International Journal of Scientific Research in Science and Technology
Available online at : www.ijsrst.com
Print ISSN: 2395-6011 | Online ISSN: 2395-602X
doi : https://doi.org/10.32628/IJSRST52411278

Synthesis & Characteristics of PPy - MgO –CuO Nanocomposite for CO_2 Gas Sensors Applications

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ARTICLEINFO

Article History:

Accepted: 20 March 2024
Published: 05 April 2024

Publication Issue :
Volume 11, Issue 2
March-April-2024
Page Number :
446-453

ABSTRACT

The MgO, CuO nanoparticles was synthesized by sol-gel method, and polypyrrole(PPy) was a synthesized by chemical oxidative polymerization technique for a period of four hours (4h) at room temperature using pyrrole monomer in aqueous solution. Unlike oxidants such as ferric chloride ($FeCl_3$) and ammonium persulphate ($N_2H_8S_2O_8$) were used. The sample PPy in the form of odorless black powder were prepared. The synthesized nanoparticles was characterized by powder X-Ray Diffraction (XRD), Scanning electron microscopy (SEM). The XRD studies of this sample confirmed the emergence of cubic structure and the particles size and lattice constant were analyzed. It shows that the morphology of PPy samples has a significant influence on the conductivity. The conducting polymer-polypyrrole has highly eolotropic of electrical conduction and operated as a CO_2 gas sensor. The different MgO-PPy, CuO-PPy , MgO-CuO Composite by weight % were prepare by the screen-printing method on Al_2O_3 layer after by glass substrate. This sensors was used for dissimilar concentration (ppm) of CO_2 gas study at room temperature. The structure and morphology of synthesized nanoparticles was investigated utilizing of X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM)

Keywords :- Polypyrrole, CuO, MgO nanocomposite, Gas Sensor, CO_2, XRD, SEM

I. INTRODUCTION

The nanocomposite material are especially important to the bridging role between the world of conducting polymers and that of inorganic materials. Nanocomposites made by the production of nanostructure material in conducting polymers had gained special attention in material science and active multidisciplinary research. [1, 2]. Carbon dioxide(CO_2) is one of the most common green house gases and is a main component among corrosive gas species . The command of CO_2 gas also plays an important role in agricultural sector. [3, 4]. Many researchers [5, 6] have grow conductive polymers for gas sensors application, such as polyacetylene(Pac), polypyrrole (PPy) and polyaniline(PANI). The superiority of conducting polymers gas sensors are low cost, suitable for manufacture on various substrates and room temperature operation [7, 8]. Polypyrrole has attracted much interest due to its easy preparation of powders and composite with good environmental balance and higher conductivity. The PPy is highly sensitive to gases but it observed saturation effect at highly concentration of gases [9] PPy have been vigorously used in many potential application such as electronic devices, sensors, batteries , microactuators, anti-electrostatics coatings, and biomedical [10, 11], and then synthesized and make ready by using different techniques such as electrochemical [12, 13] or chemical oxidation of pyrrole monomer [14, 15] in various organic solvents and in aqueous media. The use of unalike oxidants and pyrrole monomer for pure PPy and tailoring their performance on the ending properties such as electrical, thermal and morphological have not been fully utilize, and there are a few reports available in literature which use sodium dodecyl sulphate as a dopant and comparing the showing of ferric chloride and ammonium persulphate as an oxidizing agent in terms of thermal stability, conductivity, and morphology. In the evolution of Nano size materials of metal and metal oxides particles are effectively pursued because of their prominence in different field of application in science and technology. Nanoparticles of metal oxides have been used to incorporate functional properties into textiles . Attempts have been made to use common metal oxides, such as copper oxide (CuO)and magnesium oxide(MgO), for providing fabrics with functional properties. [16] Magnesium oxide (MgO) nanopowder is a non toxic white powder widely used in industrial application. The Magnesium oxide (MgO) is a versatile oxide materials, with high melting points (2850^{0}C) and high boiling points (3600^{0}C); thereby it is thermally so stable. MgO possesses inflexible properties, so can be used as a body material, furnace and crucibles. MgO compounds were ready by conventional method like combustion and thermal decomposition which yield a relative small surface area and provide low reaction activity [17]. Magnesium oxide has also shown a promising application in catalysis application of many organic reaction [18]. Many synthesis procedure such as sol-gel, hydrothermal, flame spray pyrolysis, combustion, aqueous wet chemical, surfactant and chemical gas phase deposition methods have been considered for the synthesis of MgO nanoparticles [19]. Various manufacture techniques are also employed to synthesize MgO nanoparticles having their own advantages and disadvantages [20]. Spherical shaped magnesium oxide nanoparticles were synthesized successfully by sol-gel method using magnesium nitrate and sodium hydroxide [21]. A sol gel method is an important technique for the development of magnesium hydroxide followed by annealing at room temperature to form MgO. All the metal oxide, CuO is a potential candidate for magnetic storage devices, solar energy transfer, sensor and super capacitor and especially it acts as a good catalyst in some of the chemical reaction [22]. Copper oxide act as material with semiconductor characteristics and were natural abundance of starting material. Copper oxide NPs were non –toxic and obtained easily through the oxidation reaction of copper. CuO is most of the significant metal oxide that recently attracted investigators due to availably and low cost, in addition to particular characteristics [23]. Several methodologies were employed to get ready copper oxide NPs. Sol –Gel technique have many beneficial. Solitary sol-gel installation could produce material with ultra-temperature . However, The report on the preparation and characterization of nanocrystalline CuO are relatively few to some other transition metal oxide such as Zinc oxide, titanium dioxide, Tin dioxide and Iron dioxide . In this paper, we have synthesized CuO nanoparticles with size 15-100nm. The present study deals with the Structural and morphology properties of PPy-MgO, PPy-CuO, MgO-CuO nanocomposites.

Now in this a days, there is a great interest in applying sensing devices in order to improve environmental and safety control of gases. The most used gas sensor devices can be divided in three big groups depending on the technology applied in their development :solid state, spectroscopic and optic. While spectroscopic and optic system are very expensive for domestics use and sometimes difficult to the execute in reduced spaces as car engines, the so called solid state sensors present great advantages due to their fast sensing response , simple execute and low prices [24, 25]. These solid state gas sensors are based on the change of the physical and or chemical properties of their sensing materials when exposed to different gas atmospheres. Although the number of materials used to implement this kind of devices is huge , this work were centered in studding the semiconductor properties , in those material using MgO, CuO and PPy as a sensing material.

The main work of this paper is to study new material for gas sensing elements starting from the knowledge in thick film production using screen-printing technique and the prepared samples were characterized by XRD analysis . The morphology of powders was look into by using ZEISS SCAN instrument (SEM).

II. Experimental

2. 1 Synthesis of PPy

Polypyrrole (PPy) were prepared by chemical oxidative polymerization technique using monomer pyrrole. Analytical grade ammonium persulphate (APS), (AR grade) was used as a oxidizing agent. The chemical polymerization was carried out in a beaker by mixing 0. 1 M aqueous solution of pyrrole and 0. 1 M of APS in 1:1 ratio by volume. The polymerization was carried out for a period of three hours. After termination of polymerization process, the precipitate obtained was filtered. The product was washed successively by methanol followed by distilled water.

2. 2 Synthesis of MgO

The sol-gel technique is advantageous in the synthesized of nanosized materials because it has the advantages of simple procedure, low temperature processing and low cost Initially the Magnesium Nitrate hexahydrade of wt. 5. 21gm (0. 2 M) and dissolved in 100m1 of distilled water. The 0. 8 gm (0. 2 M) of NaOH in 200m1 distilled water. The distilled water is generated from the distillation plant in our laboratory. Then 100m1 of NaOH solution is added in solution of [Mg(NO2)(H20)] drop-wise by using glass rod. After that, solution kept under magnetic stirring for 2 h after stirring the solution was kept on table at rest for 2 h so that, the precipitation is formed at the bottom of beaker. This precipitation was filtered and washed several times by using distilled water and Ethanol so as to get the final products. The final product is kept in vacuum oven (Quality Make, India) at 80 °C for 4 h for drying product and removing the moisture. This dried powder is then crush and make it very fine powder by using mortal pestle. Finally the fine powder of MgO is calcinated at 400 °C for 3 h for the removal of impurities present in the powder. So that we will get synthesized MgO possessed high crystalline with the particle size in nanosized range.

2. 3 Synthesis of nano CuO

CuO nano particles are synthesized by Co-precipitation method using copper (II) acetate [Cu(CH3COO)2·H2O)] and Ammonia (NH_3). In short, 0. 2 M copper (II) acetate solutions (100 ml) and Ammonia was added drop wise to maintained pH in a round-bottom flask and under magnetic stirrer. The colour of the solution revolve from blue to black instantaneously and a black suspension formed simultaneously. The reaction was carried out under stirring and boiling for 3 hr. The mixture was cooled to room temperature CuO precipitate was obtained. The precipitate was filtered and washed with distilled water for several times. The resulting product was dried at 60˚C for 2 hr to obtain the dry powder of CuO Nano Composite.

2. 4 Synthesis and Sensor preparation:

As mention above the aim of the present work, The work concentrates on thick film sensors of PPy, MgO and CuO. The experimental method for the preparation of material , fabrication of sensors , screen –printing method and fabrication of gas chamber and gas flow meter is discussed.

2. 5 Preparation of sensors thick films:

PPy, MgOand CuO sensors were get ready by screen-printing technique, (thick film technique)[26, 27]. The binder make ready by thoroughly mixed 8wt. % butyl carbitol (BCA) with 92wt. % ethyl cellulose. (EC) was used for the screen printing process [27, 28]. The active powder and ethyl cellulose were mixed thoroughly. During this mixing process, the BCA was added drop by drop to obtain the proper viscosity of the paste. For thyrotrophic property for printing on the substrate. Paste for screen printing was prepared by getting 60 wt. % of PPy, MgO and CuO powder with40 wt. % binder in an agate mortar and thoroughly mixing it. The paste thus get ready by screen printing onto a chemically cleaned galss substrate of size 75mm×25mm and the dried at room temperature for 24 h. The prepared film was heated at 150^0C for 60-70 min. During this stage , The volatile organic solvents was removed via decomposition and the prints adhered to the substrate. Therefore the ink solvent does not diffuse in sample. For the surface resistance measurements the electrodes of conducting silver paint were formed on adjacent sides of the film and then the films was a subjected to heating at 800C for 15min for scorching the silver paint. The electrical resistance of the film was measured by using a voltage drop method adopted by Yawale et al. [30]. The measurements were carried out in the testing ground of department of physics of Vidyabharti mahavidyalaya, Amravati. The gas chamber having dimension 30cm×30cm×30cm with an attached CO_2 gas flow meter was used for keeping the sensors for testing. The gas flow adjusted to 2min. The reading were carried out in a CO_2 gas environment at different ppm levels and various temperature . The experiments was carried out 5-6 times for reproducibility of the sensors. No change in sensors resistance was observed at the concentration and temperature. The thickness of all the prepared sensors sample were measured by digital micrometer. and following gas chamber(figure 1) is used for characterization.

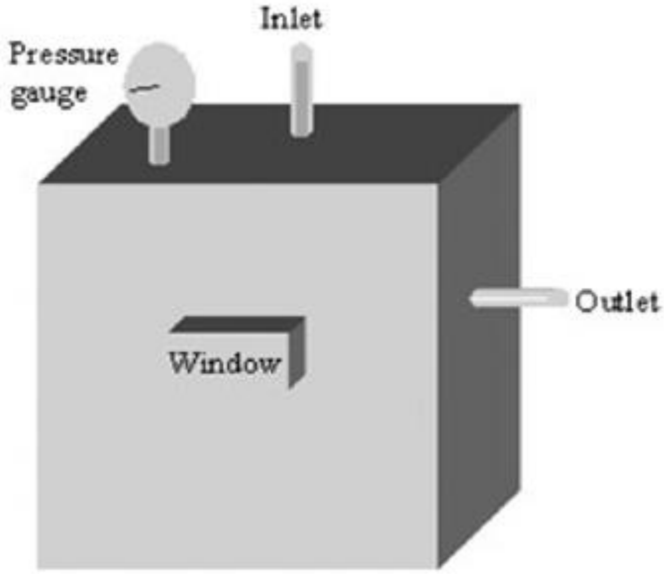


Figure 1: Gas chamber for CO_2

III. Results and Discussion

3. 1. XRD analysis

Figure (2)(a), (b), and (c) shows XRD pattern of PPy, MgO, CuO. fig. (a) It is observed thad XRD pattern contains 6-8 peaks. The (h k l) values are obtained by using 2θ and d-values from XRD pattern. Fig(2a) show a broad peak at 2 θ= 32^0 which is the characteristics the peak of amorphous nature of PPy. PPy is amorphous in nature. In fig (b) and (c) show all the diffraction peaks appearing at corresponding 2θ values at 18. 67, 29. 37, 35. 47, 38. 75 are miller indices values (001), (104), (002), (111)respectively. These result were matches with JCPDS card (no. 1010484). The result showed that the structure was in cubic structure. The average grain size calculated using Debye-Scherer's Formula [31] of these material is about nm.

$D = k\lambda/\beta \cos\theta$ (nm)

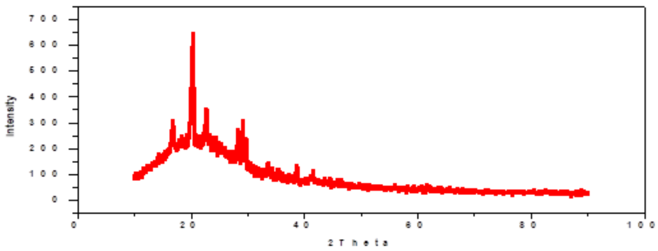
Where, D is the particle size (nm)

K is the shape factor

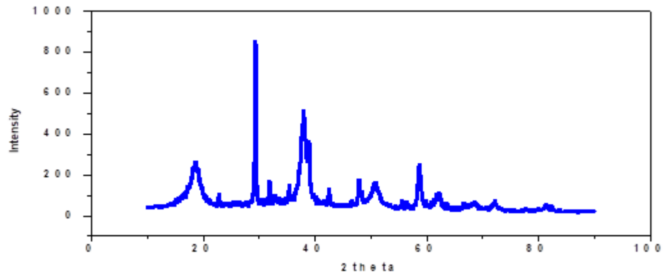
λ is the wavelength of X-ray

β is the full width at half maximum intensity

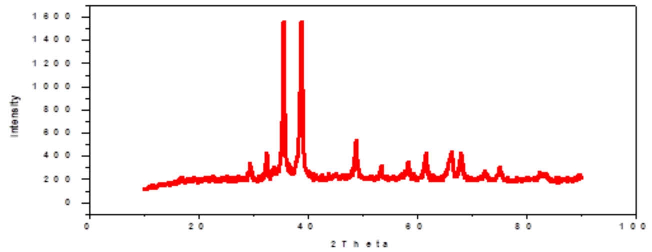
θ is the Bragg diffraction angle



Figure(2a) XRD of Pure PPy



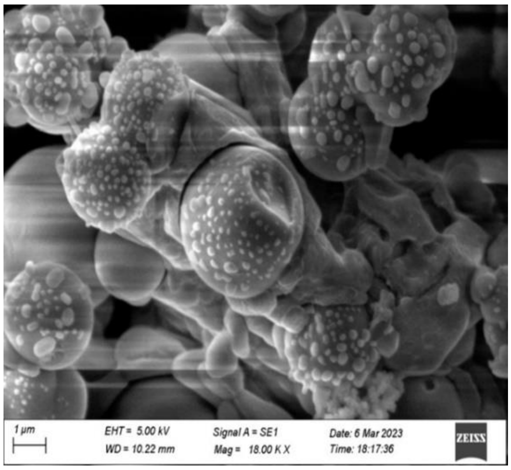
Figure(2b) XRD of Pure MgO



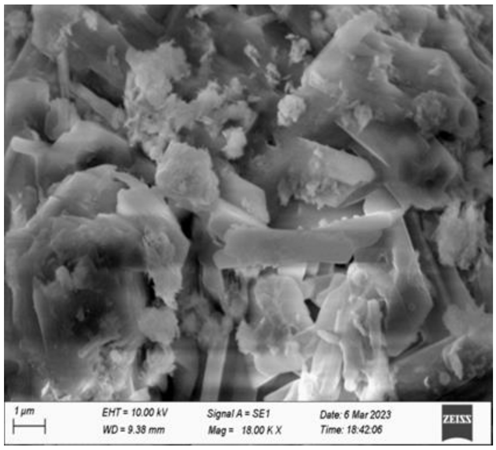
Figure(2c) XRD of Pure CuO

3. 2 SEM analysis

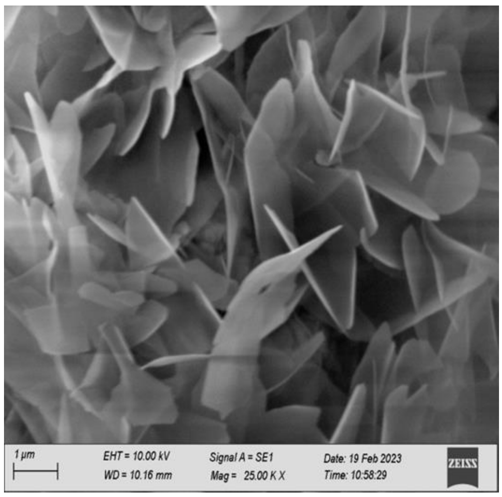
The SEM analysis examined the surface morphology of prepared samples and the representative images are shown in figure (3) (a), (b), and (c). The size and morphology of the synthesized PPy, MgO and CuO nanoparticles are visualized by Scanning electron microscope using ZEISS SCAN instrument for different magnification. The PPy , MgO and CuO nanopaerticles are presents in spherical and cylindrical in shape. The grain size of PPy, MgO, CuO are1µm. This type of morphology highly functional in gas sensing action. This film has a uniform powdered morphology. The PPy is amorphous nature show in the SEM picture. Thus, successful preparation of PPy, MgO, CuO can be confirmed by the result obtained from XRD, SEM studies.



(a)



(b)



(c)

Fig. 3 (a) Pure PPy (b) Pure CuO c) MgO

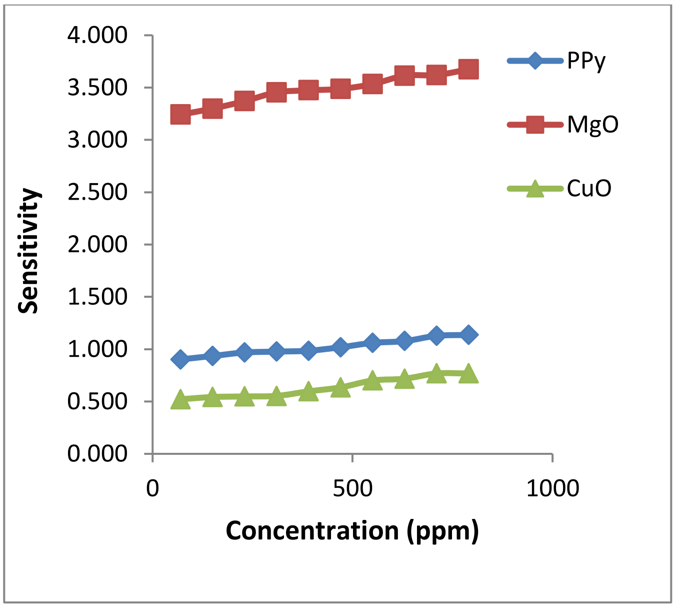
3. 3 Sensing Response

The sensor is a defined as in eq. (1)[32]

S = (Rg-Ra)/Ra (1)

= ΔR/Ra

Where, Ra is is the resistance of sensors in air and Rg is the resistance in gas, respectively. The sensing response of these film was measured for different concentration of CO_2 gas at room temperature fig (4a). The resistance of the film was considered to be decrease with concentration of CO_2 gas.

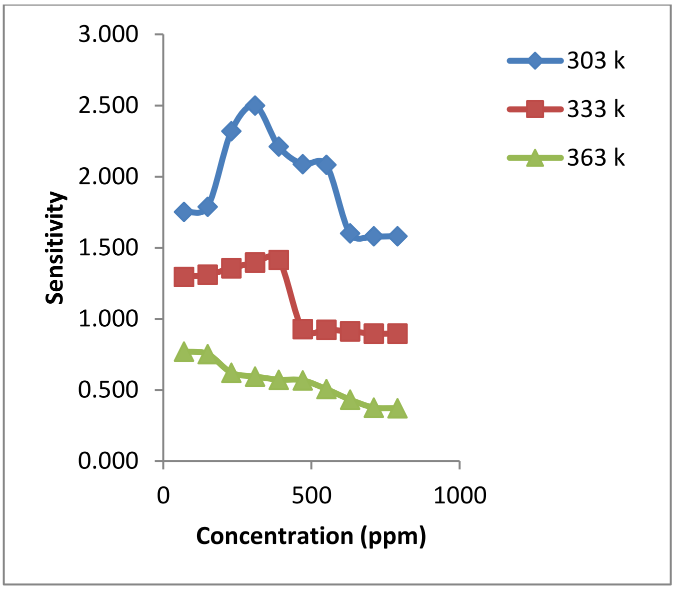


Fig(4a) Sensing response of PPy, MgO and CuO sensors as a use of CO2 gas concentration at room temperature.

The resistance of PPy, MgO, and CuO sensors is increases with CO_2 gas concentration. The relationship between sensitivity and CO_2 gas concentration for PPy, MgO, CuO sensors at room temperature (303K) display in figure (g). MgO sensor show a highly sensitivity to CO_2 gas, compare with PPy and CuO sensors. MgO sensors exhibit a good dependence on CO_2 gas concentration up to 800ppm.

3. 4 Sensing response of Optimize sample of MgO:

Fig (4b) be seen as the difference of sensitivity to CO_2 gas concentration at different temperature. It is observed that MgO at 303 k sensor show fast recovery as compared to Other sensor. Therefore MgO sensors are the best among the various reported sensors. And fig (i) show that the difference of sensitivity to 100, 300, 700 ppm CO2 at various temperature. The MgO sensors observed that its sensitivity found to be higher at 313 k in fig. (4c). which is the operating temperature of sensor.



Fig(4b) Sensing response of optimize sample MgO as a use of CO_2 gas concentration at different temperature

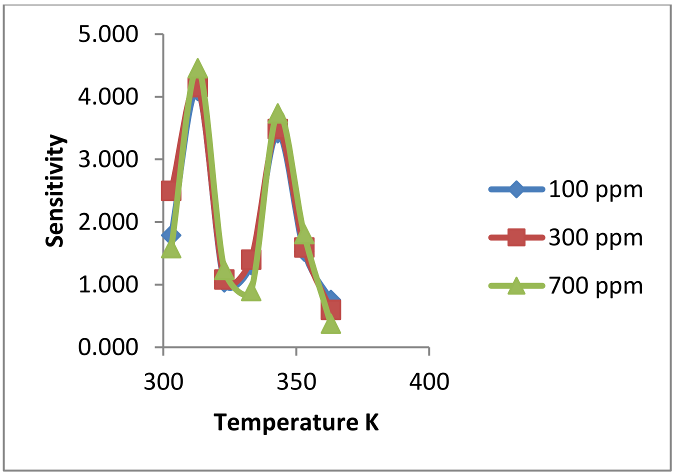


Fig. (4c) variation of sensitivity to 100, 300, 700 ppm CO_2 gas at various temperature.

IV. CONCLUSION

The study of the PPy samples were prepared using different oxidants, and there performance in terms of electrical properties has been evaluated and compared and the , MgO, and CuO nanoparticles are prepared by sol-gel method and different characteristics like XRD, SEM were studied. XRD pattern is used to determine the crystal structure, phase purity and grain size of nanoparticles. SEM image of PPy, MgO, and PPy reveals the well crystallized particles with spherical, and cylindrical like morphology. Screen printing method is a very simple method for preparation of multilayer sensors. Gas sensing characteristics shows response for CO_2 gas with operating room temperature. The MgO sensor gave high sensitivity to CO_2 gas, compare with PPy, CuO sensors. . The MgO sensors observed that its sensitivity found to be higher at 313 k in fig. (4c). which is the operating temperature of sensor.

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