

Solution Route Synthesis of PANI-ZnO Thin Films for Enhanced Gas Sensing

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ABSTRACT: The development of conducting polymer–metal oxide nanocomposites has emerged as an effective strategy for improving the performance of gas sensing materials. In this study, a polyaniline–zinc oxide (PANI–ZnO) nanocomposite was successfully synthesized using the solution route technique, and a thin film was simultaneously deposited onto a glass substrate during in situ polymerization. The synthesized nanocomposite was characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), ultraviolet–visible spectroscopy (UV–Vis), and scanning electron microscopy (SEM) to study its structural, optical, and morphological properties. XRD results confirmed the incorporation of ZnO nanoparticles within the PANI matrix, with particle size of 21.58 nm. FTIR spectra displayed characteristic vibrational bands of both PANI and ZnO confirm the presence of ZnO particle in PANI matrix, while UV-Visible spectroscopy showed absorption bands at 231 and 232 nm associated with the benzenoid and quinoid structures of PANI influenced by ZnO. SEM analysis revealed a uniform distribution of ZnO nanoparticles and a compact granular surface morphology, confirming the successful formation of the nanocomposite. The synthesized thin film then exposed to NH₃ gas with 100 ppm and recorded the response and recovery time.

KEYWORDS: PANI, ZnO, Nanocomposite, Solution route synthesis, Thin film

I. INTRODUCTION

The monitoring and detection of hazardous gases have become increasingly important due to growing environmental pollution, industrialization, and public health concerns [1]. Toxic and flammable gases such as ammonia (NH₃), nitrogen dioxide (NO₂), carbon monoxide (CO), Carbon Dioxide (CO₂) volatile organic compounds (VOCs) pose significant risks to both human health and the environment, even at low concentrations [2]. Therefore, the development of sensitive, selective, and energy-efficient gas sensors is essential for ensuring safety in industrial processes, environmental monitoring, and domestic applications [3].

Despite continuous advancements, conventional gas sensors often face several limitations, including high operating temperatures, poor selectivity, slow response/recovery times, and limited long-term stability. Metal oxide–based sensors, although widely investigated, generally require elevated temperatures (200–400 °C) to achieve sufficient sensitivity [4]. This results in increased power consumption and reduced device lifespan, making them less suitable for portable or low-power applications. Furthermore, many metal oxides show cross-sensitivity to multiple gases, which complicates accurate detection. These challenges highlight the need for new sensing materials that can operate effectively at lower temperatures while maintaining high sensitivity and selectivity [5].

Among metal oxides, zinc oxide (ZnO) has attracted significant attention due to its wide band gap in the range of 3.37 eV, large surface-to-volume ratio, and high chemical stability. ZnO exhibits excellent electron mobility and surface reactivity, making it a promising n-type semiconductor for gas sensing [6]. However, pure ZnO-based sensors typically suffer from poor selectivity and high temperature requirements. To overcome these drawbacks, researchers have explored hybrid structures that integrate ZnO with conducting polymers, enabling the combination of semiconducting and conducting characteristics in a single material system [7].

Polyaniline (PANI), a well-known p-type conducting polymer, offers several advantages such as environmental stability, reversible redox behaviour, and tunable electrical conductivity through protonic doping [8]. It has the additional benefit of functioning efficiently at or near room temperature. When PANI is combined with ZnO, a p–n heterojunction is formed at the interface, facilitating enhanced charge transfer and creating additional active sites for gas adsorption. This synergistic interaction can significantly improve the sensor's performance by lowering its operating temperature, enhancing sensitivity, and improving selectivity toward specific gases [9].

In the present work, a PANI–ZnO nanocomposite was synthesized using a simple and cost-effective chemical method [10]. The synthesis aimed to achieve a uniform distribution of ZnO nanoparticles within the PANI matrix to ensure strong interfacial contact and optimal electron transport. The synthesized samples will be characterized using FTIR, UV–Vis spectroscopy, XRD, and SEM to investigate their structural, optical, and morphological properties.

Although the current study focuses primarily on synthesis and characterization, future work will explore the gas sensing performance of the PANI–ZnO composite for target gases such as ammonia (NH_3), ethanol, and nitrogen dioxide (NO_2). Key parameters including sensitivity, selectivity, response/recovery time, and stability will be evaluated to establish its potential as a high-performance sensing material. The findings are expected to contribute to the ongoing development of low-cost, room-temperature gas sensors suitable for real-world environmental and industrial monitoring applications.

II. MATERIALS AND METHODS

A. MATERIALS: Aniline (99.99%), Ammonium persulphate (APS) (99.99%), ZnO (powder form), HCl (dil.)

B. SYNTHESIS OF PANI/ZnO NANOCOMPOSITES:

PANI/ZnO nanocomposite synthesised by using in situ oxidative polymerization of aniline, in the presence of ZnO nanoparticle using ammonium persulfate as an oxidizing agent in an acidic medium. To prepare the PANI/ZnO nanocomposite, 0.3 M of aniline add into 100 ml of 2 M HCl aqueous solutions, were vigorously stirred on a magnetic stirrer at room temperature for 30 minutes called as beaker 1. Then, in another beaker make a solution of, 0.3 M of Ammonium persulphate (APS) in 100 ml of double distilled water with 0.4 M ZnO powder with constant stirring of 30 min. Add beaker 2 solution in beaker 1 using burette dropwise with constant stirring for 2 hours and polymerization process is taking place. While adding solution from beaker 2, the colour of the solution turned blue and after 40-50 minutes it becomes green, which indicates a good degree of polymerization. Stirring was further continued for 1 h. Then, the final solution kept for overnight and after 12 hours it was filtered and precipitated was kept in vacuum oven for 24 hours for drying. The obtained product was crushed using mortar pestle to get fine powder for further characterization. This product was labelled as PANI/ZnO (0.3 M/0.4 M).

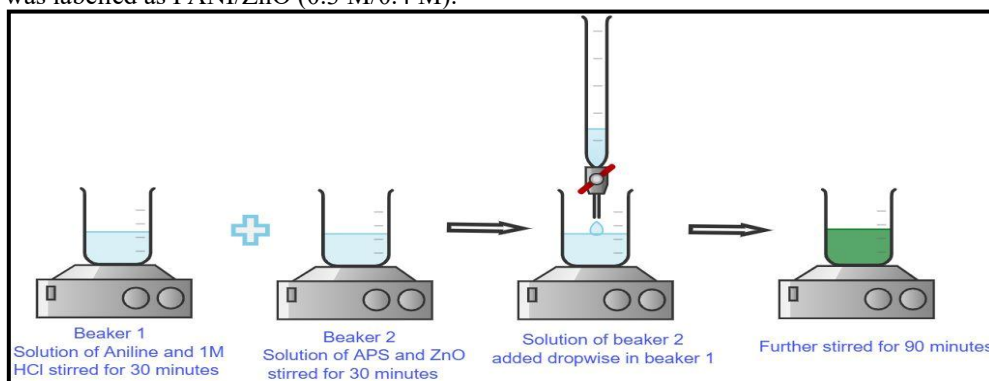


Figure 1: Synthesis of Nanocomposites

III. RESULTS AND DISCUSSION

A. X-RAY DIFFRACTION (XRD):

The X-ray diffraction (XRD) analysis of the nanocomposite was conducted using a Rigaku Mini Flex 600 diffractometer. The PANI/ZnO nanocomposite exhibited distinct characteristics in its XRD pattern. Five prominent peaks were identified at angles of 16.42° , 21.29° , 23.55° , 24.97° , and 42.05° , for nanocomposite as illustrated in Figure 2. A comparison of these peaks with the standard (h k l) planes from PDF Card No.: 2225234 reveals a strong correlation between the observed and standard values [11]. The particle size of the nanocomposite was determined using the Debye-Scherrer formula, yielding a size of 21.58 nm, confirming the presence of nanosized ZnO particles within the PANI matrix from the PANI/ZnO nanocomposites of (0.3M+0.6M) concentration as shown in figure 2.

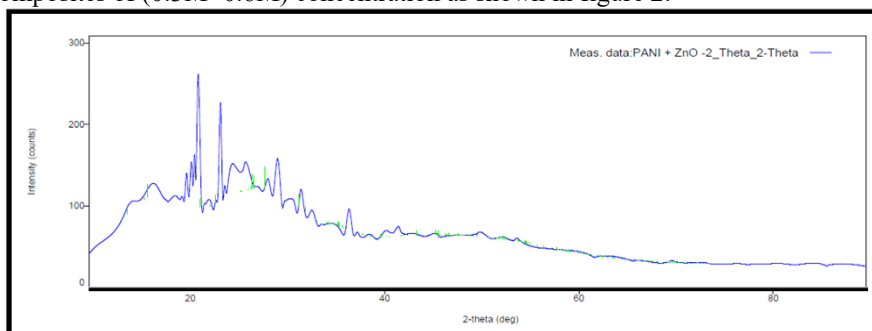


Figure 2. XRD pattern for PANI/ZnO nanocomposite

B. SCANNING ELECTRON MICROSCOPY (SEM):

SEM images shows that PANI/ZnO nanocomposites flaky shaped structures, and the size of the flakes reduced with increasing percentage of ZnO. As the molar concentration of ZnO increases the size of PANI decreases due to agglomeration, and size of PANI particles has decreased. According to Mostafaei and Zolriasatein et al, differences in PANI and PANI/ZnO size were caused by PANI agglomeration in the presence of ZnO. Increasing the amount of ZnO can reduce PANI size. This agglomeration is caused by hydrogen bonds that occur due to the interaction between ZnO and N-H groups or coordination bonds. The SEM image helped us to concluded that the increasing of ZnO percentage has a big effect on the morphology of PANI as surface to volume ratio is increased.

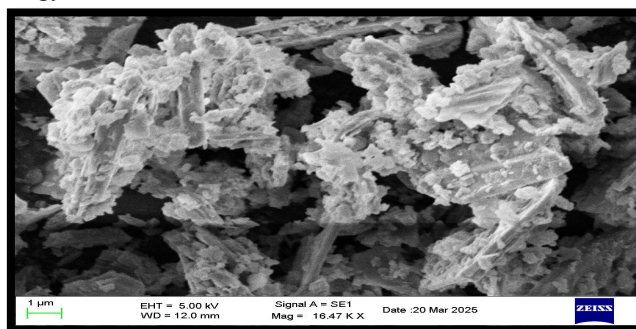


Figure 3. SEM Image of PANI/ZnO nanocomposite

C. FOURIER-TRANSFORM INFRARED SPECTROSCOPY (FTIR):

The FTIR spectra of the PANI/ZnO composite as shown in figure 4. The observed peaks at wave numbers 1625.1, 1530.58, 1187.24, 841, 675.11, 612.43, 517.91, and 405.07 cm^{-1} highlight the key characteristics of PANI [12]. The peaks at 1625.1 and 1530.58 cm^{-1} are attributed to the stretching modes of C=N and C=C in the quinoid and benzenoid rings, respectively. The peak at 1187.24 cm^{-1} is linked to C-N stretching, while the peak at 841 cm^{-1} is identified as N-Q-N stretching [13]. Furthermore, the low-frequency bands between 456, 512.91 and 675, 862 cm^{-1} are associated with Zn-O-Zn and Zn-O stretching modes, thereby confirming the incorporation of zinc oxide in the PANI matrix.

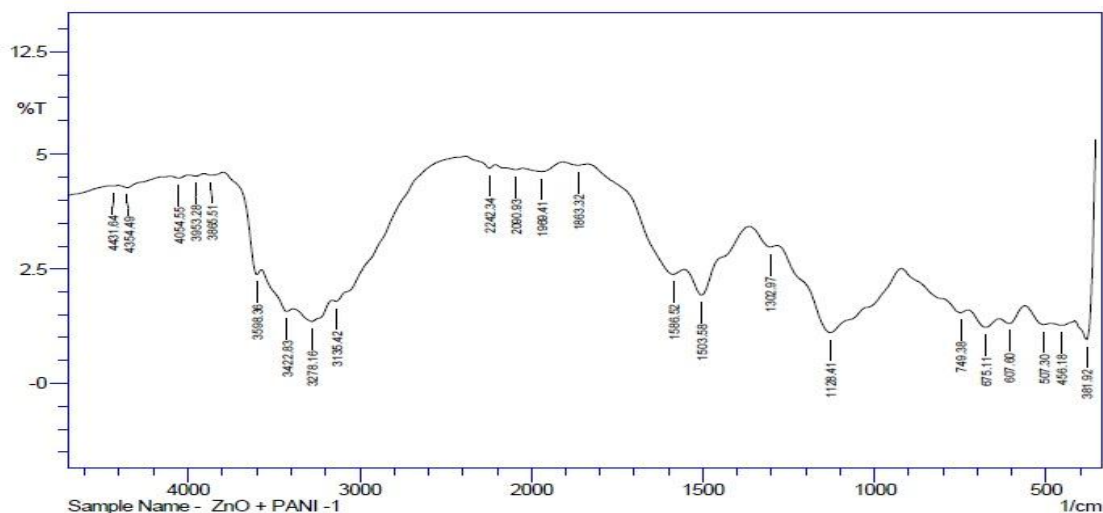


Figure 4. FTIR for PANI/ZnO nanocomposite

D. ULTRAVIOLET-VISIBLE (UV-VIS) SPECTROSCOPY:

The UV-visible spectra of PANI/ZnO nanocomposites is shown in Figure 5. PANI shows three absorption bands at 350nm, 450 nm and around 800 nm wavelengths. As reported previously by some researchers doped forms of PANI usually show three characteristic absorption bands at 320-360, 400-450 and 700-850 nm [13]. The absorption band of ZnO lies between 200- 400 nm of visible light. The peaks observed at 231 nm and 232 nm indicated that interaction of ZnO with PANI which overlaps with the absorption band of PANI at the same wavelength value for ZnO/PANI composites. From the figure of ZnO /PANI composites, the absorption bands of PANI/ZnO nanocomposites showed

blue shift which shows decrease in conjugation because of interaction between PANI and ZnO. Aniline in PANI will donate free electron pairs to ZnO and form a complex compound. This will form a polymeric ionization chain and produce an efficient electron exchange effect [14].

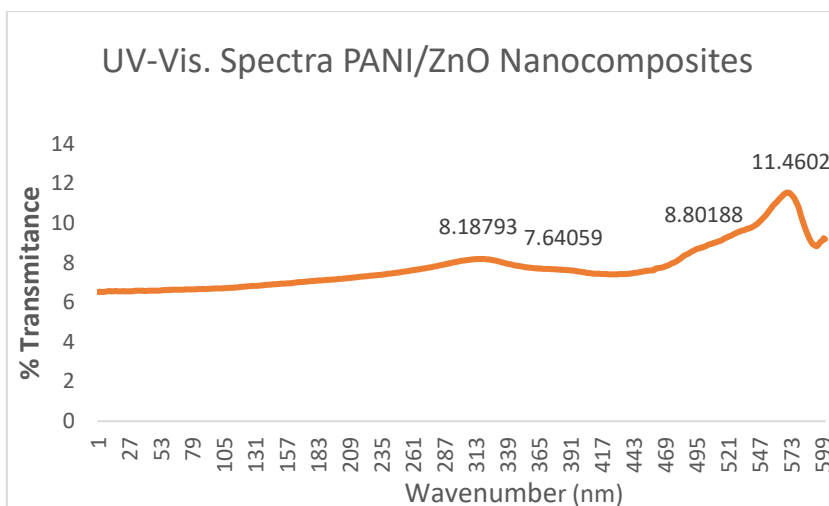


Figure 5. UV-Vis. Spectra for PANI/ZnO nanocomposite

E. GAS SENSING CHARACTERIZATION:

The synthesized PANI-ZnO (0.3M+0.6M) nanocomposite sensor films were explored to different concentrations (20-100 ppm) of NH_3 and recorded their response and recovery time as shown in graph. It was observed that resistance of thin film increase after exposure to NH_3 may be because of porous structure of PANI- ZnO films leads to the predominance of surface phenomena over bulk material phenomena. It has also indicated that surface to volume ratio of nanocomposites thin was increased.

It is observed that due to porous structure as shown in SEM images the response value increase rapidly with increasing concentration of NH_3 but it slows down at higher concentration. The response value could be increases due to availability of large number of porous space but for higher concentration it gets packed and porous space is not available in large number. It is observed that the response time and recovery time varies inversely with respect to concentration of NH_3 . The response time is recorded as to approx. 92 s and it would be decreased up to 56 sec while recovery time is up to 175 sec. and increases from 203 to 415 s with increasing NH_3 concentration from 20 to 100 ppm.

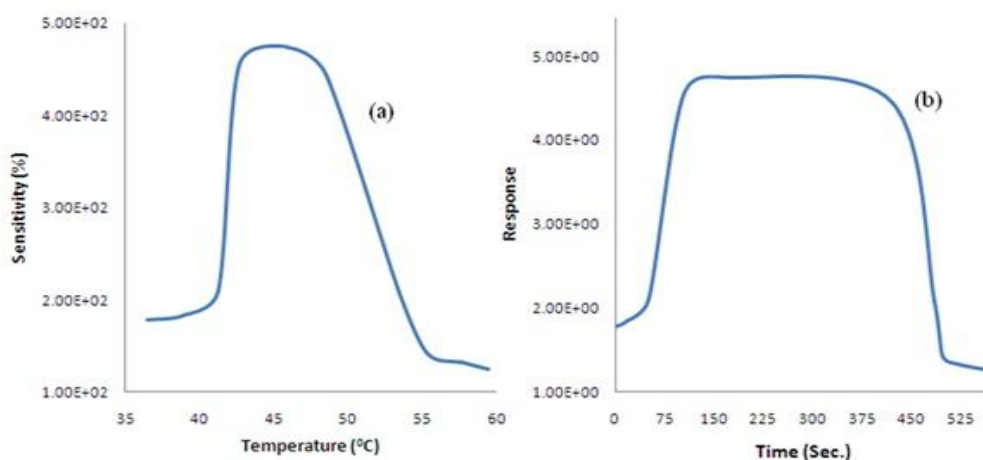


Figure 6: Sensitivity and Response Time Graph

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