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Research Paper

Nanoparticles of Ag-Doped ZnO for Ethanol Gas Sensing

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Nanoparticles of Ag-doped ZnO have been synthesized, characterized, and used to detect ethanol gas. Hydrothermal synthesis and several characterization methods were used to produce the nanoparticles. Nanoparticles created using Ag-doped ZnO have an average diameter of 217nm, are well-crystalline, and display excellent optical characteristics, according to the comprehensive characterizations. An effective ethanol gas sensor was built using the nanoparticles that had been manufactured using Ag-doped ZnO nanoparticles. At 3500C, the recorded gas response for 200 ppm of ethanol gas was 35.815, according to the thorough gas sensing studies.

Keywords: *Silver (Ag) Doped ZnO, Nanoparticles, Ethanol, Gas Sensing Properties.*

1. Introduction

Impure ZnO nanostructures have recently gained a lot of interest because they have better physicochemical, electrical, thermal, and surface characteristics than virgin ZnO nanomaterials[1]. One possible candidate for the fabrication of various optoelectronic devices, such as solar cells with a transparent surface, field effect transistors, thin-film transistors [2-5], light emitting diodes, electrochemical sensors, gas sensors, piezoelectric and pyroelectric devices [7-11]. ZnO is a semiconductor that belongs to the n-type II– VI group and has a band gap of 3.37 eV. Its exciton binding energy is significant 60 meV. Additionally, the addition of ZnO to ZnO improves the surface area and defect density, as well as customising and modifying the characteristics of the material [12]. ZnO has been doped using a variety of doping ions, all of which have been documented in the scientific literature [13-14]. Inflammable, colourless, and volatile ethanol has the chemical formula CH3CH2OH. Alcohol and consuming alcohol are typical names for it. When ethanol is released into the environment in excess, it can irritate the skin and eyes, depress the central nervous system, make people feel sick, and burn the skin when exposed to NO2. Levels between 10 and 50 ppm can irritate the nose, throat, and bronchitis, while levels over 100 ppm can be fatal due to their effects on the lungs. In this context, scientists are working hard to create nanodevices based on sensing technologies for applications ranging from the detection of harmful gases to medical diagnosis. Adsorption of gas molecules followed by the elimination of dangerous gases by conduction band electrons forms the sensor, an electron device that can sense environmental changes. Due to its nontoxicity, good electrical and thermal conductivity, and biocompatibility with ZnO, Ag is one of the most promising dopants for ZnO. Ag-doped methods include sol–gel, hydrothermal, plasma induced, solvothermal [15-16], polymer precursor, photochemical sono-mechanical and among others. Electron acceptors such Ag+ ions in doped ZnO are preferred over interstitial locations by Lupan et al [2] and Yan et al [8], respectively. Thomas et al. have shown that Ag+ ions replace Zn2+ ions in its wurtzite hexagonal phase by combining experimental and theoretical methodologies [9]. Impurity bands formed when Ag's 4d and O's 2p orbitals meet, move the Fermi level toward the valence band and give ZnO its p-type character. Lupan et al. found that Ag doped nanowire-fabricated nano and micro-devices had much quicker response and recovery times in room temperature UV and H2 gas measurements than those made without the nanowire. In a study at 3000C, Jeong et al. [3] compared the gas sensing capabilities of ZnO nanowires doped with Ag to those of ZnO nanowires doped with Ga and pure ZnO. At an ideal temperature of 2600C, sea-urchin-like Ag-doped ZnO nanoparticles were produced and employed as ethanol sensors 7] increased the surface area for gas adsorption due to Ag doping in ZnO while simultaneously reducing the band gap as well. As a result, electron excitation to the conduction band requires less thermal energy. Ag-doped ZnO nanoparticles have been synthesised, characterised, and used in gas sensing in this research. Hydrothermal method was employed to make the nanoparticles, which were then utilised as functional materials in the construction of an effective ethanol gas sensor [7-16].

2. Synthesis of Ag-Based ZnO Nanoparticles

Using a straightforward hydrothermal technique, well- crystalline Ag-doped ZnO nanoparticles were successfully produced. A 0.1 M aqueous solution of Zn(NO32, 6H2O) was created in 90 mL of DI water, and it was thoroughly mixed with 0.1 M AgNO3 and 0.1 M HMTA, both of which were prepared in 10 mL of DI water, while being stirred constantly for 20 minutes. This was a typical reaction procedure. In order to keep the pH level at 13, a few drops of an NH4OH solution were added to the final product in a dropwise fashion. The solution that was obtained was first stirred, and then it was moved to an autoclave lined with Teflon. The autoclave was then shut, and it was heated to 155 15 0C for three hours. After the appropriate amount of time had passed for development, the temperature within the autoclave was allowed to return to room temperature. After obtaining precipitates with a colour similar to off-white, they were filtered, washed in a sequence consisting of DI water and ethanol, and lastly dried at a temperature of 700 degrees Celsius for two hours. Prior to the formation of a slurry in DI water for the production of gas sensors, the Ag-doped ZnO nanoparticles were heated for three hours at a temperature of 4000 degrees Celsius. In order to achieve the desired level of homogeneity, the slurry was ultrasonically treated for a period of thirty minutes. The substrate consisted of two gold electrodes placed on the top surface of a sheet of alumina that was 0.25 millimetres thick and had a temperature-controlled micro- heater placed below it. Changes in the average temperature of the surrounding environment were tracked over time using sensors that used infrared technology. Following the application of Ag-doped ZnO nanoparticles onto the alumina substrate, the gas sensor was allowed to air-dry before being heated for two hours at 450 degrees Celsius. In addition, a quartz tube that was constructed expressly for gas sensing measurements was used. Connecting a DC 2- probe electrometer to a computer and evaluating the sensor's reaction to varying concentrations of ethanol gas (10–200 ppm) allowed for the measurement of resistance in gas and air at temperatures of 270, 320, and 370 degrees Celsius, respectively. The amount of time required to reach a steady response value of 90 percent is referred to as the reaction time (res), whereas the amount of time required for the initial response value to return to 10 percent is referred to as the recovery time (rec).

3. Results and Discussion

X-ray diffraction was used to analyse the artificially produced Ag-doped ZnO nanoparticles in order to investigate the crystallinity as well as the crystal phases (XRD). Figure 1 exhibits the typical XRD pattern of as-synthesized Ag-doped ZnO nanoparticles, which shows various well-defined diffraction peaks appearing at 2θ (degree) angles of 31.770, 34.450, 36.270, 38.260, 47.530, 56.670, 62.840, 66.390, 67.910, 69.250, 72.530 and 76.80 correspond to the wurtzite hexagonal crystal planes of ZnO (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) respectively. The observed XRD results are well matched with the reported literature and JCPDS data card no. 36-1451 In addition, a short peak appearing in the XRD pattern at 2θ = 38.260 was also seen which is due to the (111) plane of the face-centred cubic (fcc) phase of the metal. The JCPDS data card number 04-0783 and the published literature match the observed peak for Ag.

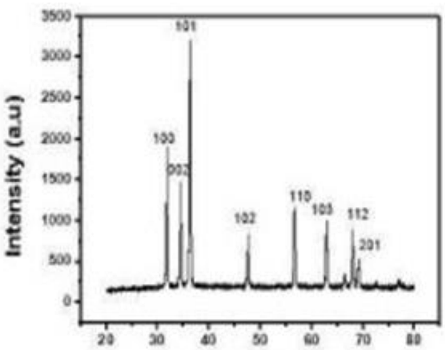

Figure 1. The typical XRD pattern of Ag-doped ZnO nanoparticles.

The technique known as field emission scanning electron microscopy, or FESEM, was used in order to look at the general morphology of Ag-doped ZnO nanomaterials (FESEM). Figure 2 contains FESEM images of a synthetic material for your viewing pleasure. The FESEM images that were taken make it abundantly evident that the material that was synthesised has morphologies in the form of particles, which were created in a high density and have dimensions on the nanoscale. Ag doped ZnO nanoparticles were found to have an average diameter of 22.7 nm. The obtained XRD pattern closely matches the observed results.

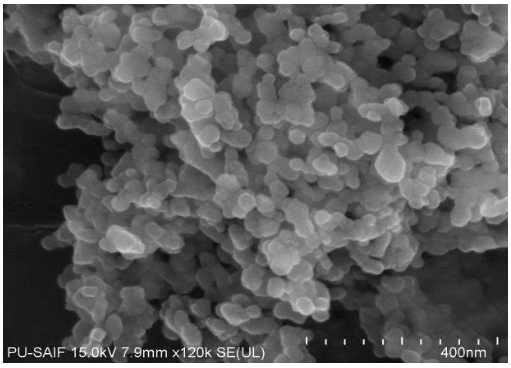

Figure 2. FESEM image of Ag-ZnO nanoparticles

UV-Visible spectroscopy was used to investigate the optical characteristics of Ag-doped ZnO nanoparticles that were produced. When the nanoparticles were produced using Ag, they displayed a single and strong absorption peak at 410 nm, which is the characteristic peak of ZnO's wurtzite hexagonal phase. This is seen in the UV-Vis. spectra in Figure 3. Planck's equation (Eq. 1) predicted a band gap of 3.04 eV for Ag-doped ZnO nanoparticles that were produced. Ag-doped ZnO nanoparticles have outstanding optical characteristics, as shown by the existence of a single absorption peak in the UV-Vis spectrum [4-7].

Eg = 1242/λmax (nm) = Eg in eV (1)

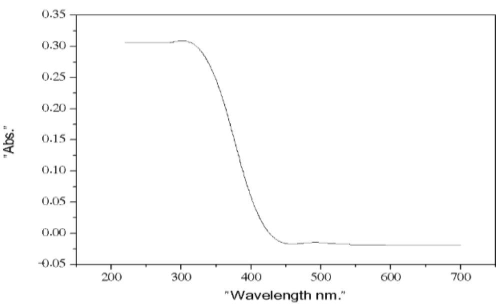

Figure 3. UV-Vis Spectroscopy of Ag-ZnO Nanoparticles

Figure 4 displays the typical FTIR spectrum of Ag-doped ZnO nanoparticles. The FTIR spectrum had well-defined peaks at 439, 919, 1425, and 3427 cm-1. At a frequency of 439 cm-1, the brilliant, forceful, and well-defined peak is produced by the metal-oxygen bonding modes (Ag–O or Zn– O). O–H stretching vibrational modes and deformations, which are induced by O–H stretching vibrational modes and physiosorbed water molecules on the nanoparticle surfaces, result in the appearance of sharp but broad bands at 3427 and 1425 cm-1 [8-9]. There is a possibility that the peak might be attributed to the in-plane vibrational modes of nitrate (NO3 ions), and this peak can be seen at 919 cm-1 [4].

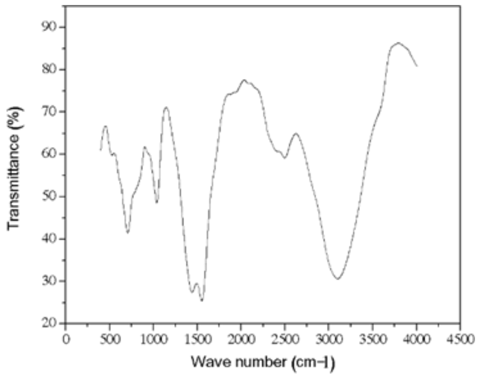

Figure 4. FTIR Spectroscopy of Ag-ZnO Nanoparticles Ethanol Gas Sensing Property of Ag-ZnO nanoparticles

Metal oxide-based gas sensors' gas response is strongly influenced by operating temperature and concentration, and this is now well-established. At very low working temperatures, there is enough power. The valance band electrons cannot be excited to the conduction band because there isn't enough activation energy available. Adsorbed O2 molecules are reduced by electrons to create analytes that are reduced by oxygenated anions. Instead, a high working temperature is advantageous. As a consequence, oxygenated species may also be desorption as atoms and molecules in the air. In regard to early temperatures, this is why employing a manufactured sensor for ethanol gas optimization, ZnO nanoparticles doped with Ag were used to make this. ZnO doped with Ag is a novel material. Sensors based on nanoparticles were subjected to a concentration of 100 ppm ethanol was heated to 270, 320, and 370 degrees Celsius in the lab. The most effective ethanol sensing temperature was determined to be atmospheric temperature, Figure 5. Equivalently, the gaseous reaction, recuperation, and resuscitation Rec timings were 12.12, 13.3, and 14.3 secs, respectively.

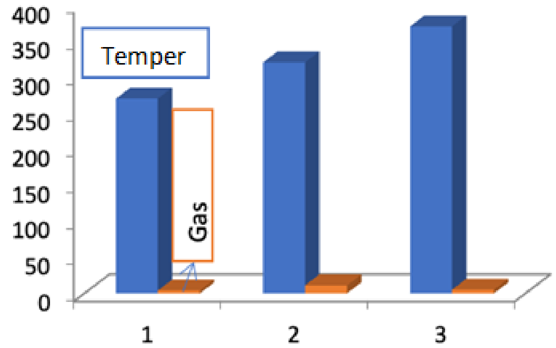

Figure 5. Ag-doped ZnO nanoparticles based sensors respond to 100 ppm ethanol.

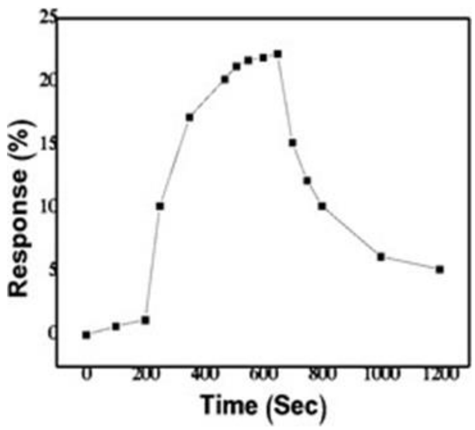

Figure 6. represents the time response curve for the selected sample.

Our response and recuperation time are also shown. The reaction time is the time it takes for the sensor to become resistant to the target gas. The time it takes to regain initial resistance. A quick response and recovery of Ag-doped ZnO nanoparticles is shown in Figure 6. Gas oxidation may have accelerated this quick reaction. The enhanced surfacto-volume relationship, defect density, and ribbon gap indicated better reaction and recovery time in tri-doped ZnO samples. This reduces the number of electron- hole combinations. Doping the ZnO crystal lattice with Ag+ ions results in an increase in the number of oxygen vacancies on the surface of Ag-doped ZnO nanoparticles, which may explain why res and rec are so short [33]. Recent studies have shown that doping ZnO nanoparticles with Ag+ ions increases charge carrier density, mobility, and resistivity [16]. The mechanism for the selected samples is refereed in the research papers. At various temperatures, Ag-doped ZnO sensors were subjected to 100 ppm ethanol. Figure 5 shows the sensor response against operating temperature graphs for all synthesised samples. The best operating temperature for pure and doped ZnO was 400°C. and 300°C. Target gas species must pass a temperature threshold to be identified. combined with adsorbed oxygen species. At optimal temperature, gas Energy-rich molecules react with surface- adsorbed oxygen, changing the sensor conductance. Doped samples have a lower optimal operating temperature of 300°C. Ag's catalytic nature contributes. Catalysts allow low-energy reactions. Under Oxygen molecules adsorb on the material's surface, generating O2. Conduction electrons, this increases the sensor air resistance. The proposed model has been presented to clarify the gas sensing mechanism, which is understood by a change in electrical resistance brought on by adsorbed oxygen. When exposed to air, ZnO absorbs oxygen molecules and changes into various ionic species, which improve sensitivity by snatching one electron from the conduction band. Due to the creation of thick layers as a result, the electrical resistance increases. Additionally, when ethanol was applied to Ag-ZnO based films, the ethanol molecules reacted with the adsorbed oxygen and released free electrons, reducing the electrical resistance and depletion layer thickness. The increase in gas sensitivity is caused by the active sites for gas adsorption that are provided by large surface areas. Metal oxide gas sensing mechanisms are always difficult to develop. It is founded on the chemiresistance theory. On the other hand, transducers and receptors were involved. Transducers convert chemical signals into electrical signals and give receptors by interaction with metal oxides as either charge carriers' donors or acceptors. The type of gas molecules and the predominant carriers determine how the resistance of a metal oxide coating changes. Normally, ZnO's surface adsorbed oxygen from the air. This adsorbed oxygen species has the ability to absorb an electron from the ZnO film surface and transform into O-, which releases oxygen. By assisting in the formation of the depletion layer on the host surface, this O- ion lowers the conductivity [6]. The electron trapped by the oxygen adsorbate will return to the ZnO layer when the sensor is exposed to donor (reducing gas), which results in a drop in the potential barrier and an increase in conductivity. Doping element addition aids in completing the ZnO structure. FESEM pictures demonstrated that surface area and density are crucial factors in gas sensing applications. This opens up more

5. Conclusion

We were able to successfully manufacture Ag-doped ZnO nanomaterials using a simple hydrothermal technique aided by HMTA. In addition, the gas sensing properties of Ag-doped ZnO nanoparticles were tested with ethanol in a subsequent study. Even at low concentrations of 10 ppm, the constructed gas sensor had a remarkable gas reaction with ethanol gas. An analyte gas's operating temperature and concentration had a substantial impact on sensor response. Since these gas sensors have low res and rec recorded, they're excellent candidates for use as sensors against lowering gases.

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