

SYNTHESIS OF NANOTUBULAR NiO-CNT COMPOSITE AND ITS APPLICATION IN TEMPERATURE INDEPENDENT CO₂ GAS SENSORS FABRICATED USING INTERDIGITATED SILVER ELECTRODE

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A nanotubular NiO/CNTs composite is by tethering NiO onto the surface of the CNTs and subsequent chemical deposition by simple hydrothermal method. CNTs increase the electrochemical utilization of metal oxide as it can provide a great reaction site because of the large specific area and high electronic conductivity. The sensor is fabricated on flexible PET substrate using silver material for making the interdigitated electrode and embedding the highly conductive sensing material on it to form the electrical contact. The gas response was found to be linear between CO₂ concentrations of 1000–4000 ppm, with a high sensitivity of 6.5% at room temperature when the concentration of ambient CO₂ gas was 4000 ppm.

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1. Introduction

Carbon dioxide is non-inflammable, odourless, colourless and not easily detectable in its vapor and fluid states. It is however a minor, but vital constituent of the environment, averaging around 0.036% to 360 ppm by volume. It is likewise a typical end-product of animal and human metabolism. Gaseous CO₂ is found in higher concentration even at low levels as the density is 1.5 times greater than air. Standards and legislative control have been implemented over years to maintain an acceptable level of exposure in domestic and industrial uses [1]. At a concentration of only 15% in air, CO₂ can cause threat to life due to its toxic effect. Toxicological symptoms of inhalation of CO₂ in humans range from headaches, increased respiratory and heart rate, dizziness, unconsciousness to coma and death depending on the concentration and duration of exposure. Hence, it is very important to develop low-cost and highly sensitive sensors for detecting CO₂ concentration in the atmosphere.

Researchers have been endeavoring to make improvements in solid state gas sensors with the aim of enhancing the properties like selectivity, sensitivity, response time and stability. Metals and metal oxides have received impressive consideration during the past decades due to their size-dependent physical, chemical, optical, magnetic and electronic properties in comparison to their bulk counterparts [2]. During the past decade, numerous efforts had been made towards the synthesis of nanomaterials with a goal of dimension and shape selectivity, elimination of risky chemical substances within the protocols with scalability and simple workup techniques [3-5]. Transition metal oxides show high electrochemical properties and are inexpensive, abundant and have low toxicity. Nickel oxide (NiO) is a

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crucial transition-metal oxide with cubic lattice structure, which has attracted increasing attention due to promising use in a array of applications such as use in a variety of applications which includes: catalysis, battery cathodes, gas sensors, electrochromic films and magnetic material [6]. It has excellent durability, exhibits anodic electrochromism and electrochemical stability, large spin optical density and offers various manufacturing possibilities [7]. Additionally as a low cost storage material, NiO semiconductor turns into a motivating topic within the new area of studies. Because of the volume effect, the quantum size impact, the surface effect and the macroscopic quantum tunnel impact, nanocrystalline NiO is predicted to possess many improved sensing characteristics [8,9]. Also, it possesses multiple oxidation states which favour rapid redox reactions, resulting in high specific capacitance. Practically, NiOx is not deployed in gas sensing applications due to long reaction/recovery time, excessive resistivity and poor long-term stability. However, nickel oxide can be combined with other components and form nanocomposites to attain higher electronic conductivity [10]. The attachment of nanoparticles (NPs) on carbon nanomaterials (CNMs), consisting of Single-walled carbon nanotubes (SWNTs), multi-walled carbon nanotubes (MWNTs), and graphene has attracted abundant interest, for the nanocomposites not only amalgamates the extraordinary properties NPs and CNMs, but as well display some new and improved properties acquired by the interactions amid them. NiOx is a material with p-type conductivity

Several influencing elements, including the characteristics and structure of the sensing layer, affect the redox reactions and hence decide the sensitivity of metal oxides as gas sensing materials [11,12]. For maximum metal oxide gas sensors, the excessive working temperature is due to the reaction temperature of O⁻. The sensitive layer needs to be preheated to a high temperature in order to increase the chance of gas molecule adsorption at the surface which might consume ions of the sensing materials. As the ions interact, the conductivity of the material will change, to enable the sensing feature [13]. Heating filaments and micro-hotplates are commonly used for this purpose, which call for more cost and complicated configurations compared to others operating at room temperature [12-15].

Conventional metal oxide sensing materials, including NiO, have to address the problem of low sensitivity at room temperature, while Carbon Nanotubes (CNTs) attract greater interest due to their distinctive properties and have come to be the foremost promising materials for highly-sensitive gas sensors [16,17]. As a form of promising sensing material Multiwalled Carbon Nanotubes (MWCNTs), are found to possess electrical properties and are sensitive to extremely small traits of gases, including alcohol, ammonia (NH₃), carbon dioxide (CO₂) and nitrogen oxide (NO_x) at room temperature, whilst other substances have to be heated by an additional heater so as to work normally. This high sensitivity eliminates the need of aiding techniques like pre-concentration, and for that reason contributes to the benefits of low cost, low weight and simple configuration. Besides, MWCNTs also outdo traditional sensing materials in terms of great adsorptive ability, larger surface-area-to-volume ratio and quick reaction time, leading to vital changes in electrical properties, like capacitance and resistance [18-20]. Furthermore, in comparison with metal oxide semiconductors that require microfabrication techniques, power source and ad-hoc electronics when applied as sensing material, MWCNTs possess top corrosion resistance and higher bandwidth. In this work, synthesis of nanotubular NiO/CNTs composite is done, and its response to CO₂ gas is studied.

2. Experimental methods

2.1. Preparation of NiO nanorods for preliminary studies

All the chemicals were of analytical grade reagents without further purification. De-ionized water was used throughout the experiments. In the typical procedure, 1:10M ratio of NiCl₂·6H₂O and CH₃COONa·3H₂O were taken. Initially, 0.1M NiCl₂·6H₂O was dissolved in ethylene glycol (HO-CH₂CH₂-OH) were kept in water bath at 60°C with continuous stirring, further addition of 1M CH₃COONa·3H₂O after 15min changed into green transparent solution. The obtained green solution was microwave heated by LG commercial domestic microwave oven with different timing 1,2,3,4 mins.

These different timing results in different colour solution from brighter green colour to gray colour. Subsequently the solution was washed by ethanol and water mixture (1:3) several times. Then, the obtained sample was dried in hot air oven at 100°C for 14 hours. Finally, the samples were calcined at 400°C for 45min and 90 min respectively

2.2. Functionalization of MWCNT

The Oxidisation using acids or their mixtures is an efficient methodology for purification of carbon nanotubes. When acids act upon CNTs, destruction of the surface of nanotubes occur and the hemispheres at the termini are split apart. Carboxyl (-COOH), carbonyl (=CO) and/or hydroxyl (-OH) groups are created at the locations of intersection. The most widely recognized chemicals utilized for this procedure include- concentrated nitric acid (HNO_3), sulphuric acid (H_2SO_4), perchloric acid (HClO_4), a mixture of concentrated nitric and hydrochloric acid or perhydrol (30% H_2O_2). The degree of functionalization of CNT walls upon oxidization depends on type of oxidiser used, process temperature and curvature of nanotubes inflicting stresses between sp^2 bonds. Walls with a larger radius of curvature show better reactivity, accordingly they have higher susceptibility to oxidation.

In the present work, to synthesize NiO/CNT nanocomposite, the surface of CNTs was functionalized as follows: MWCNTs were first refluxed first in concentrated HNO_3 for 24 h and second in H_2O_2 for 12 h. Afterwards the MWCNTs were sonicated in deionized water and KMnO_4 solution was added drop wise. The precipitate was washed with ethanol after filtration and air dried without heating to produce nanomaterials.

2.3. Preparation of CNT-NiO Nanocomposite

For NiO/CNT nanocomposite preparation, 1.5 g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 50 ml of deionized water containing 0.5 g of functionalized CNTs. This was then ultrasonicated for 10 min and magnetically stirred for 15 min at room temperature. The addition of 1 g of NaOH to the mixture and stirring for 30 min facilitated the precipitation of $\text{Ni}(\text{OH})_2/\text{CNTs}$ nanocomposite. The solution was kept in oven for hydrothermal precipitation at 120°C for 6 hours in teflon lined autoclave. The obtained black mixture was filtered, washed with absolute ethanol and deionized water, dried at 80 °C for 24 h, and finally calcined at 300 °C for 2 h in static air

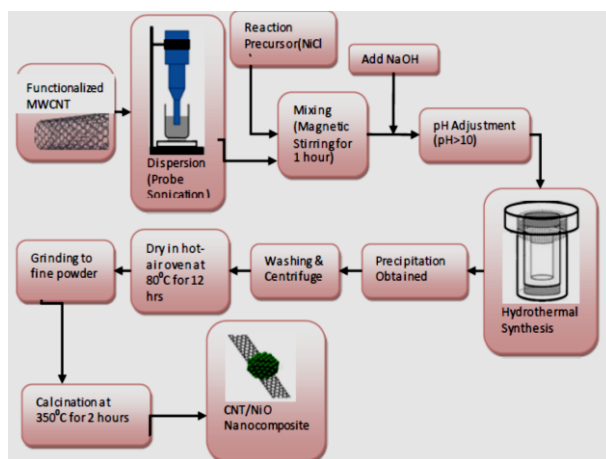


Fig 1. Preparation of CNT-NiO Nanocomposite.

3. Gas sensor fabrication and test set up

Gas sensor is fabricated on a flexible Polyethylene Tetrathalate (PET) substrate, to form a chemiresistor consisting of several pair of electrodes and conducting nanocomposite material in contact with the electrode. A constant potential is applied on the sensor and the change in electrical resistance of the sensing material on exposure to analyte gas is measured as output. To improve performance an interdigitated electrode made of silver material is used with each leg and gap between the legs have a thickness of 0.4 mm. Fig. 2 shows the design of the interdigitated electrode sensor and the testing chamber where the sensor comes in contact with the analyte CO_2 gas. The response of the sensor towards different concentrations of CO_2 is measured using Keithley Source Meter-Model No.2401.

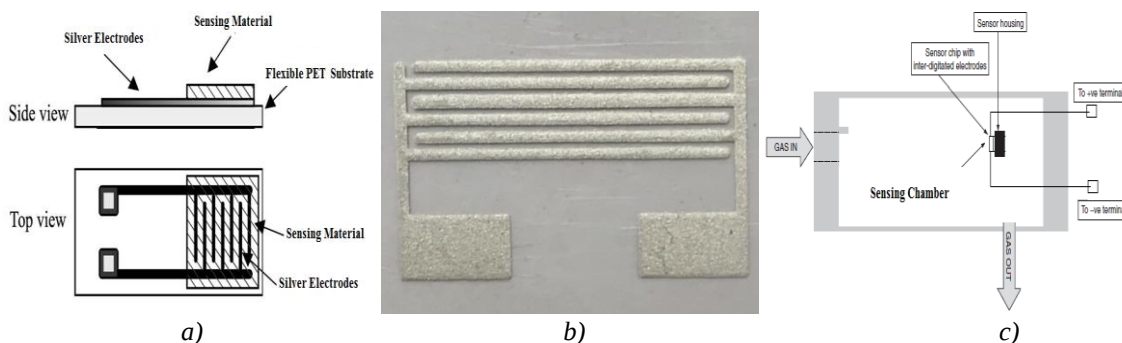


Fig. 2. (a) Schematic diagram of the sensor (b) interdigitated silver electrode (c) Schematic of gas sensing chamber.

4. Results and Discussion

The as-prepared nanomaterials were characterized and analyzed for gas sensing response towards carbon dioxide gas. Structural and morphological characterizations were done using UV-Vis Spectroscopy, Fourier Infrared Spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

4.1. UV-Visible spectrophotometry

UV-Vis spectral analysis has been performed for the prepared samples of bare NiO nanorods and CNT/NiO nanocomposite (before and after annealing). According to existing studies, NiO nanoparticles show an adsorption peak between 300 -350 nm, at the same time as doped nanoparticles display absorption above 350 nm. Rifaya et al., in 2012 reported the band gap for nickel oxide to be 3.6-4.0 eV. In figure, the spectrum reveals a function absorption edge of NiO at a wavelength of 350 nm. The strongest absorption bands at 330 nm for the NiO is shifted to a lower absorption band at around 280 nm in the presence of MWCNT indicating the successful formation of MWCNT-NiO nanocomposite.

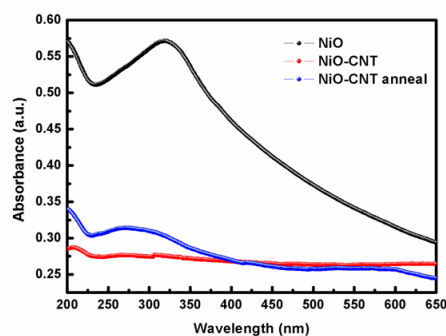


Fig. 3. UV-Vis Spectrophotometry analysis.

3.2. Fourier Infrared Spectroscopy

ATR-FTIR spectra were recorded on a Shimadzu Affinity IS Series Spectrophotometer using KBr to form pellets with tested samples. Fig. 4 shows the FT-IR spectra of the (a) functionalized CNTs, NiO nanorods (b) and CNT/NiO nanocomposites (c & d) in the 4000–500 cm^{-1} spectral location. In the high frequency region, the broad band around 3411 cm^{-1} is corresponded to the stretching vibrations of the –OH groups. The broad band around 2843 cm^{-1} is assigned to the C–H stretching vibration mode, originating from the surfaces of the tubes. The top at 2357 cm^{-1} is as a result of –CH₂ and C–CH₃ stretching vibrations at the defect sites of these tubes. The dominant height at 1735 cm^{-1} may be assigned to the acid carbonyl stretching mode. The greater height round 920 cm^{-1} inside the nanocomposites can be attributed to O–H bending vibrations mixed with metal atoms. The FT-IR spectra of the NiO primarily based nanocomposites display peaks at 415 cm^{-1} and 563 cm^{-1} which can be derived from the stretching vibration of Ni–O bond.

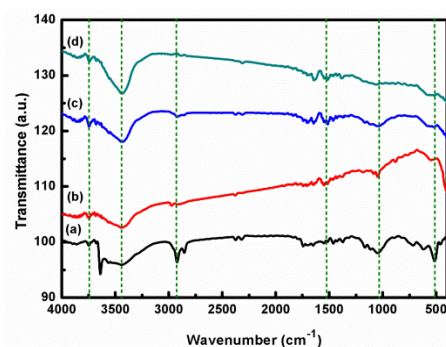


Fig. 4. Fourier Infrared Spectroscopy Analysis.

4.3. X-Ray diffraction patterns

The x-ray diffraction spectrum of NiO sample with different microwave heating and calcination timings are shown in Fig. 5(a). The crystalline structure with 3 peaks (110, 110, 111) are in same phase at microwave heating rate of 2 min followed by calcination for 45 min at 400°C, similarly another crystalline structure at the upper side has a same phase with 3 peaks (110, 111, 111) with a microwave heating of 4 min and calcination temperature of 400°C for 45 min. A mixed phase appears when the material is subjected to 3 min microwave with 5 peaks (101, 002, 110, 202, 004) with a calcination temperature of 400 °C for 90 min. The data clearly indicates that the crystal structure changes from rhombohedral to hexagonal (Joint Committee for Powder Diffraction Studies, JCPDS No: 893080 and No: 140481). The XRD pattern shows a significant amount of line broadening which indicates the formation of nanoparticles. The data exhibits prominent peaks at 31.9°, 45.5°, 56.7°, 37.2°, 43.2°, and

62.8°. In Fig. 5 (b), it can be seen that the diffractogram of pure MWCNTs exhibit its typical peaks at 25.9° and 42.7°, corresponding to the graphite (002) and (100) reflections ((JCPDS) No. 01-0646), respectively.

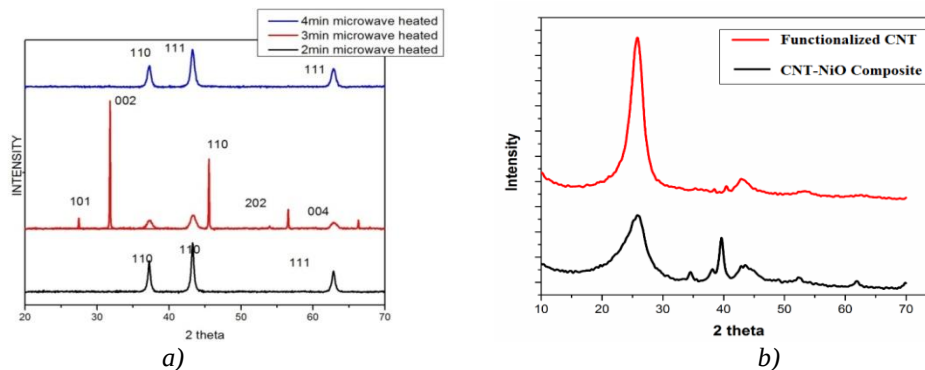


Fig. 5. X-Ray Diffraction Studies of (a) NiO nanorods at different temperatures and (b) Functionalized MWCNT and CNT-NiO nanocomposite structure.

4.4. Scanning Electron Microscope (SEM) Images

The morphological structure of the NiO nanorods and NiO/CNTs composite were investigated using Scanning Electron Microscopy (SEM, Zeiss Carl EVO 18), with the samples fixed on aluminium stubs and coated with gold. The SEM images of synthesized NiO nanorods and CNT-NiO nanocomposite are represented in fig a-d. Fig a and b indicates the formation of rod-like conglomerate structures of nickel oxide nanoparticles. Fig c and d are the SEM images of carbon nanotube materials, showing some loose curly tubes, which is the composite formed. In SEM images, NiO/CNTs composite exhibited a nearly uniform morphology, with neither NiO aggregation nor two-phase (NiO and CNTs) separation occurring. In the absence of CNTs, the NiO cannot grow on or attach to any substrates; instead, the NiO adopts an aggregation state.

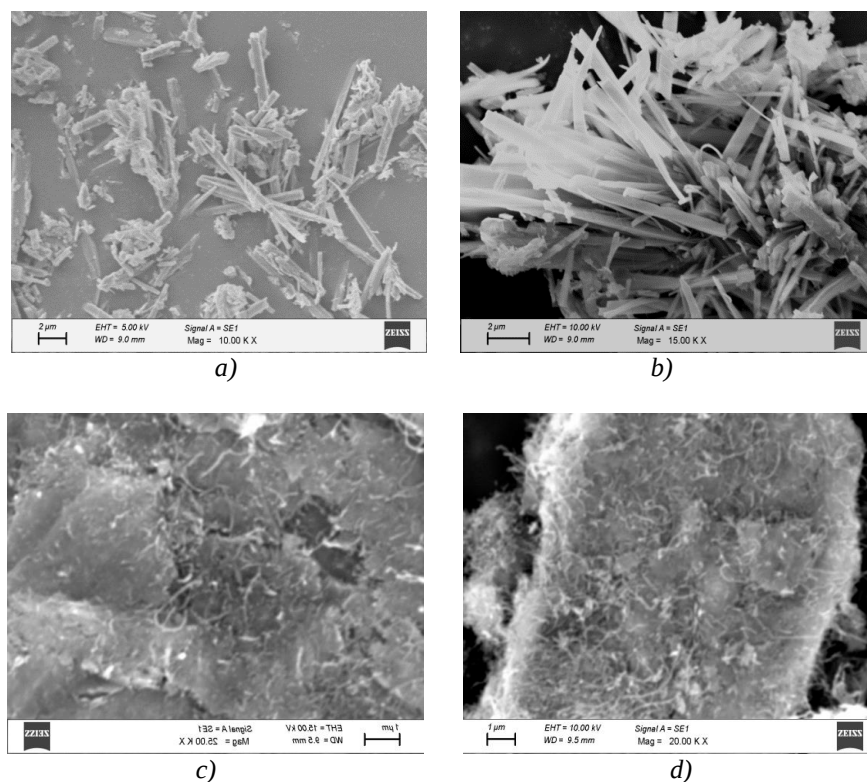


Fig. 6. SEM images of (a,b) NiO nanorods and (c,d) CNT-NiO nanotubular composites.

4.4. Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) micrographs were investigated with a JEOL JEM-2100 to confirm and observe the microstructure and phase transition directly through the oxidation of CNT by reducing NiO to nickel, selectively for NiO 50 wt% /CNT composite samples after the ex situ heat treatment at 350⁰C for 60 min.. Figure shows the TEM images, SAED pattern and EDS of the sample. Moreover, the Selected Area Electron Diffraction (SAED) pattern (Fig. 3e) exhibits concentric diffraction rings, revealing the nanocrystalline characteristics of the NiO phase in the CNTs/NiO composite. These rings shows d-spacing of 0.3440 nm, 0.2997 nm and 0.2160 nm which can be readily indexed to the (111), (101), and (110) planes of the NiO, consistent with the XRD results. No peaks for impurities are detected in EDS, indicating that hydrothermal method used in this study is responsible for formation of pure CNT-NiO nanocomposite.

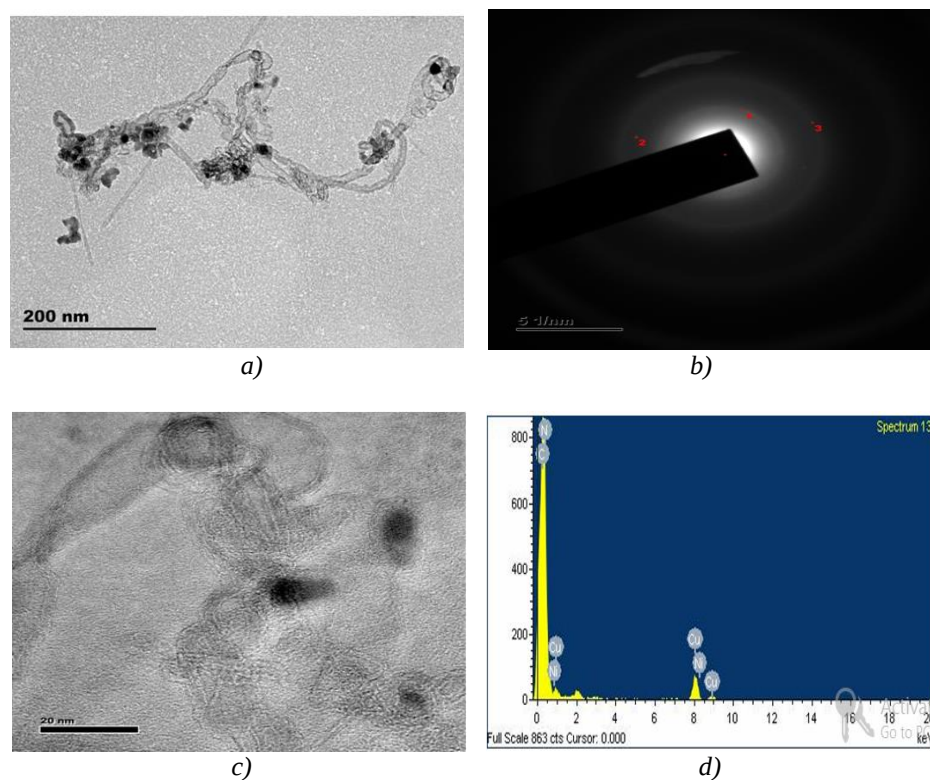


Fig. 7. (a,c)TEM images of NiO-CNT nanotubular composite, (b) SAED pattern of NiO-CNT nanotubular composite and (d) SAED pattern of the material.

4.5. Sensor response analysis towards CO₂ gas

The CNT-NiO nanocomposite solution is drop coated on the interdigitated electrode. A constant potential of 1 mV was applied on the sensor and the change in electrical resistance of the sensing material is measured. A chemical or physical change in any part of the sensor will motivate a consequential *change* in overall resistance of the device and the most crucial part is the bulk resistance. For a doped conducting chemical compound, its conductivity is mainly due to three components

$$\frac{1}{\sigma} = \frac{1}{\sigma_c} + \frac{1}{\sigma_h} + \frac{1}{\sigma_i}$$

where σ is overall conductivity, σ_c the intermolecular conductivity, σ_h the intramolecular hopping conductivity and σ_i the ionic conductivity. When react with analytes, σ_c can be altered via changing the doping stages of material by both redox reactions and acidic/basic doping/dedoping. The doping levels of conducting polymers can be effectively altered by chemical reaction and absorption of different analytes, and thus it serves as a simple method to ascertain the analyte gas. Electron transfer from or to the analyte causes the variations in resistance and work function of the sensing material.

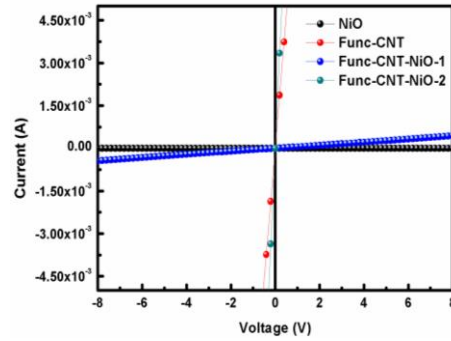
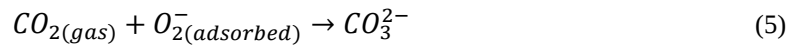
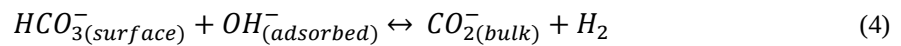
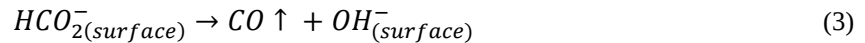
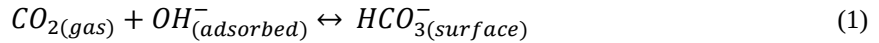


Fig. 8. I-V characteristics of pure NiO, MWCNT and of NiO-CNT nanocomposite.

I-V Characteristics shown in Fig. 8 reveals the ohmic behavior of the nanocomposite material. CNT material is highly conductive, whereas the NiO nanorods show very low conductivity at room temperature. The conductive nature of the CNT-NiO nanocomposite is due to its facile electronic nature, plus the ionic interaction between the NiO nanoparticles and MWCNTs are some of the factors responsible for this significant charge exchange. Similarly, the large surface area created by the porous MWCNT on the electrode facilitates free movement of charges between the base electrode and the electroactive composite material at the electrode surface which is another important factor for the larger conductivity at the surface.

The linear-bonded atoms of CO₂ molecule possess a stable structure and there does not exist any lone pair of electrons. At low temperatures, the dissociated hydrogen and hydroxyl ions from molecules at the surface of metal oxide react with gaseous carbon dioxide to form carbonate ions as given in equations 1-4, with intermediate ions, formate ions and bicarbonate ions. At higher temperatures, gaseous CO₂ molecules react with layered oxygen ions, to form carbonate ions.



Thus, the consumption of electrons by each carbon dioxide molecule during its interaction with metaloxide surface lead to change in conduction, which can be used for detection of CO₂. In the proposed work, CNT-NiO forms p-type material and therefore shows increase in conductivity. The response of the sensor to different concentrations of CO₂ is shown in figure. The base resistance of the sensor at room temperature is approximately 45 ohm, indicating typical well-conducting CNTs. The variation in resistance with concentration of CO₂ was analysed to determine that the speed of response and sensitivity of the fabricated sensor are favourable for its use in room-temperature. Figure plots the responses for the sensor, where change in resistance is measured in a series of CO₂ filling and pumping cycle. The electrode is kept a fixed voltage of 0.01V.

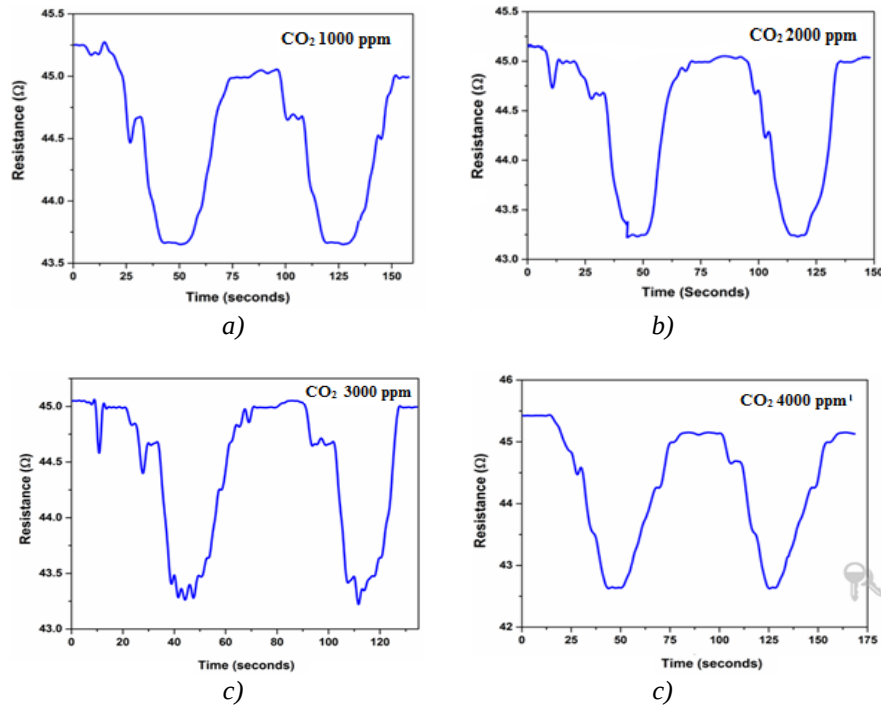


Fig. 9. Sensor response to different concentrations of CO_2 gas at room temperature.
a)1000 ppm; b)2000 ppm; c) 3000 ppm; d) 4000 ppm

Sensitivity is defined as the ratio $[(R_a - R_g)/R_g] \times 100$, where R_a is the resistance of the sensor before injecting CO_2 gas and R_g is the resistance obtained in the pumping half-cycle. At injected CO_2 gas concentrations of 1000, 2000, 3000 and 4000 ppm, the measured sensitivities were around 3.6%, 4.2%, 4.7%, 6.5% respectively. The strength of the response of the sensor maintained after repeated cycles of exposure and recovery. The performance of the sensors remained stable for a long period under normal operating conditions. Fig. 10 shows that the sensitivity increases linearly with the increase in concentration.

Table 1. Sensor response and sensitivity calculations, to different concentrations of CO_2 gas at room temperature.

Concentration	R_a	R_g	$R_a - R_g$	$\frac{R_a - R_g}{R_g}$	Sensitivity	T_a	T_g	$0.9(R_a - R_g)$
1000 ppm	45.236	43.663	1.573	0.036	3.6	0 s	42.01 s	1.4157
2000 ppm	45.147	43.317	1.83	0.042	4.2	0 s	43.19s	1.647
3000 ppm	45.117	43.084	2.033	0.047	4.7	0 s	42.05s	1.827
4000 ppm	45.415	42.632	2.783	0.065	6.5	0 s	47.40 s	2.5047

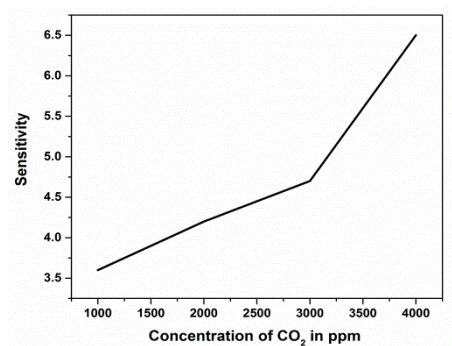


Fig. 10. Sensitivity of the NiO-CNT nanotubular material towards different concentrations of CO₂.

5. Conclusions

NiO-CNT nanotube composites were synthesized using a wet-chemical procedure under hydrothermal conditions which is economical, easy, efficient and simple to operate. Structural and morphological characterizations of the composite were conducted using UV/Vis Spectrophotometry, FT-IR, SEM, XEDS, TEM and XRD techniques. A flexible sensor was fabricated in PET substrate using silver ink material for making the interdigitated electrode and embedding the sensing material on it to form the electrical contact.

In NiO/CNT composites, CNT provide a great reaction site because of the large specific area and high electronic conduction path to the NiO, which if considered alone has relatively low conductivity. The flexible gas sensor exhibited a high sensitivity of 6.5% at room temperature when the concentration of ambient CO₂ gas was 4000 ppm. The speed and stability of the response of the fabricated sensor were both favorable and the results presented in this article clearly demonstrate the feasibility of manufacturing flexible CO₂ gas sensors using the NiO-CNT nanocomposite material.

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