

Synthesis and Characterization of Silver Oxide-Based Linde Type a Zeolite/Polypyrrole Composite for Highly Sensitive Dimethyl Methyl Phosphonate Sensor Applications

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Abstract

We report the hydrothermal synthesis of zeolite Linde type A and the chemical polymerization technique for the synthesis nanocomposite for gas sensing applications. Our prime motive is to enhance the sensing efficiency of zeolite nanocomposite. The synthesized nanocomposite was characterized by various techniques like X-ray diffraction technique (XRD), Scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDX) and Fourier transform infrared spectroscopy (FTIR). XRD analysis showed the highly crystalline zeolite, AgO-Zeolite and PPy have shown broad peaks which confirm that the samples are in an amorphous phase. SEM results elucidated that the incorporation of polypyrrole into the zeolite changed the surface morphology from rectangular to spherical. The particle size of the nanocomposite decreased thereby increasing their surface area which in turn enhanced their sensing application. The gas sensing behavior of the nanocomposite was measured on DMMP using substrate-coated copper electrodes and the nanocomposite was loaded over the electrode via the drop-casting method. Response and Recovery time, sensitivity, and selectivity of the substrate were investigated. The nanocomposite showed excellent performance for different concentrations of DMMP Toxic vapors.

Keywords: Zeolite; Synthesis; Polymer; Gas Sensor; Nanoparticle

Introduction

Detection of toxic gases is of great importance for protection against chemical weapons. In particular, organophosphates, such as sarin, damage nerve function and are fatal inhibitors of acetylcholinesterase. Dimethyl methyl phosphonate (DMMP) is a stimulant of nerve agents, because of the common occurrence of the P=O, P-CH₃ and P-OCH₃ functional groups. DMMP is a harmful, low molecular weight and volatile molecule, that must be removed from the atmosphere. Due to its organophosphorus composition, dimethyl methyl phosphonate [DMMP, CH₃PO(OCH₃)₂] is often used as a simulant for chemical warfare agents (CWAs) and insecticides such as the G-series nerve agents tabun (GA), sarin (GB), soman (GD), and paraoxon. Because of its widespread use as an anti-foaming agent, plasticizer, stabilizer, textile conditioner, and antistatic agent, DMMP has also become a serious environmental and food chain pollutant [1,3], which remains a great challenge to detect due to the lack of sensitive, selective and stable sensors. Due to safety issues, we use DMMP as a laboratory stimulant for sarin (C₄H₁₀FO₂P). Conducting polymer, conducting polymer composites and metal oxide are among the sensing materials utilized to detect DMMP. The detection of dangerous and inflammable gases is critical for climate and human health. Many researchers use metal oxide-based sensors, such as SnO₂, ZnO, In₂O₃, and NiO film, for the detection of CWA. [4]. Inorganic metal oxide has a low surface area and requires a high temperature for the gas sensing procedure. Since the surface area is vital in absorbing more gases. Because zeolite is a material with good thermal stability and a large surface area [5], many researchers have been inspired to develop new approaches based on these properties. The zeolite framework is made up of SiO₄ and AlO₄ tetrahedra units.

The silicon and aluminium atoms are bonded covalently via an oxygen bridge, and subsequently form secondary polyhedral building units that further construct molecular-scale micropores in a periodic three-dimensional arrangement. The formation of micropores inside the zeolite crystals induces a high specific surface area as compared with nonporous materials, enabling their use in diffusion-related applications such as adsorptive separation and catalytic reactions [6-9]. In addition, due to their purely inorganic framework and crystalline architecture, zeolites have very high thermal and mechanical stabilities. Linde Type A zeolite, referred to as LTA, is a highly aluminous zeolite classified as a small-pore size zeolite due to its 8-membered-ring (8MR) micropore aperture with double-four-ring

(D4R) units. Despite its small micropore aperture, LTA zeolite is one of the most important industrial zeolites that can be notably used in selective adsorption and separation of atomic, ionic, or molecular guest species [10-12]. Conductive polymers are used as gas sensors because of their excellent electrical and optical properties. Conducting polymers have many applications in day-to-day life such as anti-corrosion coatings, chemical and biosensors, light-emitting diodes, solar cells and supercapacitors [13-15]. According to several researchers, PPy has been used in gas sensors to detect a variety of gases. Polypyrrole (PPy) is another conductive polymer that has received a lot of attention due to its easy production, high electrical conductivity, low cost, and outstanding chemical and electrochemical stability [16-17], hence it is widely used as a sensing material.

In this chapter, the study of Zeolite nanoparticles was successfully synthesized by a hydrothermal method, and their composite with polypyrrole was prepared by chemical oxidative polymerization techniques as a DMMP toxic gas sensor. Here we have fabricated a sensor for detecting dimethyl methyl phosphonate (DMMP) in our laboratory. To our best knowledge, Zeolite LTA-PPy Composite is the first time reported as a gas sensor towards DMMP toxic gas. The gas sensing investigations show that DMMP gas has excellent sensing capabilities at room temperature, with low concentration, quick reaction, and recovery time.

Experimental

Chemicals

All of the chemicals used in this study were analytical grade and were purchased from various companies such as CDH, Merck and Fisher scientific. Sodium hydroxide (NaOH), sodium aluminate (Na AlO₂), Sodium metasilicate (Na₂SiO₃), Silver Nitrate (AgNO₃), Potassium permanganate (KMnO₄), ammonia persulfate ((NH₄)₂S₂O₈), pyrrole (C₄H₅N), Hydrochloric acid (HCl) and Ethanol (C₂H₅OH).

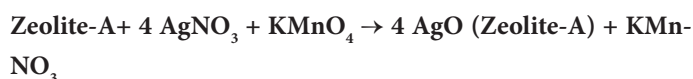
Synthesis of zeolite Linde Type A [LTA]

Zeolite A was synthesized by the low-cost, eco-friendly hydrothermal method. In the typical process, 1.446 g of NaOH was dissolved in 160 ml of water. The solution was equally divided into two parts and placed in two different beakers. Add 16.516 g of sodium aluminate to the first beaker and stirred for about 30 minutes until a clear solution was formed and transferred into a polyethylene bottle. In the second beaker add 30.96g of sodium

metasilicate and this solution is added to the first one, and a thick gel-like substance was formed. The polyethylene bottle containing this gel-like substance was sealed and placed in a hot air oven maintained at a constant temperature of 140 °C for 3 hours. After the reaction parameters were met, the oven was turned off and the polyethylene bottle was naturally cooled to Room temperature. The product was washed, collected, and dried.

Modified zeolite A

Parent Zeolite A was modified by silver ions via using the ion-exchange technique. In this procedure, 1.70 g of AgNO₃ was added to 1.5 g of zeolite LTA in 10 mL of distilled water and stirred at room temperature for 5 hours. In the separate beaker, 0.395 g of Potassium permanganate dissolved in 12.5 ml of de-ionized water and finally it was slowly added to the above already prepared solution, which was then stirred for 3 hours. This obtained product was filtered and washed with distilled water and the final product was dried at 100°C. After this process, it was calcined at 550°C for 4 hours.



Preparation of polypyrrole

The Chemical oxidative polymerization method was used to synthesize polypyrrole. 1 mL of pyrrole monomer was dissolved in 70 mL of 1.5 M HCl solution in a beaker. 2 g ammonia persulfate (oxidant) was dissolved in 20 mL of deionized water in another beaker. Then, a solution of ammonia persulfate was dropped slowly into the pyrrole solution. The complete solution was then stirred at RT for 4 hours. After the polymerization was completed, the final solution was filtered, washed several times with deionized water and ethanol (1:1), and dried at 100°C for 3 hours.

Preparation of Composite

The polymerization technique was used to synthesize zeolite/PPy composite. In the first step, 1 ml of pyrrole-monomer solution and 1 g of zeolite were dissolved in 70 ml of a 1.5 M Hydrochloric acid solution with constant stirring for about 30 minutes in a beaker. In a separate beaker, 2 g of ammonia persulphate was dissolved in 20 mL of deionized water. In the second step, the ammonia persulphate solution was added dropwise to the already prepared solution. The entire solution was then stirred at room temperature for 4 hours. After the polymerization was completed, the entire solution was filtered, washed with deionized water/ethanol several times, and dried in a hot air oven at 100 °C for 3 hours.

Result and Discussion

X-ray Diffraction Analysis

The X-Ray Powder Diffraction technique was used to study the structural properties of the synthesized samples. Figure 1 (a, b, c and d) represents the XRD spectra of all synthesized samples. Figure 1 (a) shows the XRD spectrum of zeolite-A with corresponding peaks such as 7.37°, 10.42°, 12.54°, 16.2°, 20.6°, 21.9°, 24.25°, 27.29°, 30.1°, 32.7°, 34.3°, 47.54°, 52.7°, 69.2° (-JCPDS#43-142) which resembles the reported literature of zeolite -A [18]. Figure 1 (b) represents the XRD pattern of modified zeolite-A with AgO. With the incorporation of AgO in zeolite-A, the peak intensity as well as a moderate shift of peaks occur. Figure 1(c) shows the polypyrrole XRD, with a diffraction peak at 26° with the corresponding plane (112). Figure 1(d) represents the XRD spectrum of Zeolite-A -AgO/PPy composite in which some peaks merge due to the overlapping of polymer ions on the zeolite-A surface.

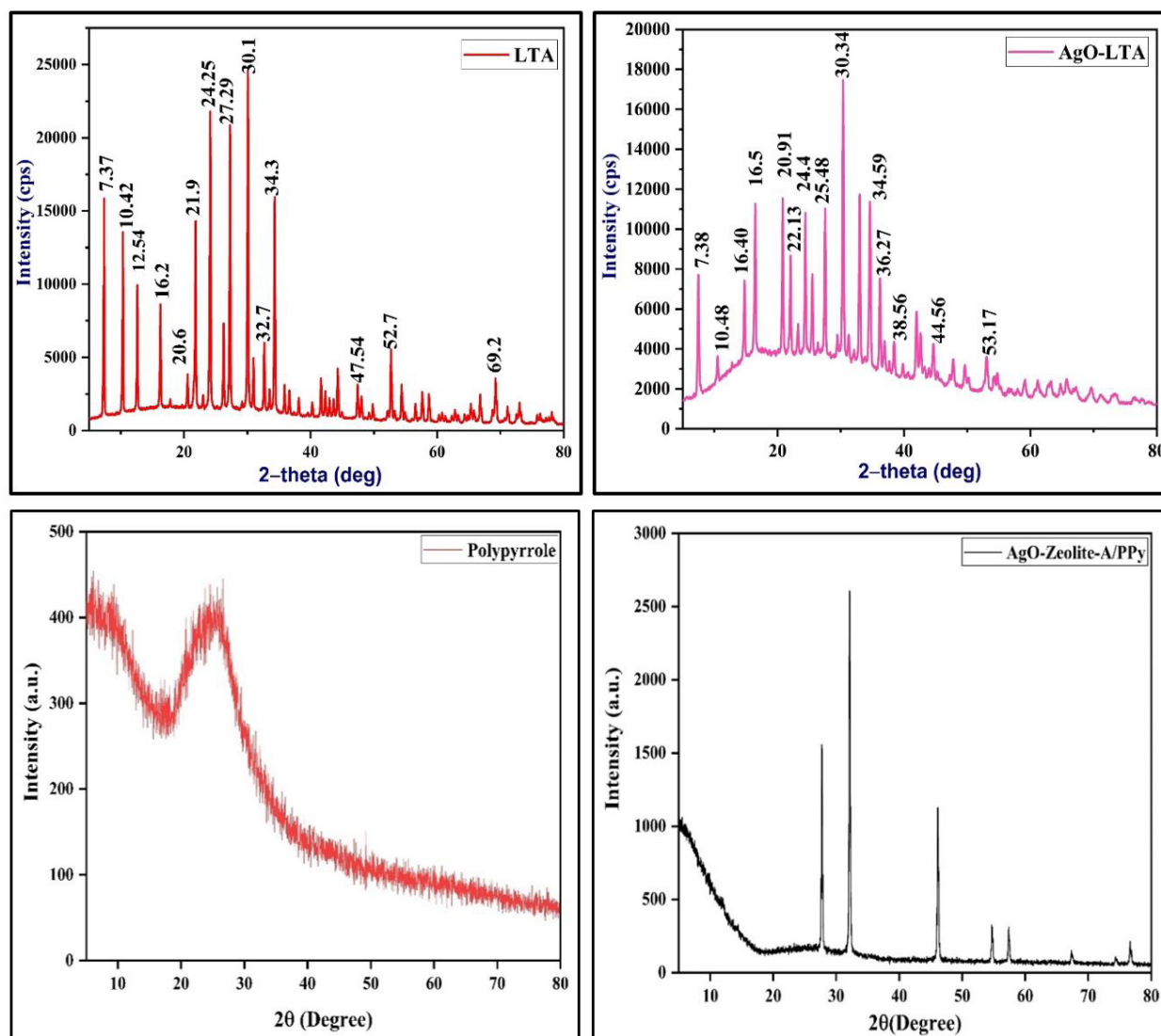


Figure 1: XRD spectra of (a) pure zeolite A, (b) modified zeolite, (c) PPy, and (d) composite

The crystallite size of all the synthesized samples was calculated by using Debye Scherrer's formula

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad [1]$$

Here, D is the crystallite size, 0.9 is the shape coefficient, λ is the wavelength, β is the full width at half maximum (FWHM), and θ is the diffraction angle.

FTIR Analysis

FTIR technique was used to find the functional groups present in the materials. Figure 2 shows the FTIR spectra of synthesized samples. Figure 2(a) represents the FTIR spectrum of zeolite -A and its modified form. Zeolite - A has Symmetric stretching vibration with a frequency of 650 cm^{-1} and asymmet-

ric stretching vibration has a frequency of 950 cm^{-1} , and also bending vibration of the Al-O-Al bond and the SiO_4 groups have absorption bands nearly at 460 cm^{-1} and 533 cm^{-1} , respectively. Figure 2(b) shows the FTIR spectrum of PPy, the peaks detected at 1542 and 1466 cm^{-1} are related to the fundamental vibration of PPy. The broad peak at about 3400 cm^{-1} refers to N-H stretching. The peak at 1375 cm^{-1} is related to C-N asymmetric vibration, whereas the peak at 1045 cm^{-1} is related to C-H deformation. The peak at 2928 cm^{-1} is associated with C-H stretching vibrations. The band at 1624 cm^{-1} can be assigned for the C=C bond. The peak for C-N stretching is at 778 cm^{-1} . Figure 2(c) represents the composite of zeolite-A with polypyrrole, all the peaks mentioned above are present in the spectrum of composite material that confirms the formation of the composite.

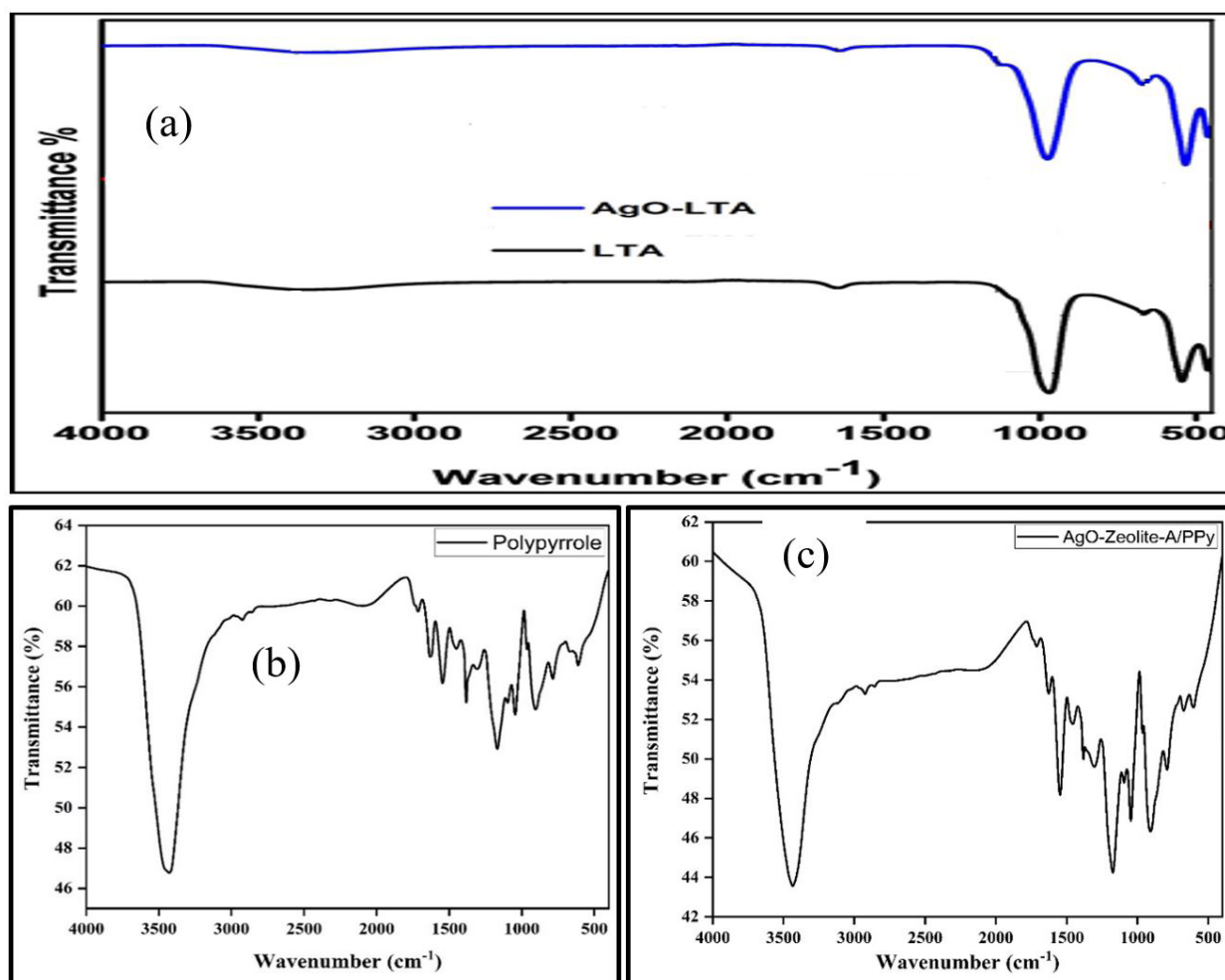


Figure 2: FTIR spectra of (a) pure zeolite A, modified zeolite and (b) PPy, and (c) composite

SEM-EDX Analysis

The morphological properties and elemental composition of the synthesized samples were determined by SEM and EDX techniques. Figure 3(a) shows the SEM and EDX of sample zeolite -A. From the SEM micrograph zeolite- A has a cuboid shape with excellent crystal edges. The formation of such a shape is due to the high dielectric constant and high polarity of water used as the reaction medium. EDX shows all the elements used are all in the stoichiometric ratio that results in the formation of

zeolite -A. Figure 3(b) represents the modified form of zeolite-A having the same shape. Figure 3(c) represents the conducting polypyrrole having a cauliflower-like structure with identical shape and size. EDX shows that carbon, nitrogen, oxygen, and sulfur are in atomic percentage, shows the formation of polypyrrole. Figure 3(d) shows the micrograph of the zeolite-A/polypyrrole composite. In the composite, both the polypyrrole and Zeolite-A are present, shows the cuboid as well as cauliflower-like structures that confirm the formation of the composite.

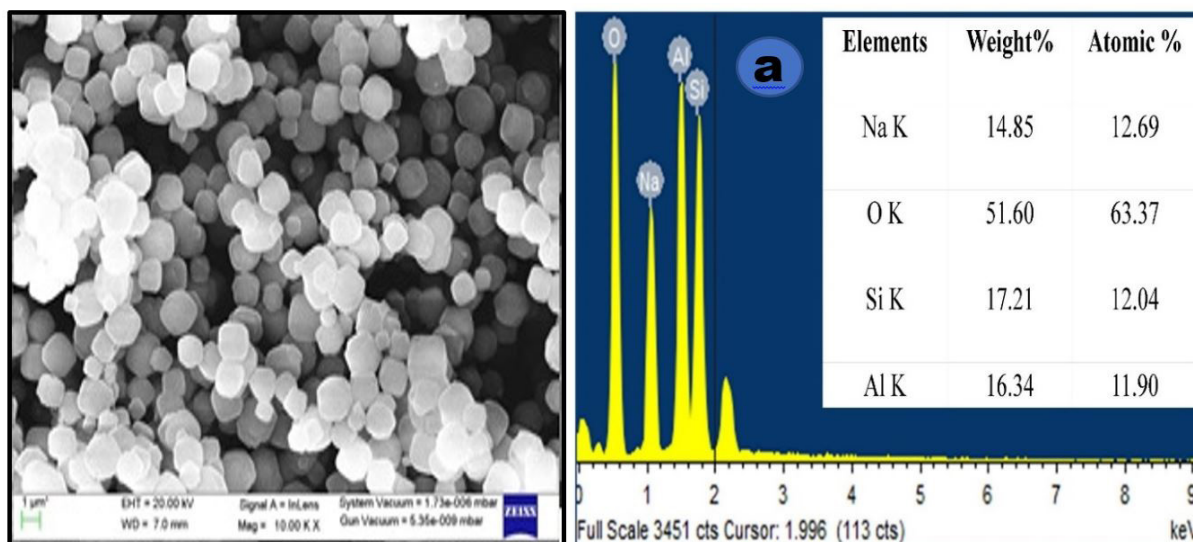


Figure 3(a): SEM and EDX analysis of Zeolite-LTA

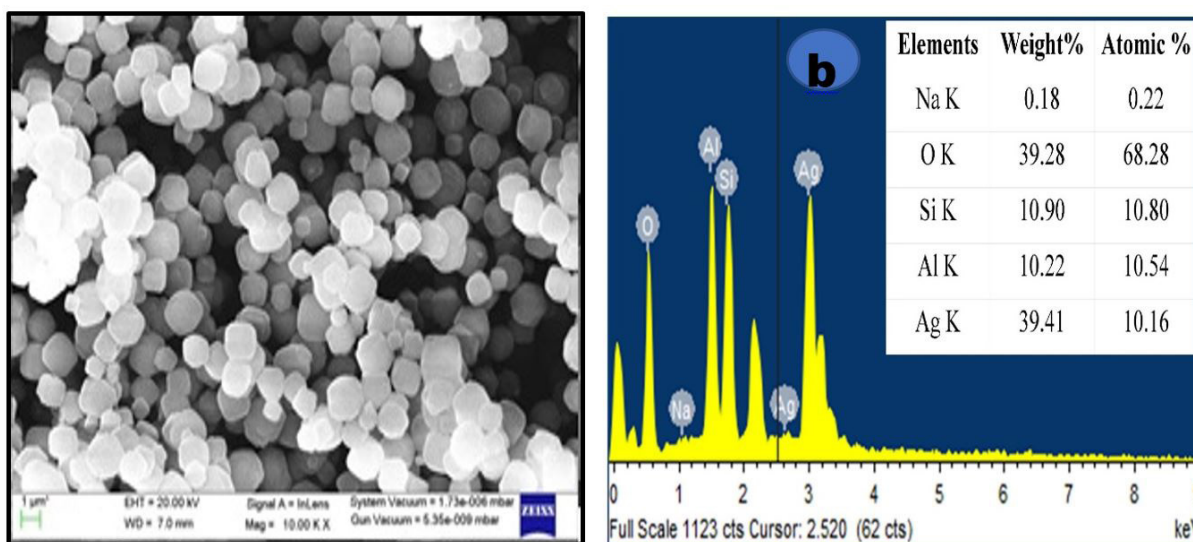


Figure 3(b): SEM and EDX analysis of AgO-Zeolite-LTA

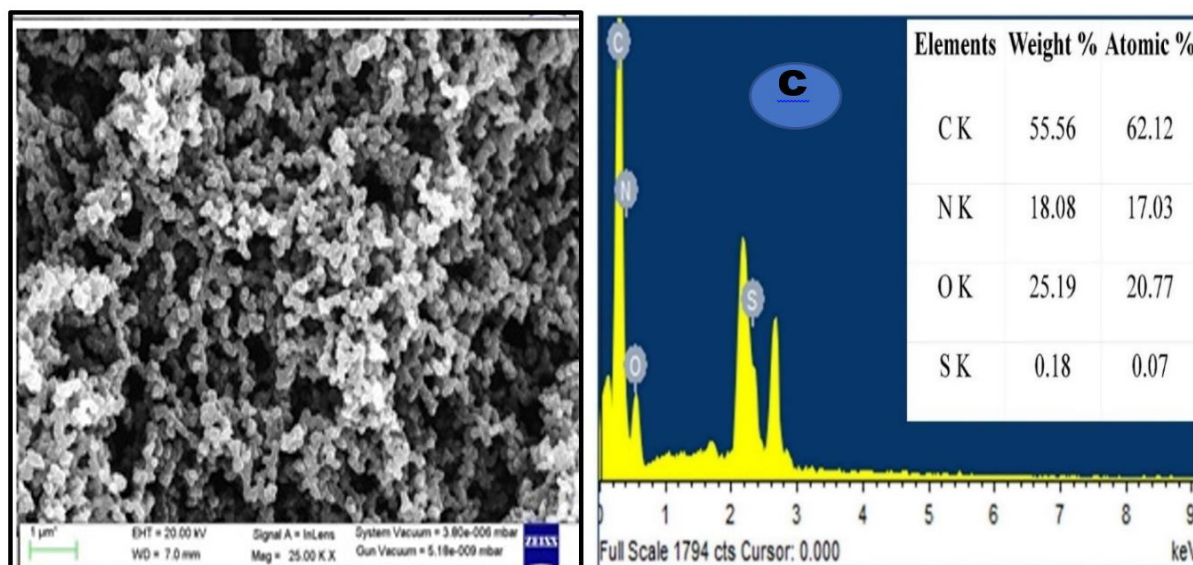


Figure 3(c): SEM and EDX analysis of PPY

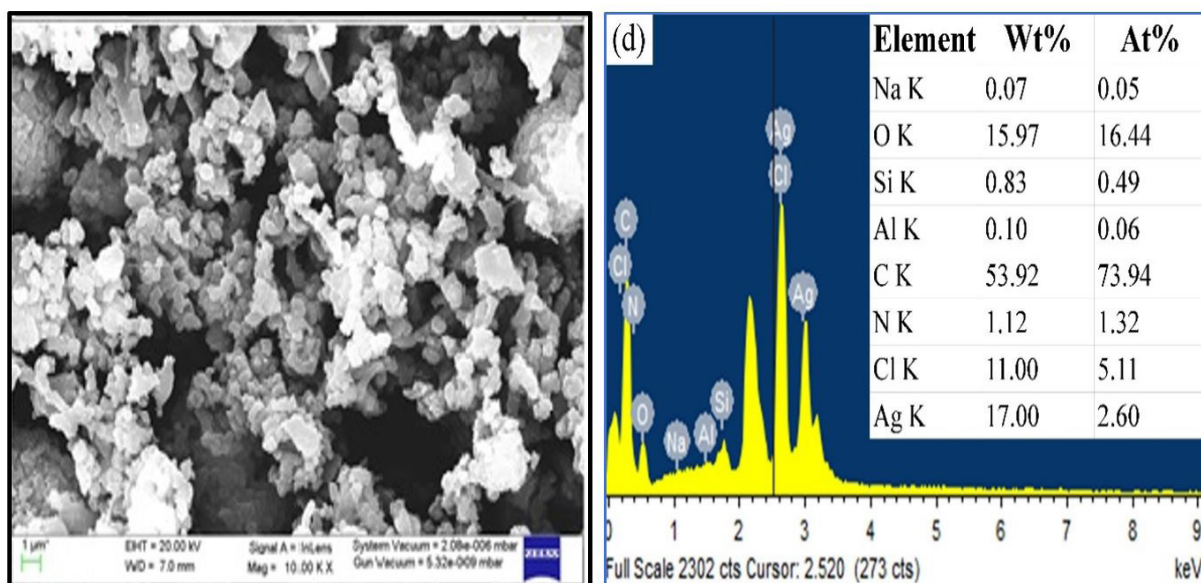


Figure 3(d): SEM and EDX analysis of PPy/Zelite

Gas sensing Analysis

Gas sensing setup and measurement

The synthesized material was taken for gas sensing study in a homemade glass chamber of volume 1 Litre as shown in Figure 4. The sensing material was drop casted between the two copper electrodes and was connected to a multimeter. The change in the resistance of the sensing material occur when the ammonia gas was introduced and the resistance was recorded on the digital multimeter (PHILIPS DM-441B) as shown in Figure 4. Different concentration of DMMP vapor gas was introduced into the gas chamber time by time and after every exposure of DMMP gas, recovery of the sensing material was carried out by passing nitrogen with a temperature of 320-350°C into the chamber. The required concentration of DMMP vapor gas was calculated by using the following equation [19].

$$C = \frac{22.4pTV}{273MV} \times 1000 \quad (2)$$

where C (ppm) is the desired target gas concentration, q is (g ml⁻¹) the density of the liquid (gas), V' is the volume of the liquid (gas), T is the temperature in Kelvin, M is the molecular weight of the liquid (g mol⁻¹) and V is the volume of the chamber (L). The sensing response by the sensor was calculated by using the below equation [20].

$$R\% = \frac{R_{\text{gas}} - R_{\text{air}}}{R_{\text{air}}} \times 100 \quad (3)$$

Where R_{gas} is the resistance of the gas in the chamber and R_{air} is the resistance of the gas in the atmosphere.

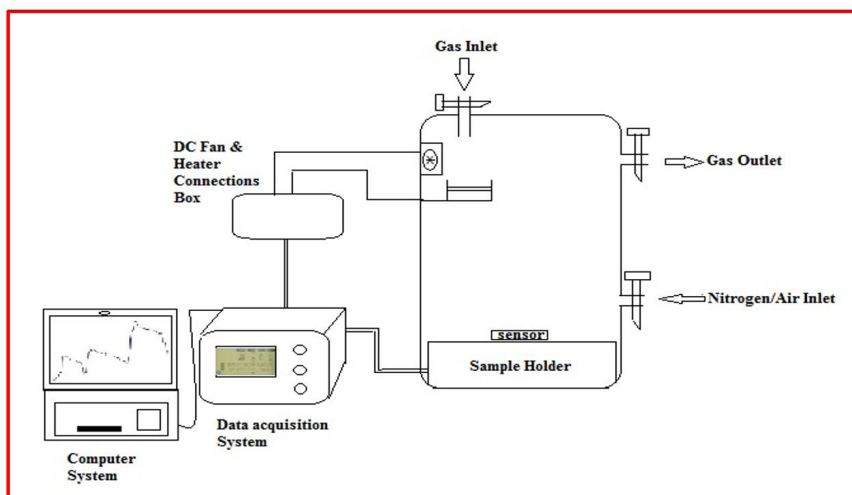


Figure 4: Gas sensing setup

Mechanism of the Gas sensing

The mechanism of the gas sensing can be explained by the electronic structure of the composite Ag-LTL/PPy. Polypyrrole has p-type semiconductor properties and the majority of charge carriers are holes. The basic structural properties of Polypyrrole having a positive charge on holes can interact readily with DMMP gas. As the PPy reacts with (DMMP) through the electronic interactions, there occurs decrease in charge carrier density and hence increase conductivity. Upon exposure to DMMP gas, the molecules of the DMMP gas are physically bound with the PPy polymer chain Figure 5 and 6.

On increasing the concentration of DMMP vapor gas, the sensing response of the sensor increases due to the higher

charge carrier density provided by the gas to the sensing material as well as the oxidation nature of the DMMP gas capable of donating electrons. Thus, when the material remains physically bound with DMMP gas, the resistance of the sensing material increases. After heating the material with nitrogen gas exposure at a temperature of 320-350 °C, decreases the resistance of the PPy. The mechanism of the gas sensor can determine the sensitivity of the different concentrations of gas sensor to various detectable signals like resistance. The operating principle of the present sensor is based on the change in resistance caused by the reaction between the gas molecule and the surface of the sensing material. In this process, the sensor was first introduced into the air, then this oxygen is adsorbed on the surface of the material, and free electrons surround the surface of the synthetic material to form O_2 , O_2^- , O_2^{2-} and other oxygen ions. The reactions are as follows:

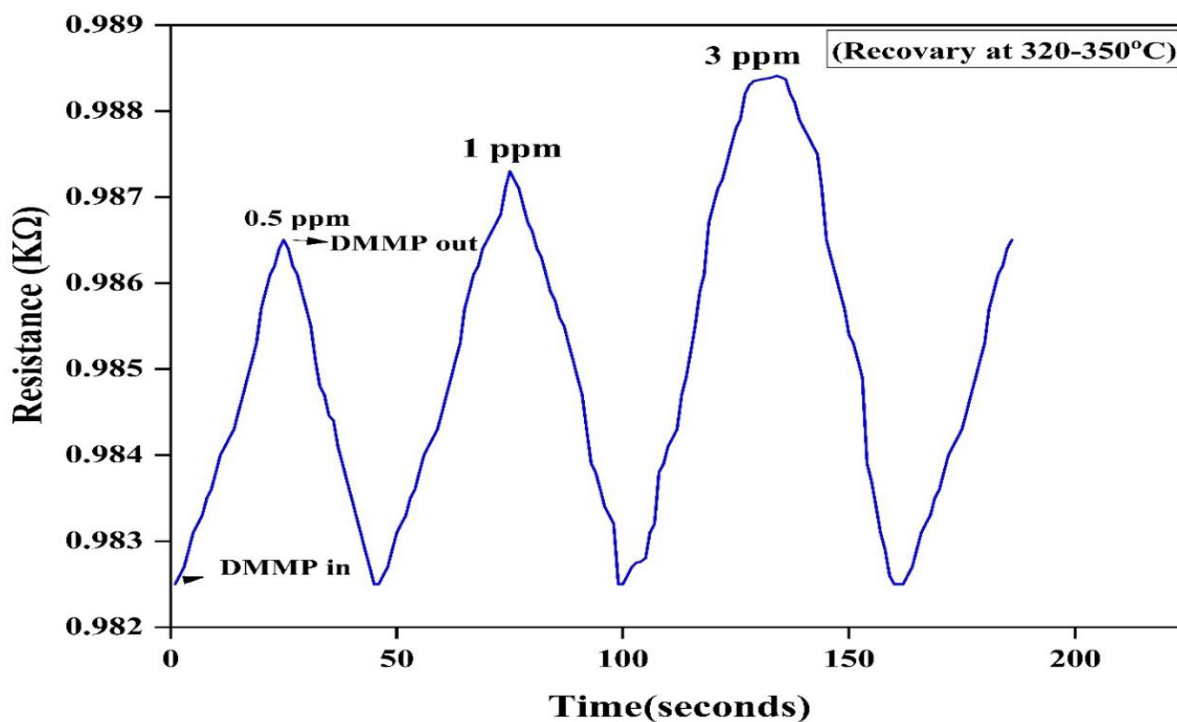
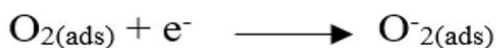


Figure 5: Graph between Resistance Vs Time

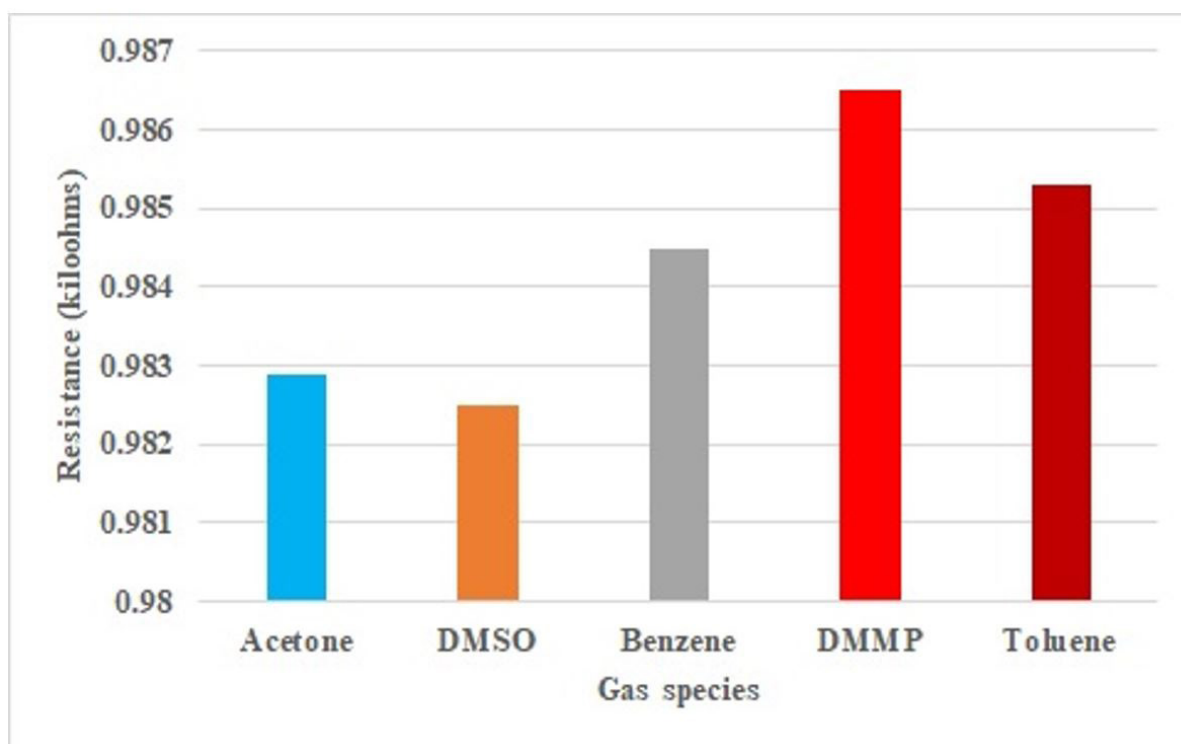


Figure 6: Selectivity

Conclusion

This study focuses on successfully synthesizing zeolite-A nanoparticles by using a hydrothermal method and such zeolite-A nanoparticles are modified by the ion-exchange method. The preparation of the composite was done by using the chemical oxidative polymerization method. These synthesized materials were characterized by XRD, FTIR and SEM with EDX. XRD and FTIR show the formation of zeolite-A, Polypyrrole and composite material. XRD confirms that all the synthesized materials have crystalline nature. SEM micrograph shows that zeolite-A has a cuboid shape and polypyrrole has cauliflower-like structures. SEM of composite material has both the cuboid and cauliflower-like structures that confirms the formation of the zeolite-A/polypyrrole composite. EDX analysis confirms that all elements present in zeolite-A, modified zeolite-A and composite are in stoichiometric ratio. A thick film of AgO-zeolite-A/polypyrrole composite sensor was fabricated on the PCB substrate by the drop-casting method. Studies of the gas sensor have

shown that the sensor exhibits a fast response of 63 seconds and a recovery time of 102 seconds. The sensitivity of the sensor was determined to be 14%. The composite sensor shows good sensing property towards DMMP toxic vapors. The AgO-Zeolite-A/PPy-based Sensor can be used in various concentrations with increasing response time. Sensor reproducibility has been tested for approximately one month, and the results show good outcomes. The sensor also offers excellent reproducibility and extensive stability. This outstanding sensing performance indicates that Zeolite with silver ions encapsulated polypyrrole is a promising candidate for making real-life good in the future.

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