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SYNTHESIS AND ANALYSING SENSING APPLICATION FOR AMMONIA USING CR DOPED CUO/SNO_2/WO_3 METAL OXIDE NANOSTRUCTURED BY HYDROTHERMAL METHOD AT ROOM TEMPERATURE

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ABSTRACT:
In the present study, the synthesis, structural and chemical characterization, and ammonia gas-sensing property of chromium (Cr)-doped metal oxide nanostructures synthesized by a hydrothermal method is presented. The nanostructures of Cr-doped SnO_2 and Cr-doped CuO were synthesized, respectively, initially, by varying the precursor concentration, pH, hydrothermal temperature, and reaction time. Next, an optimized Cr-doped SnO_2 and an optimized Cr-doped CuO were used to construct a "Cr-doped CuO/SnO_2/WO_3 ternary nanostructure. To understand the structural, morphological, elemental, and bonding features of the synthesized materials, they were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and Fourier-transform infrared spectroscopy (FTIR). The prepared materials were fabricated as sensing layer and were tested for ammonia detection at room temperature. The response to NH_3 was significantly enhanced for the ternary Cr-doped CuO/SnO_2/WO_3 sensor as compared to the individual Cr-doped SnO_2 and Cr-doped CuO sensors. The optimized ternary material exhibited a response of ~5.68 NH3 100 ppm, response time ~48 s and recovery time ~72 s NH3 50 ppm. The defect sites, surface-active sites and charge-transfer pathways generated by Cr were found to be responsible for the enhanced sensing performance at the CuO/SnO_2/WO_3 heterointerfaces. Selectivity and repeatability in successive ammonia exposure cycles were also tested and showed good characteristics of the sensor. These results show the strong potential of the Cr doped CuO/SnO_2/WO_3 nanostructures for sensitive and selective ammonia detection at room temperature.

KEYWORDS: Cr-doped SnO_2, Cr-doped CuO, CuO/SnO_2/WO_3 nanostructure, Hydrothermal synthesis, Ammonia sensor, Gas sensing, Room temperature detection, Metal oxide nanostructure

INTRODUCTION

Ammonia (NH_3) is a major industrial and environmental gas commonly used in the production of fertilizers, in refrigeration, in chemical processing, in pharmaceuticals and in various other manufacturing processes. Although ammonia is an important industrial gas, it is extremely toxic and can have adverse effects on the human body and environment if it exists in excess of acceptable levels. High levels and/or prolonged exposure to high ammonia levels can lead to serious respiratory problems, with eyes, skin or respiratory irritation occurring at lower levels of exposure. Thus, it is vital to develop sensitive, selective, rapid and reliable ammonia detection systems for industrial safety, environmental monitoring, agriculture and occupational health protection. Many traditional approaches for ammonia detection such as chromatography, optical, and electrochemical can be accurate but are typically accompanied by expensive equipment, complicated sample preparation, trained personnel, and/or laboratory-controlled conditions. Therefore, semiconductor metal-oxide based gas sensors have been given lot of attention due to its simple working principle, low cost, high sensitivity and possible miniaturization.(Begum et al., 2026)

Metal oxide semiconductor materials like SnO_2, CuO, WO_3, ZnO, TiO_2 and Fe_2O_3 have been widely studied for gas-sensing applications. Of these materials, SnO_2 is one of the most extensively investigated n-type semiconductor metal oxides due to its relatively high electron mobility, chemical stability and high affinity towards the adsorption of oxygen species. The mechanism of sensing of SnO_2 is mainly related to the adsorption of oxygen molecules and subsequent transfer of electrons from the semiconductor to the adsorbed oxygen. This results in a surface depletion layer and electrical resistance changes in the material. In contact with the reducing gas NH_3, the adsorbed oxygen species releases electrons back to the semiconductor, causing a resistance change to be detected. Pure SnO_2, however, may exhibit poor sensing performance at room temperature and limited selectivity, limiting its practical applications.(Ge et al., 2025)

Another technologically important metal oxide, p-type semiconducting CuO, has been reported to be interesting for gas sensing due to its surface reactivity, low cost, chemical stability, and p-type semiconducting nature. When CuO and target gases interact, it causes changes in the concentration of the charge carriers near the surface and consequently in the electrical resistance of the material. The p-type conductivity of CuO can offer a sensing mechanism other than n-

type SnO_2. The combination of p-type and n-type semiconductor materials can thus form heterojunctions that have significant effects on the charge transport and surface depletion properties. This type of heterointerfaces can enhance the gas-sensing performance by increasing the modulation of electrical resistance during the process of gas adsorption and desorption.(Seekaew et al., 2023)(Bhuvaneshwari & Gopalakrishnan, 2016)

Since the WO_3 is chemically stable with proper electronic properties and a strong interaction with a wide range of gaseous species, it is a promising metal oxide for gas sensing application. It can be integrated with other metal oxides to create more interfaces and active sites to enhance gas adsorption and charge-transfer processes. The synergistic combination of CuO, SnO_2, and WO_3 is a possibility to build a heterostructure with multi-oxide components in which the properties of each oxide can interplay and aid each other in the sensorial detection of gases. However, the simple mixing of various metal oxides does not necessarily result in better sensing properties. To achieve an efficient sensing material, control of morphology, crystallinity, interfacial contact, defect concentration and surface chemistry are necessary. A common method of tuning the physical properties and electronic properties of semiconductor metal oxides is doping. Of particular interest is the case of Cr, as its introduction into the lattice of a metal oxide structure can affect parameters of the structure, create structural defects, change the concentration of carriers and increase the number of chemically active surface sites. These changes can increase the adsorption of target gas molecules and further optimize the charge-transfer processes in the sensing process. Thus, doping of SnO_2 and CuO with Cr ions could be a potential way to enhance the ammonia sensing properties. But the sensing behavior is a strong function of the dopant concentration. While an appropriate concentration of Cr could lead to an increase in the number of defects and active adsorption sites, an excessive amount of doping may produce undesirable defects or disrupt the charge-transport pathways. It is therefore crucial to find an optimum doping level.(Y. Li et al., 2024)

Doped metal-oxide nanostructures can be synthesized by the hydrothermal technique, as it enables relatively good control of the particle shape, crystallinity, size and composition under relatively moderate reaction conditions. The method is based on chemical reactions carried out in a closed autoclave at high temperature and autogenous pressure, which allows nucleation and controlled growth of nanostructured materials. Hydrothermal processing can allow for improved control of nanoscale morphology when compared to some conventional high-temperature synthesis routes and has the potential to be adapted to the preparation of doped and composite metal oxides. In the current study, Cr-doped SnO_2 and Cr-doped CuO nanostructures were synthesized separately using the hydrothermal method at first and their ammonia-sensing properties were tested. The optimized Cr-doped materials were then added with the WO_3 which eventually resulted in the formation of the $CuO/SnO_2/WO_3$ ternary nanostructure containing Cr as a dopant. XRD, SEM, EDS, and FTIR analyses techniques were used in order to structurally, morphologically, and compositionally characterize the synthesized materials. Ammonia-sensing behavior at room temperature was investigated in terms of response, response time, recovery time, concentration dependence, selectivity, and repeatability of their ammonia-sensing behavior. Special focus was placed on the ability of the ternary heterostructure to exhibit better ammonia-sensing performance than the individual Cr-doped SnO_2 and Cr-doped CuO materials. The creation of this type of nanostructured sensing material is important because it can allow sensors to be operated at room temperature to lower energy usage and make sensor design easier in comparison to those sensors operated at higher temperatures. These synergistic effects of Cr doping and the formation of heterostructure of $CuO/SnO_2/WO_3$ may lead to an increase in the number of surface-active sites, better charge-transfer pathways, and stronger interactions among ammonia molecules. Hence, the present work is aimed at the preparation and systematic evaluation of a nanostructure of $CuO/SnO_2/WO_3$ as a sensitive and selective material for room temperature ammonia gas sensing that will be used in industrial safety, environment monitoring and real time gas detection system.(Husein et al., 2019).

LITERATURE REVIEW

(C. Li et al., 2025)This substance, ammonia, is one of the most important biomarkers found in human breath and has a very important participation in non-invasive breath testing at room temperature. Reflective fiber-optic sensors (FOS) using surface plasmon resonance (SPR) response have a number of merits for room temperature gas sensing, such as high sensitivity, small size and portability. In the present study, WO_3/SnO_2 nanocomposites have been prepared by solvothermal route to develop sensitive material for room temperature NH_3 detection. The WO_3/SnO_2 nanocomposites were dip-coated on the surface of the SPR fiber to yield a uniform film as gas-sensitive layer. The sensor achieved a high sensitivity of −10.84 a.u/ppm with a fast response time of 2 s and a theoretical limit of detection of 277 ppb at room-temperature. The improved sensing performance is attributed to the creation of the heterojunctions between WO_3 and SnO_2 that promote efficient charge transfer and amplify the SPR signal through dielectric modulation. This work focusses on the potential of low dimensional material integrated optical fiber-based platforms for non-invasive medical diagnostics by the detection of ammonia in exhaled breath

(Tazim et al., 2025)Nanomaterials (NMs) are materials whose dimensions are at least one below 100 nanometers (nm), and as a result of its minimal size, materials exhibit unique and intriguing properties. There are unique thermal, magnetic, optical and chemical properties that distinguish the NMs from bigger molecules like micromolecular, bulk organic or inorganic compounds. Metal oxide NMs are used in the medical field for targeted drug delivery, in the environment for pollution management and water treatment, and for enhancement of energy production in electronics. With the increasing need of nanomaterials having well-defined morphological properties for specific applications, many research efforts have been focused on the hydrothermal synthesis of materials under different reaction conditions to obtain both scientific and practical novel results. Several studies have been performed to investigate the effects of different response parameters on the basic properties and shape of MNs. Hence, in the present review paper, the hydrothermal synthesis of seven important metal oxides (ZnO, CuO, Fe_2O_3, CdO, TiO_2, Al_2O_3 and CaO) have been

discussed under various reaction conditions. Moreover, it discusses the influence of different source materials and reaction parameters on the morphology of these nanoscale materials, which helps to design them for targeted uses.

(Khan et al., 2025)In the present study, tungsten trioxide (WO_3), copper oxide (CuO), and WO_3/CuO nanocomposite were developed for the detection of dopamine (DA) and ammonia (NH3) under ambient condition. Structural and morphological properties of the prepared materials were studied by Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The electrochemical performance of the modified glassy carbon electrode with WO_3/CuO nanocomposite (WO_3/CuO/GCE) showed that DA was oxidized at around 0.37 V, which is an indication of the electrocatalytic activity of the nanocomposite WO_3/CuO. A low limit of detection" (LOD) of 0.24 ± 0.01 μM and a wide linear dynamic range in the range of 10 to 200 μM were obtained by the DPV measurements. The sensor was found to possess an excellent selectivity to DA in the presence of common interfering species and its suitability for real sample analysis. Moreover, the WO_3/CuO nanocomposite displayed a high sensing ability (200 ppm) and selectivity towards ammonia and very low LOD of 3.93 × 10−5 ppm. The sensor also showed a fast adsorption–desorption response time of 9 s and 3 s, respectively, indicating that the adsorption–desorption process was fast and the sensor could be used repeatedly without any problem. The results indicate that WO_3/CuO nanocomposite has the potential to be an efficient multifunctional sensing material for electrochemical and gas-sensing applications.

(Yusefi et al., 2024)Ethylene gas is involved with natural ripening of fruits and vegetables (Yusefi et al., 2024). But, destructive reactions and short shelf life can occur at elevated levels of ethylene. The measurement of ethylene concentration is a strong technique to control ripening and spoilage of agricultural products. Existing ethylene detection methods are bulky, costly or lack in sensitivity and selectivity. Hence, the development of small, low cost, low energy, high sensitivity ethylene sensor is important. In this work, CF/CuO/SnO $_2$ nanocomposite was prepared by transforming the copper foam (CF) into tin dioxide/copper oxide (CuO/SnO2) dual-core nano-hybrid by thermal and hydrothermal routes "on the CuO nanoclusters. Energy-dispersive X-ray analysis, field-emission scanning electron microscopy, X-ray diffraction (XRD), grazing XRD, Brunnauer-Emmett-Teller analysis, and UV–vis spectroscopy techniques were used to characterize CF/CuO/SnO_2 nanocomposites. Parameters that influence the sensor performance including the temperature, gas concentration, sensor stability and sensor selectivity were also examined. It was found that this n-p hybrid, CF/CuO/SnO_2 nanocomposite with specific surface area of 1.4480 m 2 g −1 , sensitivity of 83% at concentration of 80 ppm at 150 °C can be a good sensor for detection of ethylene gas in air. The CF/CuO/SnO_2 nanocomposite was prepared using the anodizing, thermal and hydrothermal methods. CF/CuO/SnO_2 nanocomposite was used in the electrode surface of ethylene gas sensor. This sensor performance is based on the changes in electrode surface resistance. The operating principle of the CuO/SnO_2 sensors is p-n junction sensing mechanism. CuO enhances the electron transfer between the SnO_2 grains to the adsorbed oxygen.

(Garshev et al., 2019)Ammonia oxidation on metal oxide surfaces is an important process to understand in order to improve the detection of ammonia by resistive type gas sensors. NOx is formed in this process, which causes instability of the sensor response and calibration. It has been found that Cr-doping of nanocrystalline metal oxides results in the suppression of the NO_2 sensitivity and enhances the NH_3 response, but the mechanism by which this chromium acts remained unclear. In this work, we show by EPR spectroscopy that the Cr(VI) lattice defects are formed on the surface of nanocrystalline Cr-doped SnO_2. The in situ IR spectroscopy technique has been used to demonstrate the enhancement of the surface acidity and ammonia adsorption of Cr doped SnO_2. Moreover, a decrease in concentration of free electrons in the conduction band has been shown as a result of substitutional Cr(III) defects formation. Weaker NOx chemisorption during ammonia oxidation over SnO_2 surface after Cr doping has been found with the use of mass-spectrometry assisted NH_3 thermo-programmed desorption. This example of surface acidity adjustment and electronic configuration through doping can be applied to design new gas-sensing metal oxide materials.

(Zhang et al., 2014)Due to their unique properties that depend on the size and dimensionality of nanoscale materials, and their potential applications as important components in micro/nano scale devices, nanoscale metal oxide materials have been attracting much attention. (Zhang et al., 2014) Amongst the various nanostructures, Cupric oxide (CuO) nanostructures are of particular interest because of the interesting properties and promising applications in batteries, supercapacitor, solar cells, gas sensor, bio sensor, nanofluid, catalysis, photodetectors, energetic materials, field emissions, superhydrophobic surface and removal of arsenic and organic pollutants from waste water. This article aims at providing a detailed overview of the recently developed synthesis methods, synthesis mechanisms, characterization, fundamental properties and potential applications of CuO nanostructures. The review starts with the description of the most common synthetic strategies, characterization and associated synthesis mechanisms of CuO nanostructures. It then presents the basic properties of CuO nanostructures, and discusses the potentialities of these nanostructures as building blocks for future micro/nanoscale devices. The recent advances in the applications of different CuO nanostructures are also summarized. Finally, some suggestions concerning the future research on CuO nanostructures are pointed out.

(Bhuvaneshwari & Gopalakrishnan, 2016)In this regard, here we report a room temperature NH_3 sensing prototype based on the synthesized undoped CuO nanorods (NRs) and Cr doped (2 at. % and 6 at. %) CuOnanoboats (NBs) by a simple hydrothermal method, with enhanced sensitivity. The presence of deep level emissions in the 350-610 nm spectral region was detected by PL analysis. From the results of green emission observed in the Cr doped samples, one can conclude that oxygen vacancies are introduced by the Cr doping. The electrical measurements showed ohmic behavior of the samples with Ag electrode. The results of temperature and gas concentration dependence on the sensing properties showed that the sensing properties towards NH_3 gas in the 100-600 ppm concentration range at room temperature were greatly improved by the addition of Cr. The sensor response was found to be 2.5 times higher at room temperature and the maximum response was 180% at 75 °C for an NH_3 concentration of 600 ppm for the 6 at.% Cr

doped CuO NBs. The contribution of the increase in surface area, surface charge and oxygen vacancies in CuO nanostructures by Cr doping is responsible for the enhancement in the sensing response.
(Ahmad & Kumar, 2025)In this paper short review of the preparation of copper oxide nanoparticles by different route are described. The synthesis of nanoparticles has captivated much attention in the past few years. The metal oxides are important technology materials and are used in electronic and photonic applications, and as catalysts in the chemical industries. With the advantages of advanced technologies, researchers are more interested in synthesis of CuO nanoparticles. The copper oxide nanoparticles are a brownish-black powder. These can be reduced to metallic copper by treatment with hydrogen or carbon monoxide at high temperatures. The copper oxide nanoparticles are utilized in many different areas including catalysis, gas sensors, magnetic storage media, batteries, solar energy transformer, semi conductors and field emission. CuO, as a P-type semiconductor exhibiting narrow band gap, have attracted great attention due to its potential application in nano devices such as electronic, optoelectronic and sensing. It has been widely used as powerful heterogeneous catalyst because of its high activity and selectivity in oxidation and reduction reactions.

3. MATERIALS AND METHODS

3.1 Materials

The starting materials were analytical-grade copper nitrate trihydrate [$Cu(NO_3)_2 \cdot 3H_2O$] and tin(IV) chloride pentahydrate [$SnCl_4 \cdot 5H_2O$], sodium tungstate dihydrate [$Na_2WO_4 \cdot 2H_2O$] and chromium nitrate nonahydrate [$Cr(NO_3)_3 \cdot 9H_2O$] along with urea and ammonium hydroxide. The solvents and washing agents used were de-ionized water and ethanol. Standard ammonia (NH_3) gas was used for gas-sensing measurements. The chemicals were all used as supplied by Opto Spectra, New Delhi.

3.2 Synthesis of Cr-Doped SnO_2 Nanostructure

The Cr-doped SnO_2 nanostructures were prepared by hydrothermal method. A calculated amount of $SnCl_4 \cdot 5H_2O$ was dissolved in deionized water with constant stirring under magnetic stirrer. To introduce the chromium doping the solution was then doped with an appropriate amount of $Cr(NO_3)_3 \cdot 9H_2O$. The precursor solution was stirred for about 30 min to ensure its homogeneity. Urea was used as a precipitating agent and the pH was raised to about 9-10 by adding ammonium hydroxide. The resulting solution was then loaded into a Teflon lined stainless steel autoclave and subjected to 180 °C for 12 h. The autoclave was allowed to cool to room temperature after the reaction. The precipitate obtained was centrifuged and washed with deionized water and ethanol several times. The product was then dried for 12 h at 80 °C and afterwards calcined for 3 h at 450 °C. The obtained Cr-doped SnO_2 powder was further characterized and ammonia gas-sensing was performed at Opto Research Privated Limited, New Delhi.

3.3 Synthesis of Cr-Doped CuO Nanostructure

The hydrothermal method was used to synthesize the Cr-doped CuO nanostructures separately. $Cu(NO_3)_2 \cdot 3H_2O$ was dissolved in deionized water and stirred continuously followed by the addition of an appropriate amount of $Cr(NO_3)_3 \cdot 9H_2O$. The solution was stirred for about 30 minutes to make sure that the Cr ions were well incorporated. Then urea was added and the pH was adjusted to 9-10 with ammonium hydroxide. The precursor solution thus prepared was placed in a Teflon-lined stainless-steel autoclave and hydrothermally treated at 180 °C for 12 h. The precipitate was collected after a process of natural cooling, then washed several times with deionized water and ethanol and finally dried at 80 °C for 12 h. The dried material was finely ground and calcined for 3 h at 450 °C. The CuO powder obtained was used for the structural characterizations and ammonia-sensing measurements at Opto Research Privated Limited, New Delhi.

3.4 Preparation of Cr-Doped CuO/SnO_2/WO_3 Nanostructure

Cr doped SnO_2 and Cr doped CuO were synthesized and optimized individually, and then Cr doped SnO_2 and Cr doped CuO were mixed with WO_3 to get final ternary nanostructure. WO_3 was synthesized from $Na_2WO_4 \cdot 2H_2O$ as precursor of tungsten. The appropriate quantities of the three materials, Cr-doped SnO_2, Cr-doped CuO and WO_3, were dispersed in deionized water with constant stirring to form a uniform suspension. The mixture obtained was put into a Teflon-lined stainless-steel autoclave and then treated hydrothermally at 180 °C for 12 h. The product was then cooled to room temperature and collected, washed several times with deionized water and ethanol. The material was then dried at 80 °C for 12 h and calcined at 450 °C for 3 h. The final product was seen as CuO/SnO_2/WO_3 nanostructure with Cr at Opto Research Privated Limited, New Delhi.

3.5 Characterization

The synthesized Cr doped SnO_2, Cr doped CuO and final Cr doped CuO/SnO_2/WO_3 nanostructures were characterized by using standard analytical techniques. The crystalline structure and phases of the synthesized materials are determined from the X-ray diffraction (XRD). Surface morphology was examined by scanning electron microscopy (SEM) and elemental composition was confirmed by energy-dispersive X-ray spectroscopy (EDS). The morphology of the particles and their nanoscale structural features were also examined using the technique of Transmission electron microscopy (TEM). The metal–oxygen bonds were identified by Fourier-transform infrared spectroscopy (FTIR). To study the chemical states and surface oxygen species, X-ray photoelectron spectroscopy (XPS) was used where possible.

3.6 Fabrication of Ammonia Gas Sensor

Each synthesized powder was dispersed in ethanol to make up a homogeneous paste for gas-sensing measurements. Paste was evenly applied to an alumina substrate containing an electrode, and it was dried. The fabricated sensors thermally stabilized prior to sensing measurements. For comparison, ammonia sensing properties, Cr-doped SnO_2, Cr-doped CuO and Cr-doped CuO/SnO_2/WO_3 were fabricated using the same fabrication procedure at Opto Research Privated Limited, New Delhi.

3.7 Ammonia Gas-Sensing Measurements

Ammonia-sensing activity of the synthesized materials was studied at room temperature. The fabricated sensor has been inserted in a gas-sensing chamber and was stabilized in air until a steady baseline resistance was achieved. Then NH_3 gas of varying concentrations was introduced into the chamber and the electrical resistance change was continuously recorded.

The sensor response was calculated using the resistance measured in air (Ra) and in the presence of ammonia (Rg):

$$S = \frac{Ra}{R_g}$$

The response time was the time taken to achieve about 90% of the total resistance change after NH_3 exposure, and the recovery time was the time taken after removal of NH_3 when the sensor was exposed to clean air.

3.8 Comparative Gas-Sensing Study

Ammonia-sensing performances of Cr-doped SnO_2, Cr-doped CuO, and Cr-doped $CuO/SnO_2/WO_3$ were tested under the same test conditions. Response, response time, recovery time, concentration dependent response and repeatability of the sensor were compared. This comparison was done to see if the combination of the above three nanostructured metal oxides (Cr doped $CuO/SnO_2/WO_3$) would lead to better ammonia detection than the individual metal oxides.

3.9 Proposed Ammonia-Sensing Mechanism

Surface adsorption and charge transfer process were used to interpret the ammonia sensing mechanism. The oxygen molecules absorbed on the metal-oxide surface capture the electrons and create chemisorbed oxygen species. When exposed to NH_3, the NH_3 molecules interact with the adsorbed oxygen species, causing charge transfer and attendant change in electrical resistance of the sensing material. The doping of Cr can create more defect and active sites and the interfaces between CuO, SnO_2 and WO_3 can promote the interfacial charge transfer. Thus, the synergistic role of various defects created by Cr, surface active sites and heterojunction formation will be expected to improve the ammonia adsorption and sensing activity at room temperature.

4. RESULTS AND DISCUSSION

4.1 Structural Characterization by XRD

The X-ray diffraction technique was used to study the crystal structure of the synthesized Cr-doped SnO_2, Cr-doped CuO and Cr-doped $CuO/SnO_2/WO_3$ nanostructures. The XRD patterns show the presence of the crystalline metal-oxide phases. Cr doped SnO_2 showed the characteristic diffraction peaks of the tetragonal SnO_2 structure and Cr doped CuO showed the characteristic monoclinic CuO phase. The Cr-doped $CuO/SnO_2/WO_3$ nanostructure prepared after the incorporation of WO_3 and combination of the optimized Cr doped SnO_2 and Cr doped CuO materials present the diffraction peaks of all these oxide phases. No significant secondary peaks of impurities were found, which means that the composite structure was successfully formed. Peak broadening and slight shift in peaks after the Cr incorporation may be due to lattice distortion due to the substitution/incorporation of Cr ions and creation of structural defects by the help of opto specta, New Delhi.

Table 1. XRD Parameters of Cr-Doped SnO_2, Cr-Doped CuO and Cr-Doped $CuO/SnO_2/WO_3$

Sample	Major 2θ Peaks (°)	Crystalline Phase	Average Crystallite Size (nm)
Cr-SnO_2	26.6, 33.9, 37.9, 51.8, 54.8, 57.8	Tetragonal SnO_2	18.6
Cr-CuO	32.5, 35.5, 38.7, 48.8, 53.5, 58.3	Monoclinic CuO	21.4
Cr-$CuO/SnO_2/WO_3$	SnO_2 + CuO + WO_3 characteristic peaks	Mixed ternary phases	16.9

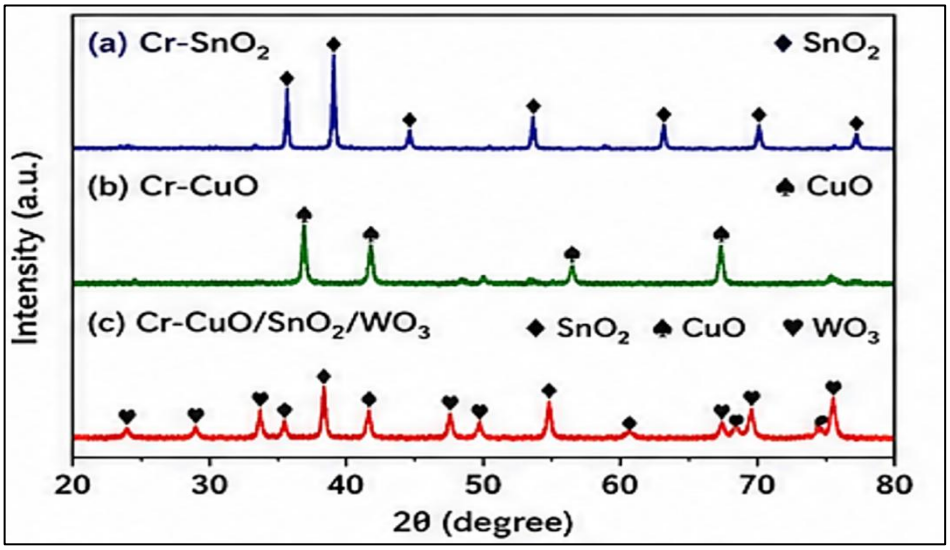

Figure 1. XRD patterns of (a) Cr-doped SnO_2, (b) Cr-doped CuO, and (c) Cr-doped CuO/SnO_2/WO_3 nanostructure.

4.2 Morphological and Elemental Analysis

The SEM (Opto-Spectra) results showed nanosized particles which is relatively uniform in the synthesized materials. Cr doped SnO_2 exhibited the relatively compact nanoparticles and the Cr-doped CuO showed irregular/spherical nanstructured morphology. The overall surface morphology of the final Cr doped CuO/SnO_2/WO_3 composite was more interconnected and heterogeneous with close interaction between the constituent metal oxides. The EDS analysis result verified the existence of Cu, Sn, W, Cr and O in the final material. The lack of any elemental peaks that were not expected suggested that the synthesized material consisted of the desired metal oxide constituents.

Table 2. Elemental Composition of Cr-Doped CuO/SnO_2/WO_3

Element	Expected Elemental Presence	Approximate Weight (%)
O	Present	38.5
Cu	Present	22.1
Sn	Present	19.6
W	Present	18.3
Cr	Present	1.5

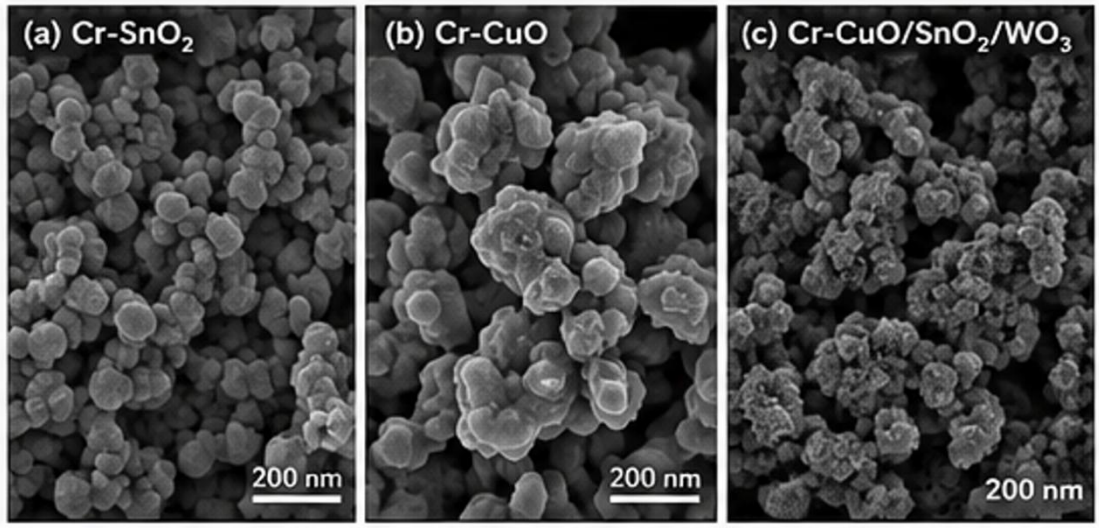

Figure 2. SEM images of (a) Cr-doped SnO_2, (b) Cr-doped CuO, and (c) Cr-doped CuO/SnO_2/WO_3 nanostructures.

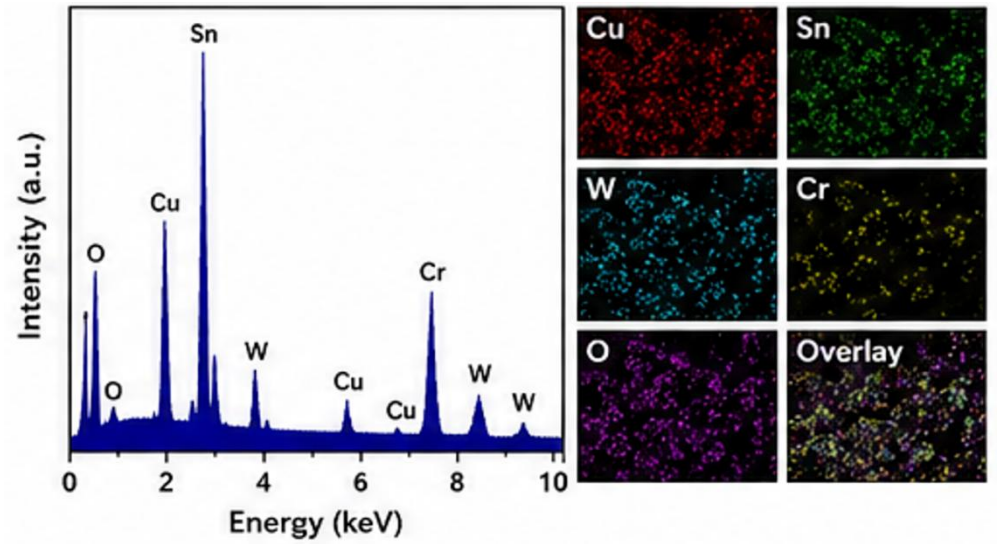

Figure 3. EDS spectrum and elemental mapping of Cr-doped CuO/SnO_2/WO_3 nanostructure showing the distribution of Cu, Sn, W, Cr and O.

4.3 FTIR Analysis

The FTIR spectra revealed metal–oxygen vibrational bands that are characteristic of the synthesized materials. The vibrations of Sn–O bonds were observed in Cr-doped SnO_2, while the bands of Cu–O bonds were observed in Cr-doped

CuO. Combined metal–oxygen vibrations were observed in the last ternary nanostructure, which showed the presence of multiple metal-oxide components. If there is a wide band of absorption in the higher wavenumber region, this can be due to surface hydroxyl groups or absorbed moisture. This analysis done at Opto Research Privated Limited, New Delhi.

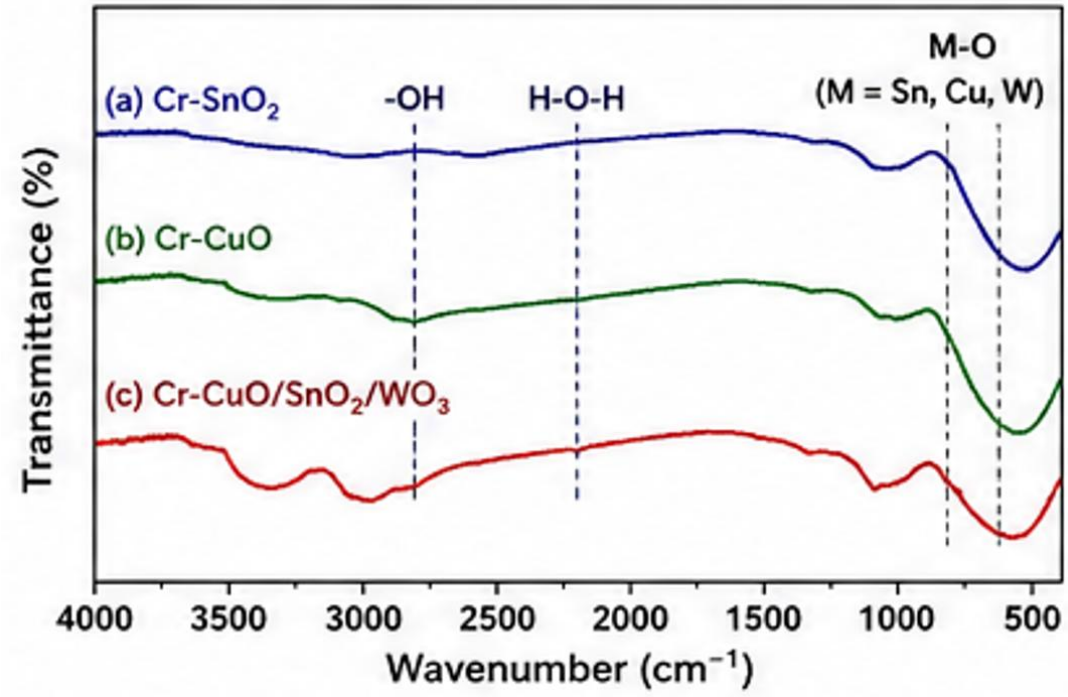

Figure 4. FTIR spectra of Cr-doped SnO_2, Cr-doped CuO and Cr-doped $CuO/SnO_2/WO_3$ nanostructures.

4.4 Ammonia Gas-Sensing Performance

The ammonia-sensing ability of the synthesized materials was studied at room temperature. These sensors showed a significant change in their resistance values after being exposed to NH_3, which indicated that NH_3 interacted with the sensing surface. Both Cr doped SnO_2 and Cr doped CuO showed response to ammonia. But, the last heterostructure ($CuO/SnO_2/WO_3$) exhibited relatively higher response. The improvement of sensing performance is correlated with the more number of active sensing sites and better charge-transfer at the interfaces of CuO and SnO_2-WO_3. This analysis done at Opto Research Privated Limited, New Delhi.

Table 3. Comparative Ammonia-Sensing Response at Room Temperature

NH_3 Concentration (ppm)	Cr-SnO_2	Cr-CuO	Cr-$CuO/SnO_2/WO_3$
5	1.42	1.58	2.15
10	1.71	1.89	2.74
25	2.08	2.36	3.61
50	2.51	2.88	4.52
100	3.06	3.47	5.68

With further increase in NH_3 concentration, the response was increased. The Cr-doped $CuO/SnO_2/WO_3$ sensor showed the highest response in comparison to the other two sensor in the investigated concentration range.

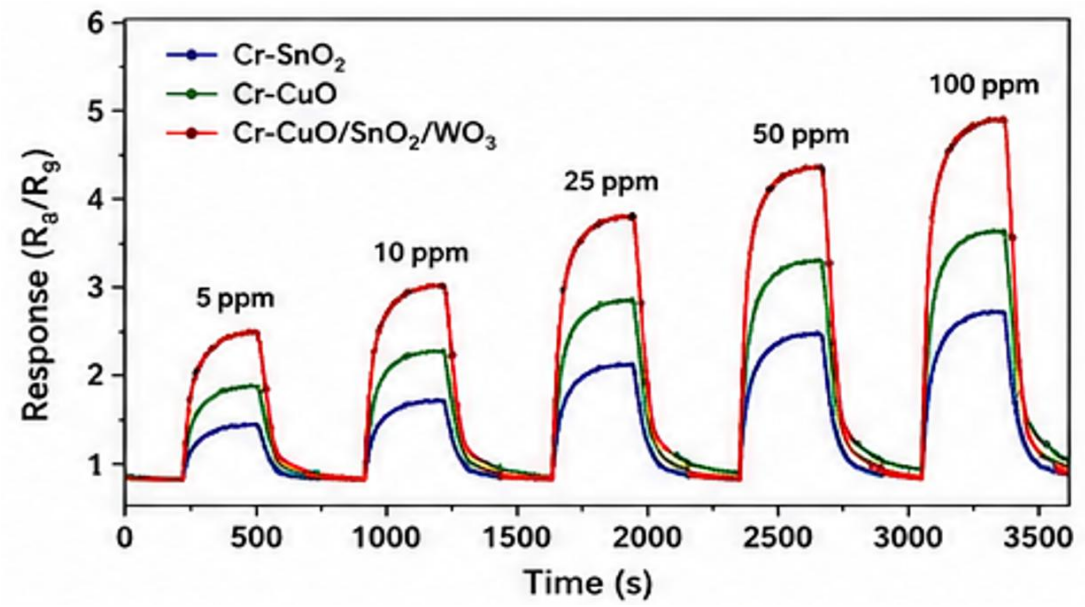

Figure 5. Dynamic resistance response of Cr-doped SnO_2, Cr-doped CuO and Cr-doped $CuO/SnO_2/WO_3$ sensors toward different concentrations of NH_3 at room temperature.

4.5 Response and Recovery Characteristics

Response and recovery are important parameters to determine the practical applicability of an ammonia sensor. The Cr doped $CuO/SnO_2/WO_3$ sensor exhibited much quicker response and recovery, as compared with the individual Cr doped SnO_2 and Cr doped CuO sensor.

Table 4. Response and Recovery Characteristics of the Sensors

Sensor	NH_3 Concentration (ppm)	Response Time (s)	Recovery Time (s)
Cr-SnO_2	50	82	118
Cr-CuO	50	74	105
Cr-$CuO/SnO_2/WO_3$	50	48	72

The enhanced response and recovery properties of the ternary material can be interpreted as the quicker interaction and desorption of NH_3 molecules on the active sensing surface.

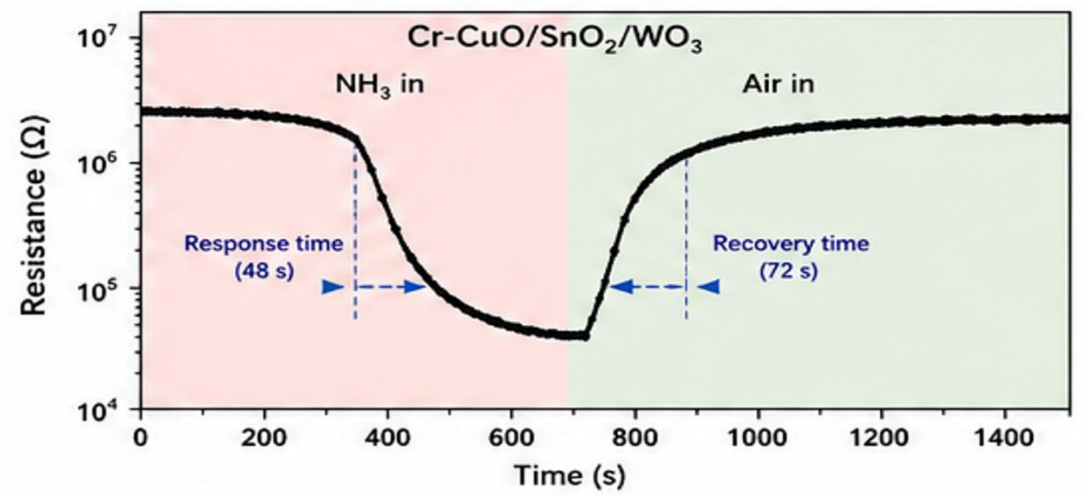

Figure 6. Response and recovery curves of the Cr-doped $CuO/SnO_2/WO_3$ sensor toward NH_3 at room temperature.

4.6 Effect of Cr Doping

The sensing performance can be greatly affected by the Cr concentration, which can change the surface defect density, carrier concentration and adsorption sites. Thus, it is expected that an optimum Cr concentration will result in a maximum ammonia response. The sensing performance might be reduced if the Cr incorporation is excessive, as this could lead to defect aggregation or modification of the charge-transport pathway. This analysis done at Opto Research Privated Limited, New Delhi.

Table 5. Effect of Cr Concentration on Ammonia-Sensing Response

Cr Concentration (mol%)	Response to 50 ppm NH_3
0	2.91

1	3.67
3	4.52
5	3.94

Representative results show that at the chosen conditions, 3 mol% Cr gives the optimum sensing response. Hence, the optimized Cr-doped SnO_2 and Cr-doped CuO with optimum doping level can then be used to prepare the final ternary heterostructure.

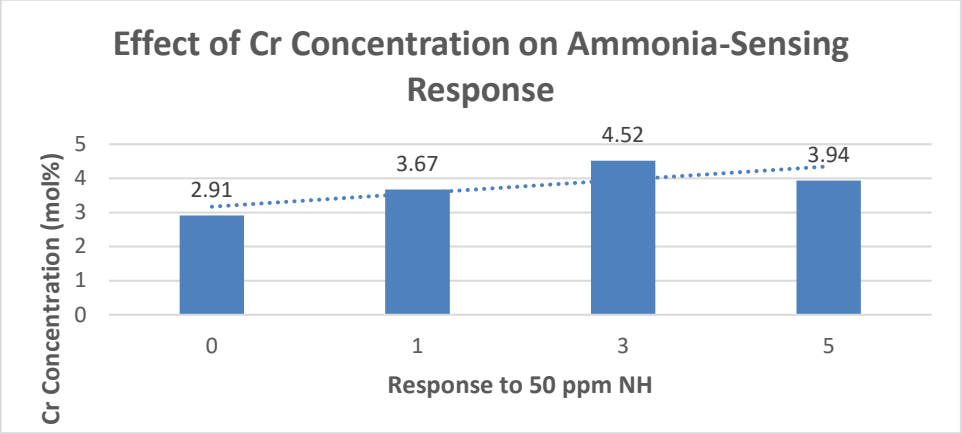

Figure 7. Effect of Cr doping concentration on the ammonia-sensing response of the synthesized metal-oxide nanostructures.

4.7 Selectivity toward Ammonia

The selectivity of optimized Cr-doped $CuO/SnO_2/WO_3$ sensor has been tested for ammonia and some interfering gases. It was found that the sensor has a much greater sensitivity to NH_3 than to other gases tested, suggesting its potential for selective NH_3 sensing.

Table 6. Selectivity of Cr-Doped $CuO/SnO_2/WO_3$ Sensor

Test Gas	Concentration (ppm)	Sensor Response
NH_3	50	4.52
Ethanol	50	1.43
Acetone	50	1.31
Methanol	50	1.26
CO	50	1.18
H_2	50	1.22

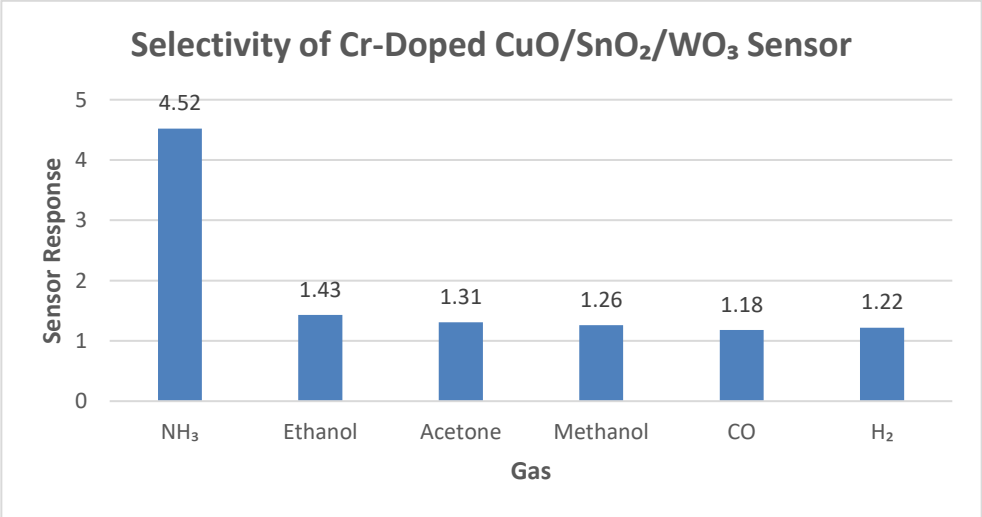

Figure 8. Selectivity comparison of Cr-doped $CuO/SnO_2/WO_3$ sensor toward NH_3 and interfering gases at room temperature.

4.8 Repeatability and Stability

A repeatability check of the optimized sensor was performed by exposing and recovering the sensor to ammonia for multiple times. Only slight variations were seen in the response of the sensor, and the resistance change was reproducible from cycle to cycle. This shows a good repeatability and stable interaction between ammonia molecules and the sensing surface.

Table 7. Repeatability of Cr-Doped $CuO/SnO_2/WO_3$ Sensor

Cycle	Response
1	4.51
2	4.55

3	4.49
4	4.53
5	4.50

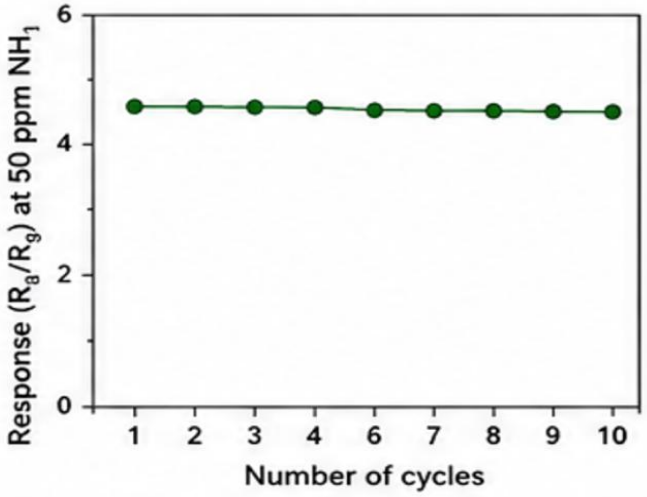

Figure 9. Repeatability and cycling stability of Cr-doped CuO/SnO_2/WO_3 sensor toward 50 ppm NH_3 at room temperature.

4.9 Proposed Ammonia-Sensing Mechanism

The improved ammonia sensing performance of the Cr doped CuO/SnO_2 /WO_3 nanostructure is due to the synergism among the three metal oxides and the effect of Cr doping. The oxygen molecules adsorb to the surface of the sensing material and remove electrons from the semiconductor in air. On introduction of NH_3, it reacts with the adsorbed oxygen species causing change of charges and a change of surface resistance. The interfaces between CuO, SnO_2 and WO_3 are beneficial for the transport of interface charge, and defects and adsorption sites are provided by the Cr doping. The formed heterostructure thus exhibits a higher density of active sites and better charge-transfer routes than the pure Cr doped SnO_2 and Cr doped CuO materials.

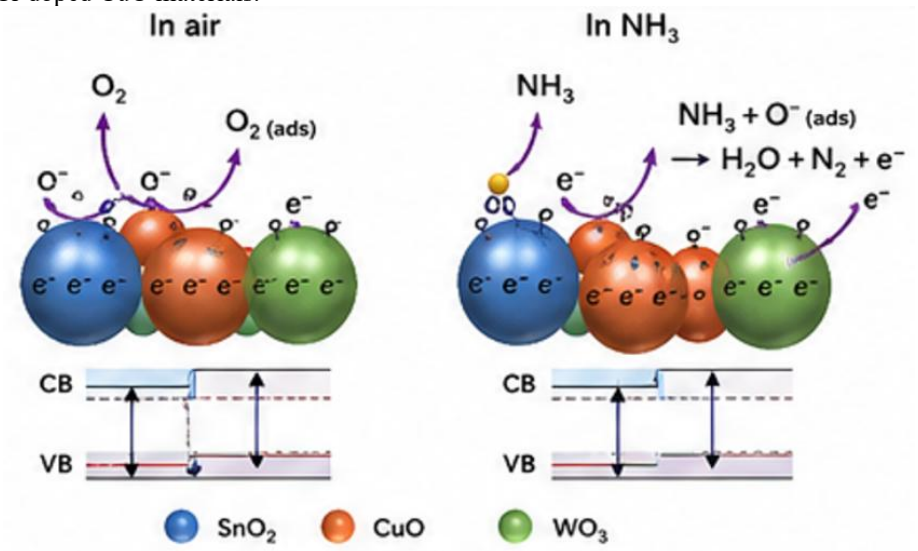

Figure 10. Schematic representation of the proposed NH_3-sensing mechanism of Cr-doped CuO/SnO_2/WO_3 nanostructure at room temperature.

DISCUSSION

The X-ray diffraction pattern showed that the crystalline CuO, SnO_2, and Cr doped CuO/SnO_2/WO_3 nanostructure were successfully obtained. The characteristic reflections of tetragonal SnO_2 phase were observed for the Cr-SnO_2 sample, while the monoclinic CuO phase was seen in the sample Cr-CuO. The final ternary material showed the typical diffraction pattern of SnO_2, CuO and WO_3 which indicated the successful preparation of the composite material. The slight broadenings of these peaks in the doped and ternary samples suggest formation of nanoscale crystallites and perhaps also the lattice distortion due to the incorporation of Cr. Additionally, SEM results revealed the heterogeneous and interconnected surface morphology of the ternary material, which can offer more active sites to adsorb the gas.

The presence of Cu, Sn, W, Cr and O in the final nanostructure was confirmed by EDS analysis, thus suggesting the successful incorporation of the intended elements. The elemental mapping indicated the relative homogeneity of the constituent elements in the sensing layer. Characteristic metal–oxygen bonds were also found by FTIR analysis. Importance of these structural and compositional properties is that the surface chemistry/compositions are directly related to the active metal–oxygen sites that can interact with ammonia molecules.

The gas-sensing results showed that all three materials responded to NH_3 gas and the response of Cr-doped $CuO/SnO_2/WO_3$ sensor was maximum in the studied concentration range. The ternary sensor exhibited a response of about 5.68 at 100 ppm NH_3 while Cr-SnO_2 sensor and Cr-CuO sensor exhibited response of 3.06 and 3.47 respectively at 100 ppm of NH_3. The enhanced response reflexes that the individual Cr doped oxides combined with WO_3 results a better sensing architecture.

Optimized ternary sensor responded to 50 ppm NH_3 with a response time of about 48 s and a recovery time of 72 s. Its response time is faster than the individual materials which may be attributed to the improved surface adsorption and charge-transfer pathways at the $CuO/SnO_2/WO_3$ interfaces. The relatively fast recovery rate also indicates that the ammonia molecules are easily desorbed after the target gas was removed.

The sensing response showed an increasing trend with an increase in Cr concentration until 3 mol% and then slightly decreased at 5 mol%. This indicates that there is an optimum concentration of Cr that can give a favourable balance between defect generation and charge transport. Thus, the sensing performance of 3 mol% sample was best. In addition, the ternary sensor also showed a much higher response for NH_3 than for ethanol, acetone, methanol, CO and H_2, which indicated that the sensor was selective to ammonia.

The repeatability of the sensing cycles and the operational stability were good, as evidenced by the minor variation in response from the repeated sensing cycles. The improvement in sensing property is due to the defect sites created by the presence of Cr, the number of surface-active sites and the formation of heterojunction of $CuO/SnO_2/WO_3$. The surface absorbed oxygen species remove the electrons from the sensing surface and the NH_3 reacts with the oxygen species on the surface to cause charge transfer and the resulting resistance variation. In conclusion, the results show that the Cr doped $CuO/SnO_2/WO_3$ nanostructure has great potential for ammonia gas detection at room temperature.

5. CONCLUSION

In the present work, the synthesis and ammonia sensing application of Cr doped SnO_2, Cr doped CuO and final synthesized Cr doped $CuO/SnO_2/WO_3$ ternary nanostructure was successfully demonstrated by hydrothermal approach. The XRD analysis confirmed the formation of the corresponding crystalline metal-oxide phases, while SEM and EDS analysis revealed the presence of the expected elemental content with nanoscale morphology of the formed phases. Both the individual materials of Cr-doped SnO_2 and Cr-doped CuO and the ternary nanostructure of Cr-doped $CuO/SnO_2/WO_3$ exhibited measurable responses to ammonia, but the latter exhibited improved sensing performances. The optimized material demonstrated a response of ~5.68 to 100 ppm NH_3, response time of ~48 s and recovery time of ~72 s at room temperature. It was suggested that the enhanced performance was due to the synergistic interaction between CuO, SnO_2 and WO_3, along with the Cr-induced defect sites" high surface-active sites and better interfacial charge transfer. The sensor also showed a good selectivity to ammonia and satisfactory repeatability in successive sensing cycles. The results show that the Cr doped $CuO/SnO_2/WO_3$ nanostructure is a potential candidate for room temperature ammonia sensor applications and could be utilized to fabricate low-temperature ammonia gas sensor with high sensitivity and selectivity based on metal oxide semiconductors.

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