig. 4 Scanning electron microscopy images for Na_3BiO_4 - Bi_2O_3 mixed oxide nanoplates (a) top view (b) cross sectional view

3.3 Structural studies

X-Ray diffraction pattern shows that the prepared sample is polycrystalline in nature (figure 5). Major diffraction peaks correspond to Na_3BiO_4 (JCPDS 01- 071-1583) and Bi_2O_3 (JCPDS 00-041-1449). Both the oxide phases Na_3BiO_4 and Bi_2O_3 exhibit monoclinic structure. Semiquantitative concentration analysis (PANalytical X'pert Highscore) shows that the relative fraction of Na_3BiO_4 and Bi_2O_3 phases are 20 % and 80 % respectively.

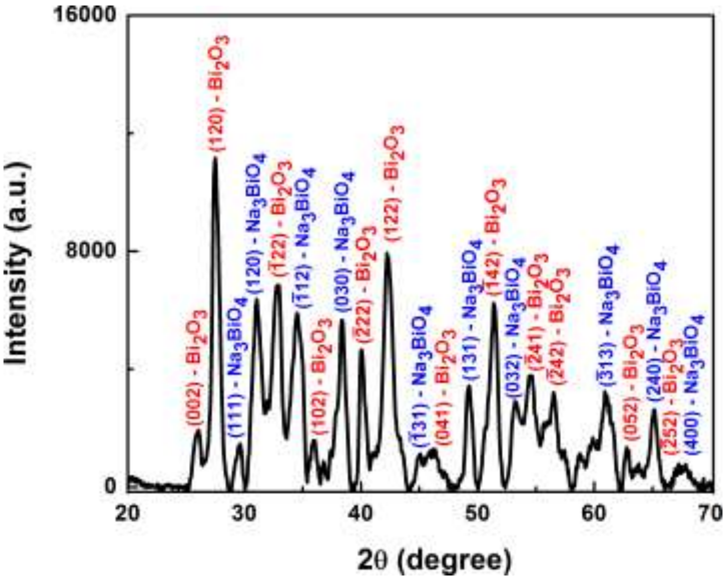

Fig. 5 X-ray diffraction pattern for Na_3BiO_4 - Bi_2O_3 mixed oxide nanoplates

3.4 Gas sensing

The percentage response of the Na_3BiO_4 - Bi_2O_3 mixed oxide nanoplates towards CO_2 was determined by measuring the change in resistance of the sample on exposure to carbon dioxide using the formula: Response (%) = $((R_o\text{-}R_g)/R_g)*100$ Rella et al (1997). R_o is the resistance of sample in presence of air while R_g is the resistance in presence of CO_2 gas. These measurements were initially carried out at 90 psi CO_2 pressure for 50° C, 75° C and 100° C (figure 6). At first, CO_2 gas was flushed trough the chamber to remove the air present in the chamber. The output valve was then closed and the required CO_2 pressure was built up (indicated by CO_2 ON). In the third step (indicated by CO_2 OFF), inlet valve was closed and the outlet valve was opened to release the CO_2 pressure. Percentage response of 0%, 15.5% and 276.8 % was seen at 50° C, 75° C and 100° C respectively.

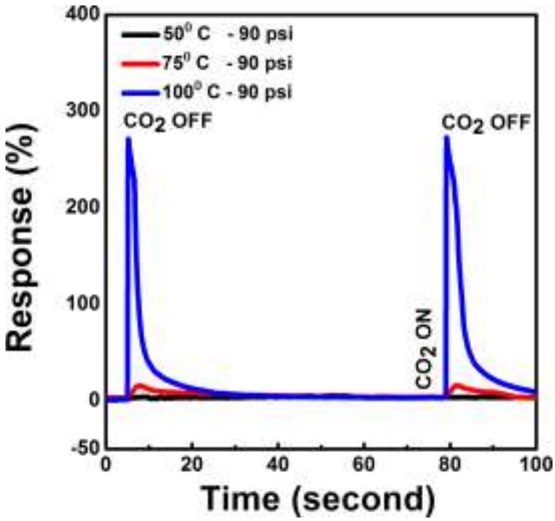

Fig. 6 Percentage response at 90 psi CO_2 pressure at (50° C, 75° C and 100° C) for Na_3BiO_4 - Bi_2O_3 mixed oxide nanoplates

Effect of variation in CO_2 pressure was further evaluated at different pres- sures and at a fixed temperature of 100° C. Figure 7 (a), (b) and (c) shows the percentage response curve for 90 psi, 60 psi and 30 psi CO_2 pressures respec- tively at 100° C. Comparison of response time at different pressures is shown in figure 8. Details of percentage response, response time and recovery time are shown in Table 1.

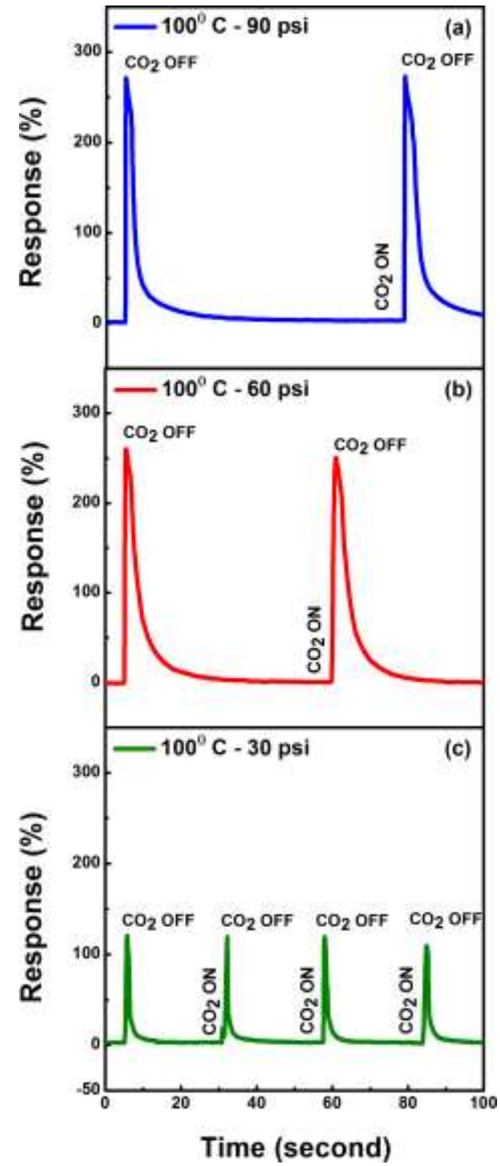

Fig. 7 Percentage response curves for Na_3BiO_4 - Bi_2O_3 mixed oxide nanoplates

Table 1 Percentage response, response time and recovery time at 90 psi, 60 psi and 30 psi CO_2 pressure (100° C) for Na_3BiO_4 - Bi_2O_3 mixed oxide nanoplates

Pressure (psi)	Response (%)	Response Time (ms)	Recovery Time (s)
90	276.8	250	78.0
60	254.5	500	53.5
30	116.5	650	24.5

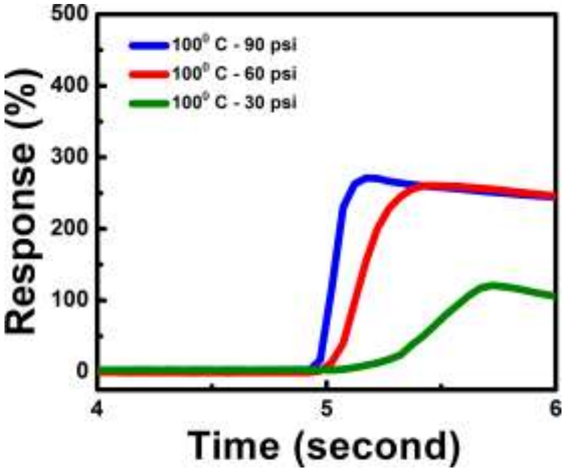

Fig. 8 Comparison of response time at different pressures for Na_3BiO_4 - Bi_2O_3 mixed oxide nanoplates

Highest percentage response value of 276.8 % is obtained at 90 psi, which decreases to 254.5 % & 116.5 % at 60 psi and 30 psi respectively for Na_3BiO_4 - Bi_2O_3 mixed oxide nanoplates. Response time increases (250 ms at 90 psi, 500 ms at 60 psi & 650 ms at 30 psi) while recovery time decreases (78 s at 90 psi, 53.5 s at 60 psi & 24.5 s at 30 psi) as the pressure is decreased from 90 psi to 30 psi This may be due to deeper adsorption of gas molecules at higher pressures. Bi_2O_3 nanoplates prepared by the similar route do not show significant percentage response (3.5 % at 100° C and 90 psi gas pressure) while ITO substrate shows no sensitivity at all. To further analyze the relationship between CO_2 pressure and percentage response, a linear fit is plotted (figure 9). A sensitivity of 3.2 %/psi is seen (R^2 = 0.94).

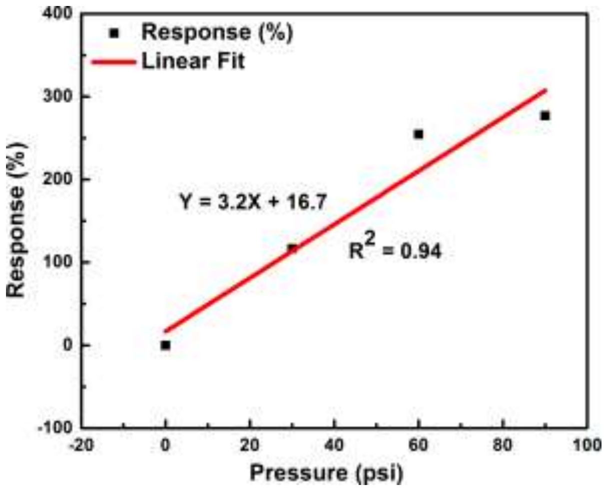

Fig. 9 Linear fit of percentage response for Na_3BiO_4 - Bi_2O_3 mixed oxide nanoplates in the range 0 psi to 90 psi (at 100° C)

Repeatability studies are shown in figure 10 for 90 psi pressure. Each successive cycle shows similar characteristics with almost equal values for percentage response, response time and recovery time.

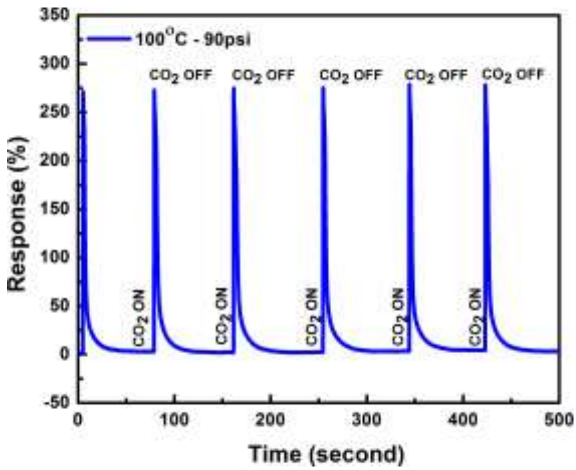

Fig. 10 Percentage response (6 cycles) at 90 psi (100° C) for Na_3BiO_4 - Bi_2O_3 mixed oxide nanoplates

The gas sensing mechanism can be explained by taking into account the interaction of CO_2 with the surface nanoplates (figure 11). An almost instantaneous decrease in resistance is seen on exposure to CO_2 gas.

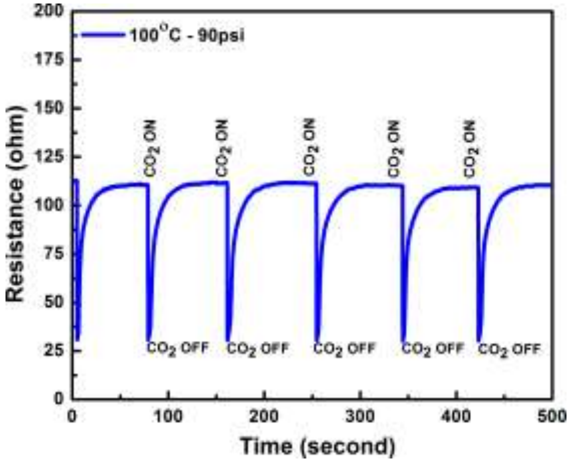

Fig. 11 Resistance change at 90 psi CO_2 pressure and 100° C for Na_3BiO_4 - Bi_2O_3 mixed oxide nanoplates

When the heated metal oxide nanoplates are exposed to air, oxygen gets adsorbed on the surface. At temperatures < 150° C, oxygen is predominantly adsorbed as O^{2-} Ranwa et al (2014). The detailed mechanism can be explained with the help of following equations:

$$\mathbf{O_2\ (air) \longrightarrow O_2\ (adsorbed)} \tag{1}$$

$$\mathbf{O_2\ (adsorbed) + 2e^- \longrightarrow 2O^{2-}} \tag{2}$$

In this process, oxygen takes up electrons from the conduction band. This leads to the formation of an electron depletion layer for an n-type material or a hole accumulation layer for a p-type material. When an oxidizing gas like CO_2 gas is introduced on to a n-type metal oxide semiconductor surface, the gas molecules gets adsorbed onto the surface of the material by taking up free electrons. The mechanism of CO_2 adsorption can be understood with the help of following equations Bhande et al (2011):

$$\mathbf{CO_2 \longrightarrow CO + O} \tag{3}$$

$$\mathbf{O + 2e^- \longrightarrow O^{2-}} \tag{4}$$

CO_2 breaks up into CO and O on surface interaction. The oxygen atoms released takes up electrons from the surface forming O^{2-}. This causes a further expansion of electron depletion layer which in turn causes a decrease in conductivity. However when a p-type material is involved, CO_2 causes an expansion of hole accumulation layer thereby causing an increase in conduc- tivity or decrease in resistance Hung et al (2017).

In the present work, a significant decrease in resistance is observed for Na_3BiO_4 - Bi_2O_3 mixed oxide nanoplates on introduction of CO_2 gas (figure 11). This suggests that this material is behaving as a strong p-type semicon- ductor (figure 12). Nanoplates offer a very large surface area leading to good adsorption. Results suggests that this adsorption is reversible and the original conductivity of the material is restored after the gas is removed.

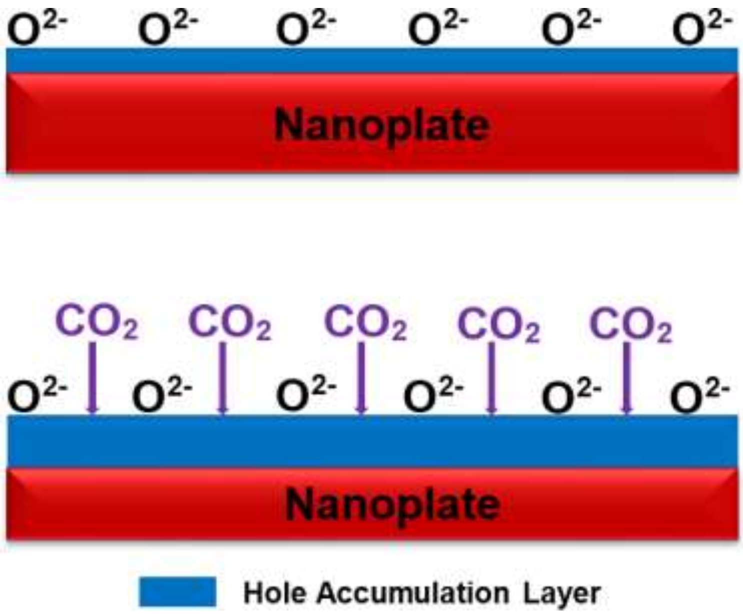

Fig. 12 Schematic diagram of the CO_2 gas sensing mechanism for Na_3BiO_4 - Bi_2O_3 mixed oxide nanoplates

4 Conclusion

Na_3BiO_4 - Bi_2O_3 mixed oxide nanostructures have been synthesized using potentiostatic electrodeposition. XRD analysis shows peaks corrsponding to monoclinic Na_3BiO_4 and Bi_2O_3 with weight percentage of 20 % and 80 % respectively. SEM studies reveals the presence of horizontally aligned nanoplates with thickness ranging from 40 nm to 75 nm. The percentage response shows a linear dependance on pressure in the range 0 psi to 90 psi and 100° C ($R^2 = 0.94$). A sensitivity of 3.2 %/psi is observed. These mixed oxide nanoplates shows a very quick response to CO_2 gas, which is a highly sought after characteristic for a gas sensor. Repeatability and stability makes this material an ideal candidate for sensor development.

Acknowledgments. The authors are thankful to UGC DAE CSR, Indore (CSR-IC/CRS-73/2014/435) for providing financial support. We are also thankful to MRC, MNIT Jaipur for providing characterization facilities.

Declarations

- Ethical Approval
  The authors provide ethical approval for this study.
- Consent to Participate
  The authors provide their consent to participate in this study.
- Consent to Publish
  The authors provide their consent to publish this study.
- Availability of Data and Materials
  The autors confirm that the data and materials used in this study are available on request.
- Funding
  The authors are thankful to UGC DAE CSR, Indore (CSR-IC/CRS- 73/2014/435) for providing financial support. We are also thankful to MRC, MNIT Jaipur for providing characterization facilities

- Competing interests
  The authors have no relevant financial or non-financial interests to disclose

- Authors' contributions
  Sandeep Gupta: Sample preparation, data acquisition and writing the draft manuscript.
  Anoop Mampazhasseri Divakaran : Gas sensing set-up designing and XRD data analysis.
  Kamlendra Awasthi: Supervision of data analysis
  Vaibhav Kulshrestha, Divesh N. Srivastava and Manoj Kumar:
  Conceptualization of research problem and supervision of experiments.

References

Barsan N, Koziej D, Weimar U (2007) Metal oxide-based gas sensor research: How to? Sensors and Actuators B: Chemical 121(1):18–35

Bhande SS, Mane RS, Ghule AV, et al (2011) A bismuth oxide nanoplate-based carbon dioxide gas sensor. Scripta Materialia 65(12):1081–1084

Cabot A, Marsal A, Arbiol J, et al (2004) Bi2o3 as a selective sensing material for no detection. Sensors and Actuators B: Chemical 99(1):74–89

Dimitriou K, Bougiatioti A, Ramonet M, et al (2021) Greenhouse gases (co2 and ch4) at an urban background site in athens, greece: Levels, sources and impact of atmospheric circulation. Atmospheric Environment 253:118,372

Fine GF, Cavanagh LM, Afonja A, et al (2010) Metal oxide semi-conductor gas sensors in environmental monitoring. Sensors 10(6):5469–5502

Fried I (2012) The Chemistry of Electrode Processes. Elsevier Science

Gou X, Li R, Wang G, et al (2009) Room-temperature solution synthesis of bi2o3 nanowires for gas sensing application. Nanotechnology 20(49):495,501

Gurlo A (2011) Nanosensors: towards morphological control of gas sensing activity. sno2, in2o3, zno and wo3 case studies. Nanoscale 3(1):154–165

Hung CM, Le DTT, Van Hieu N (2017) On-chip growth of semiconduc- tor metal oxide nanowires for gas sensors: A review. Journal of Science: Advanced Materials and Devices

Jiang C, Zeng X, Wu B, et al (2017) Electrochemical co-deposition of reduced graphene oxide-gold nanocomposite on an ito substrate and its application in the detection of dopamine. Science China Chemistry 60(1):151–156

Morales J, Sanchez L, Bijani S, et al (2005) Electrodeposition of cu2o: An excellent method for obtaining films of controlled morphology and good performance in li-ion batteries. Electrochemical and solid-state letters 8(3):A159–A162

Philip B, Abraham JK, Chandrasekhar A, et al (2003) Carbon nanotube/p- mma composite thin films for gas-sensing applications. Smart materials and structures 12(6):935

Rai P, Jeon SH, Lee CH, et al (2014) Functionalization of zno nanorods by cuo nanospikes for gas sensor applications. RSC Advances 4(45):23,604–23,609

Rai P, Majhi SM, Yu YT, et al (2015) Noble metal@ metal oxide semiconductor core@ shell nano-architectures as a new platform for gas sensor applications.

RSC Advances 5(93):76,229–76,248

Ranwa S, Kulriya PK, Sahu VK, et al (2014) Defect-free zno nanorods for low temperature hydrogen sensor applications. Applied Physics Letters 105(21):213,103

Rella R, Serra A, Siciliano P, et al (1997) Co sensing properties of sno2 thin films prepared by the sol-gel process. Thin Solid Films 304(1-2):339–343

Rivera M, Martinez-Vado F, Mendoza-Huizar L, et al (2017) Morphological and local magnetic properties of cobalt clusters electrodeposited onto indium tin oxide substrates. Journal of Materials Science: Materials in Electronics pp 1–7

Sadale S, Patil P (2004) Nucleation and growth of bismuth thin films onto fluorine-doped tin oxide-coated conducting glass substrates from nitrate solutions. Solid State Ionics 167(3):273–283

Seiyama T, Kato A, Fujiishi K, et al (1962) A new detector for gaseous compo- nents using semiconductive thin films. Analytical Chemistry 34(11):1502– 1503

Shahbazi H, Abolmaali AM, Alizadeh H, et al (2021) Development of high-resolution emission inventory to study the relative contribution of a local power plant to criteria air pollutants and greenhouse gases. UrbanClimate 38:100,897