International Journal for Research in Engineering Application & Management (IJREAM)
ISSN : 2454-9150 Vol-08, Issue-01, APR 2022

Ammonia Gas Sensing Properties of Aloevera Capped ZnO-CuO Mixed Nanomaterial

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Abstract - ZnO-CuO mixed nanomaterials have been synthesized using Aloe vera (Aloe Barbadansis) as a capping agent by adopting the chemical co-precipitation technique. The decomposition temperature of basic carbonate precursor for the preparation of ZnO-CuO mixed nanostructure is obtained from the thermogravimetric analysis. On the basis of TGA/DTA results, the prepared Aloevera capped carbonate precursor was decomposed at 350^{0}C for 3 hours to obtain the ZnO-CuO mixed nanomaterial. The elemental composition of the prepared sample was confirmed from EDS spectroscopy. The structural and morphological characterization of the prepared nanomaterials were investigated using XRD and SEM analysis. XPS spectra was used to analyze the surface composition of biologically capped ZnO-CuO mixed nanomaterial The optical gas sensing property of ZnO-CuO mixed nanomaterial was investigated by recording PL spectra in the presence of ammonia gas.

Keywords - Mixed nanomaterial, Capping agent, precursor, Spectrophotometer, Optical gas sensing.

I. INTRODUCTION

Gas sensors or gas detectors are electronic devices, which detect the presence and concentration of different types of gases. Gas sensors are commonly used to detect toxic and explosive gases. Based upon the concentration of gas to be detected, the gas sensor produces a difference in potential due to the change in resistance of the material inside the sensor. This potential difference can be measured as the output voltage of the sensor. Depending on the type of sensing element, gas sensors are classified into different types, including metal oxide-based sensors, optical gas sensors, capacitance-based sensors, calorimetric gas sensors, electrochemical gas sensors etc. Metal oxide semiconductors are widely used for the fabrication of gas sensors because of their various useful features such as easy processing, simplicity in fabrication, low material cost and improved sensitivity to the ambient conditions [1]. Recently optical gas sensors using metal oxide semiconductors as the sensing medium have been widely reported for their room-temperature operation and improved sensitivity.

The performance of a sensor strongly depends on the nature, morphology and size of the sensing material. The sensitivity of metal oxide sensors can be improved by changing their properties by doping, annealing and changing their size. ZnO based sensors are much attractive due to their wide bandgap, nontoxic nature, and improved electrical properties. A large number of researches have been made to improve the sensing capacity of ZnO by changing its nanostructures with the help of other metal oxides. CuO is also an important inorganic semiconductor with emerging sensor applications. Hetero structures of metal oxides are more attracted to the field of sensing due to the possibility to integrate their physical and chemical characteristics [2]. Both ZnO and CuO semiconductors play an important role in the field of gas sensing. The mixed oxides and composites of ZnO and CuO exhibit a super sensing performance compared to their individual components due to the presence of an additional depletion layer in the interface of the materials. Nanostructures of ZnO-CuO heterojunctions have shown research interest due to their potential applications in the field of chemical sensors, especially for the sensing of reducing gases and humidity. Researchers reported that ZnO-CuO mixed nanomaterials show better sensing properties as compared to their individual metal oxides due to the formation of p-n heterojunctions in mixed nanostructures [2].

Ammonia is a highly toxic and flammable gas widely used in various industries such as textile, automobile, paper, fertilizer and food as a coolant [3]. A large amount of ammonia gas is released from these industries in the form of aerosols and smog. Exposure to ammonia gas causes severe health problems in humans. So, the monitoring of the leakage of this gas is highly essential. Metal oxide-based gas sensors are extensively developed for the sensing of NH_3 gas due to their high sensitivity towards this gas. In this study, the optical gas sensing property of ZnO-CuO mixed nanomaterial synthesized using Aloevera capping agent was investigated and reported. The sensitivity of the sample was studied by recording PL spectra after and before filling the sample holder with ammonia gas.

Various researchers have synthesized and characterized ZnO-CuO nanostructures to study their applications in the

 DOI : 10.35291/2454-9150.2022.0125

ISSN : 2454-9150 Vol-08, Issue-01, APR 2022

field of sensing, catalysis and optoelectronics [4, 5]. Yang et al reported the gas sensing properties of ZnO-CuO hybrid nanostructure for the detection of gases like ethanol, xylene and acetone [6]. Literature reported that the enhanced surface area and highly porous nature of the composite are responsible for the gas sensing property of the material. Vijayalakshmi et al reported the optical and PL emission properties of ZnO-CuO nanostructure and its usage in optoelectronic devices. Optical transmittance is an important phenomenon in optoelectronics. Literature reveals that the transmittance of ZnO-CuO mixed nanostructures is about 85% higher than its individual components. This may be due to their highly crystalline nature and homogeneity. Ashok et al prepared ZnO-CuO nanostructures for humidity sensor applications and it is found that the sensing factor of mixed structure is higher than their individual components. This increased sensitivity of the material is attributed to the decreased resistance due to the attachment of cations of the mixed nanostructure with the hydroxyl group of adsorbed water on its surface [7]. XPS analysis was done here to study the chemical nature of the sample and to identify the presence of surface absorbed oxygen species in the sample. The absorbed oxygen species on the surface of nanomaterials enhance the characteristic sensing properties of the nanomaterials. The gas sensing property of ZnO-CuO mixed nanomaterial was investigated by recording PL spectra in the presence of ammonia gas and the results were analysed and reported in details.

II. EXPERIMENTAL

Analytical grade zinc acetate dihydrate [$(CH_3\ COO)_2$ Zn $2H_2O$], copper acetate monohydrate [$(CH_3\ COO)_2$ Cu H_2O] and ammonium carbonate [$(NH_4)_2\ CO_3$] were used as the starting material for the synthesis of ZnO-CuO nanomaterial. To prevent the growth of nanomaterial during the chemical reaction, sample preparation was carried out using Aloe vera Extract (Aloe Barbadansis) as capping agent. For the preparation of ZnO-CuO mixed nanomaterial, 0.1 Molar Zinc Acetate, Copper Acetate, and Ammonium Carbonate were added drop by drop to a solution containing 5 ml Aloevera extract and 95ml distilled water under vigorous stirring using a Magnetic Stirrer. The resultant solution was stirred for 12 h at room temperature. The obtained carbonate precursor was centrifuged, washed sequentially with distilled water and acetone several times in order to remove the unreacted ions, and then dried naturally at room temperature to obtain the carbonate precursor powder. The decomposition temperature of the prepared ZnO-CuO mixed nanomaterial was obtained from TGA/DTA analysis. Thermo Gravimetric Analysis of the as-prepared basic carbonate precursor precursors was taken using the Perkin-Elmer diamond TGA/DTA apparatus. The weight loss and stability of the materials were observed from room temperature to 500^0C at a heating rate of 15^0C per minute under a nitrogen atmosphere.

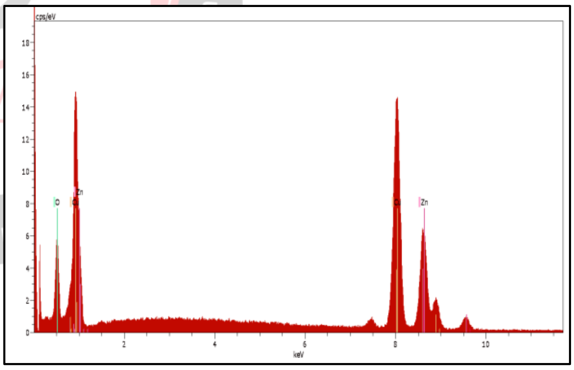
Figure 1(a) shows the TGA/DTA curves of EDTA and Aloe vera capped samples. In the figure, the decomposition of as-synthesized basic carbonate precursor started at a temperature of about 200°C and decomposition was completed at a temperature of about 300°C producing ZnO-CuO mixed nanomaterial. From the graphs, it is clear that there is a weight loss between 200^0C and 300^0C indicating the conversion of carbonate precursor to an oxide material. The small weight loss in between room temperature to 200^0C is due to the evaporation of water molecules present in the samples. Here the decomposition temperature of as prepared carbonate precursor was fixed at a temperature of 350^0C for 3 hours to obtain ZnO-CuO mixed nanomaterial. The sample code assigned is CZA.

III. CHARACTERIZATION

1. Energy Dispersive X-ray Spectroscopy

To understand the correct elemental composition and the presence of impurities if any, the EDS of ZnO-CuO mixed nanomaterial was recorded and analyzed. The EDS spectrum was recorded using the Oxford instrument swift model 7582 energy-dispersive spectrometer.

Figure 1 (b) shows the EDS spectrum of ZnO-CuO mixed nanomaterials synthesized using Aloe vera extract as capping agent. As expected, the spectra clearly show the presence of zinc, copper, and oxygen indicating that all the samples were ZnO-CuO mixed nanostructures. No peaks corresponding to other materials or chemicals were found, which indicates the purity of prepared samples.



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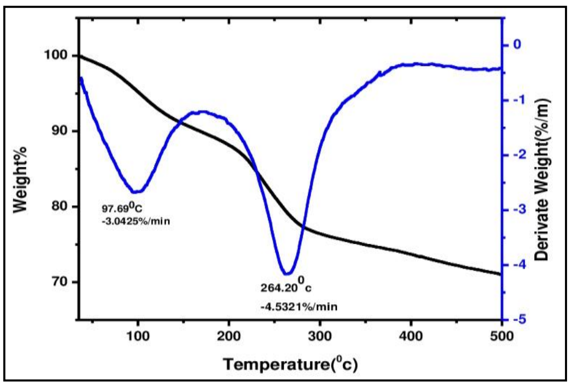


(b)

 DOI : 10.35291/2454-9150.2022.0125

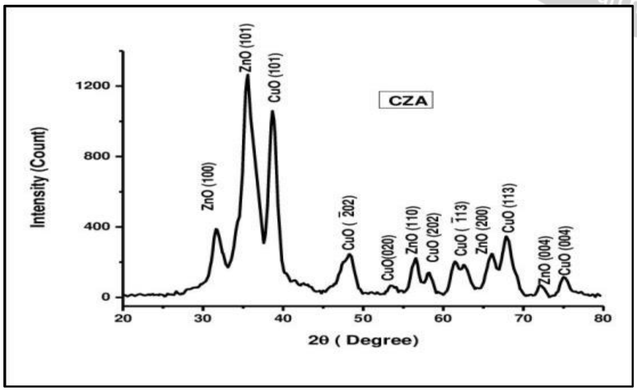
Figure 1 (a) TGA/DTA Curves of Basic Carbonate Precursor for the Synthesis of ZnO-CuO Mixed Nanomaterial (b) EDS Spectra of ZnO-CuO Mixed Nanomaterial

2. X-Ray Diffraction Analysis

The size of the prepared ZnO-CuO mixed nanomaterial was confirmed by X-ray diffraction analysis. Figures 2 (a) show the XRD pattern of ZnO-CuO mixed nanostructure synthesized using Aloe vera extracts as a capping agent. The formation of ZnO-CuO mixed nanostructure was confirmed from the peaks obtained in the XRD patterns. The obtained XRD pattern display a pair of well-defined diffraction peaks indicating the crystalline and nanoscale nature of the prepared nanostructure. Both ZnO and CuO peaks appear in the pattern which confirm the presence of both the materials. The diffraction peaks in the samples were in close agreement with reported values in ICDD card numbers 36-1451 and 45-0937 corresponding to hexagonal ZnO and monoclinic CuO respectively. The sharp, strong and intense nature of diffraction peaks in the sample indicate the highly crystalline nature of the nanomaterial [8]. No other characteristic peaks were observed in the XRD spectra indicating the phase purity of the sample. The broadening of diffraction peaks is due to the crystalline nature of the sample. In order to calculate the crystallite size, the full width at half maximum (FWHM) of the X-ray diffraction peak was determined. The crystallite size can be calculated by using Debye Scherer's equation,

$$D = \frac{k\lambda}{\beta \cos\theta}$$

Where k is the shape determining factor, its value lies between 0.94 and 1.15 depending on the shape; k=1 for spherical crystallites. D is the mean diameter of the crystallites, β is the size induced line broadening (FWHM), **λ** is the X-ray wavelength and **θ** is the diffraction angle [9]. The obtained crystallite size of the prepared sample is 7nm.



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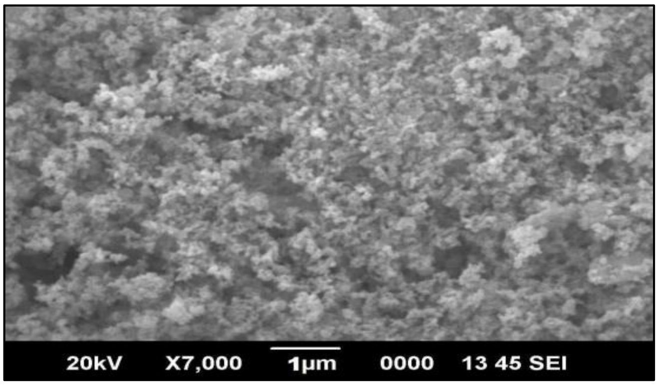


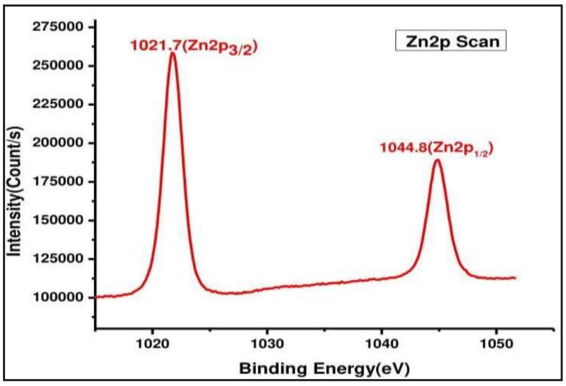
(b)

Figure 2 (a) XRD Pattern and (b) SEM Image of ZnO-CuO Mixed Nanomaterial

3. X-ray Photoelectron Spectroscopy (XPS)

XPS is one of the most important tools to identify the oxidation states and composition of the materials in the sample. In this study, XPS was used to analyze the surface composition of chemically and biologically capped ZnO-CuO mixed nanomaterial. In addition to this, here XPS spectrum of ZnO-CuO mixed nanomaterial was successfully used to identify the presence of surface absorbed oxygen species, which plays an important role to enhance the sensing property of the material.

Figure 3 shows the Zn2p, Cu2p and O1s scans of ZnO-CuO mixed nanomaterial. In the sample Zn $2p_{1/2}$ and Zn $2p_{3/2}$ peaks are observed at binding energy values of 1044.8 and 1021.7 eV, respectively. Therefore, the bonding energy difference between these two peaks is estimated to be about 23.1 eV. This value indicated the presence of Zn^{2+} species, thus strengthening the claim of ZnO formation, which is in accordance with the previously reported values [10]. In the Cu2p scan, the peaks correspond to the Cu $2p_{3/2}$ and Cu $2p_{1/2}$. In addition, there are two satellite peaks centered at about 942 and 962 eV, demonstrating the bivalence oxidation state of elemental Cu. The O1s scan of CZA also shows two peaks of oxygen corresponding to O_2^- and absorbed oxygen at 529.5eV and at 531.4eV [11] Here the intensity absorbed oxygen peak dominate O_2^- indicate the presence of more oxygen molecules absorbed on the surface of biologically synthesized ZnO-CuO mixed nanomaterial.



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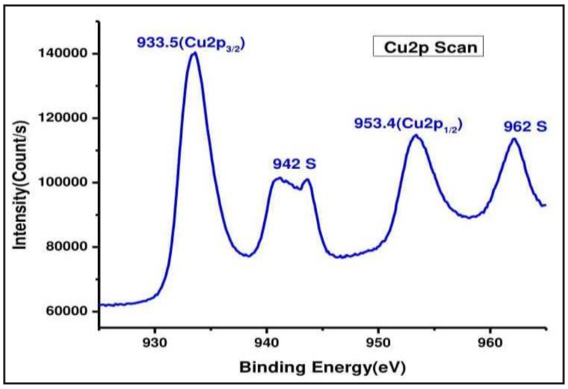

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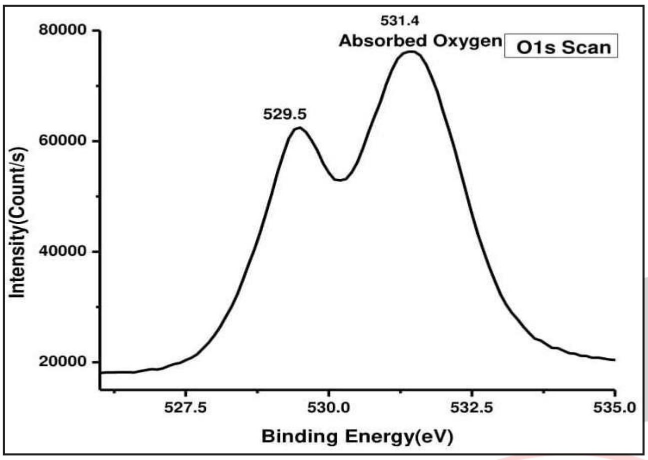

Figure 3 XPS Spectrum of ZnO-CuO mixed Nanomaterial Zn2p, (b)Cu2p and (c) O1s Scans

IV. AMMONIA GAS SENSING PROPERTY

The optical gas sensing property of biologically capped ZnO-CuO nanomaterial was obtained by recording the PL spectra. The spectrum of the sample was recorded using JASCO-FP-750 spectro-photometer. During the measurement, the sample was excited by a Xenon laser source at an excitation wavelength of 320nm. To record the spectra, the sample was placed inside the sample holder with and without filling the holder with ammonia gas. The spectra were recorded before and after the exposure of ammonia gas. The gas sensing capability of the material was analyzed by filling the sample holder with ammonia gas of measurements concentration 20ppm. PL spectra were taken 15 and 30 minutes after the exposure of gas.

Results and Discussion

The figure 4 shows the PL spectrum of Aloevera assisted ZnO-CuO mixed nanomaterial, recorded with and without the presence of ammonia gas. To study the behavior of PL spectrum, the measurements were taken at regular intervals of time. The spectrum exhibit a strong emission peak at 409nm in all measurements. The figure shows a large enhancement in PL intensity when the spectra is recorded with the presence of ammonia gas. The intensity of emission peak again increases when the time of exposure of ammonia gas increases from 15 to 30 minutes. The sensitivity of ZnO-CuO nanomaterial is strongly related to the presence of pores and void spaces in between the particles. It can be seen from the SEM image of ZnO-CuO mixed nanomaterial shown in figure 2(b). These pores and void spaces act as active centers for the adsorption of ammonia gas. The ammonia gas molecules can easily access the surface of ZnO-CuO nanomaterial by diffusing through these pores. Apart from defects and morphology, the heterojunction formed on the interface between ZnO and CuO in ZnO-CuO mixed nanomaterial plays an important role in the sensing mechanism. These heterojunctions provide free electrons for the adsorption of oxygen species on the surface. The change in PL intensity is due to the absorption and desorption of oxygen on the surface of sensing materials. Ammonia gas sensing property of ZnO-CuO mixed nanomaterial was proposed to be related to the surface adsorbed oxygen species [12].

In ZnO-CuO mixed nanomaterial, ZnO is an n-type semiconductor whereas CuO is p-type. The contact of two different metal oxide semiconductors results in the formation of a p-n heterojunction at the interface between the two semiconductors, CuO and ZnO. When ZnO-CuO mixed nanostructure was exposed to air, oxygen molecules get absorbed on the surface of the material and capture free electrons from them to form chemisorbed oxygen species. The presence of surface absorbed oxygen can be confirmed from the XPS spectra of ZnO-CuO mixed nanostructure [Figure 3]. Thus the carrier concentration inside the material decreases. As a result, resistance increases and conductivity decreases and hence PL intensity become low. When ammonia gas is exposed to this ZnO-CuO mixed nanomaterial, the reaction between NH_3 and oxygen species happens to release electrons back to their respective oxides. Which leads to an increase in carrier concentration inside the mixed nanostructure. Through this procedure, the photoexcited ZnO-CuO nanomaterial promotes the formation of excitons and reduces the tendency of nonradiative transitions. As a result, the PL intensity increases [13]. Figure 5 shows the schematic representation of the possible mechanism behind the gas sensing property of ZnO-CuO mixed nanomaterial.

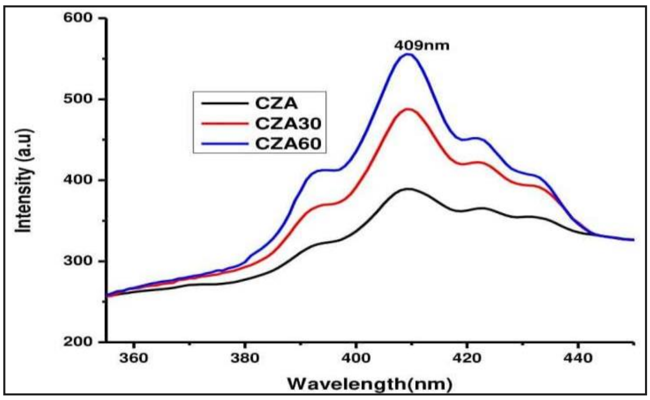

Figure 4 PL Spectra of ZnO-CuO Mixed Nanomaterial in the Presence of Ammonia Gas

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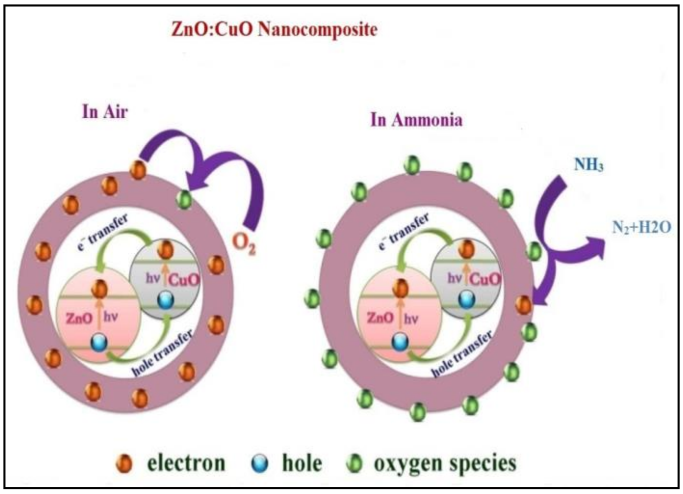

Figure 5 Schematic Representation of Ammonia Gas Sensing Mechanism in ZnO-CuO Mixed Nanomaterial [Ref: 14 and 15]

V. CONCLUSION

XPS spectroscopy confirmed the presence of oxygen molecules absorbed on the surface of the nanomaterial, which is responsible for the enhanced gas sensitivity of the nanostructure. ZnO-CuO mixed nanomaterial was used as a sensing material for the detection of ammonia gas. The optical gas sensing property of ZnO-CuO mixed nanomaterial was investigated by recording PL spectra in presence of ammonia gas. It is seen that there is an increase in the intensity of PL emission peak when the sample was exposed to ammonia gas. The unique morphology, defects, and formation of p-n junctions are responsible for the sensitivity of the material. The results revealed that, ZnO-CuO mixed nanomaterial is a promising candidate for the room temperature sensing of ammonia gas.

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