Synthesis and Characterization of Polyvinyl Alcohol-Based NiO Nanocomposites for Enhanced Sensing Properties

Carlos Rivera [1] & Lucia Hernandez [2]
***[1] Assistant Professor of Physics, University of Barcelona, Barcelona, Spain**
***[2] Assistant Professor of Physics, University of Madrid, Madrid, Spain**

ABSTRACT

Sensor Studies of polyvinyl alcohol (PVA)/NiO nanocomposite films have been studied in the present work.NiO nanoparticles have been synthesized using Low Solution Combustion method. The composites were prepared by solution-casting technique. The prepared PVA/NiO composites have been characterized by X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR), which confirmed the presence of NiO in polyvinyl alcohol and the formation of the composites. It is observed that the PVA/1% NiO nanocomposite sensor shows the highest response of 9.60% towards NO2.

Keywords: *Polyvinyl alcohol, Nano nickel oxide, X-ray diffraction, Sensors..*

I. INTRODUCTION

Polyvinyl alcohol is a polyhydroxy polymer generally obtained by the hydrolysis of poly (vinyl acetate). PVA has a carbon chain backbone with hydroxyl groups attached to methane carbons; these groups can be a source of hydrogen bonding and hence assist the formation of polymer composite [1]. The hydroxyl groups of PVA have a strong affinity for water, but strong hydrogen bonding between the intramolecular and intermolecular hydroxyl groups greatly inhibits its solubility in water [2]. PVA has different internal structure which may be amorphous or semicrystalline. The semicrystalline structure of PVA showed an important feature rather than of amorphous one. This may be because semicrystalline PVA leads to formation of both crystalline and amorphous regions [3]. Nickel oxide (NiO) is a transition metal oxide and a metal deficient p-type semiconductor [4] that crystallizes in a rock salt structure and has a wide energy band gap in the range from 3.6 to 4.0 eV [5]. It usually exhibit p-type conductivity due to holes generated by Ni vacancies in the lattice and therefore NiO is an interesting candidate for materials research. It has a wide range of applications due to its good chemical stability as well as for its excellent optical and electrical properties [6]. They have been used as catalysts [7], electrochromic display devices [8], fuel cells [9], gas sensors [10]. In the present work, attempts have been made to synthesize the nano nickel oxide particles by low solution heat combustion method and PVA/NiO nanocomposites by solution casting method.These polymer nanocomposites have been characterizedby using various techniques such as X ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy(FTIR). Room temperature gas sensing studies were carried out for NO_2 .

II. EXPERIMENTAL

Materials

Polyvinyl alcohol of analytical grade was obtained in the powder form from Nice Chemicals Pvt. Ltd. Cochin, with the average molecular weight of 125,000. Nickel nitrate [$Ni(NO_3)_2\,6H_2O$] is purchased from S.D. Fine-Chem. Ltd. Mumbai.

Synthesis of Nano nickel Oxide (NiO)

For the preparation of nano nickel oxide, Low Solution combustion (LSC) technique is employed . In this method of preparation, hydrated nickel nitrate [$Ni(NO_3)_2\,6H_2O$] is used as the metal precursor. The stiochiometric ratio of nickel nitrate and fuel were taken into the cylindrical Petri dish of ~300 ml and well dissolved in double distilled water. Then the resulting mixture is placed into a pre-heated muffle furnace maintained at (400 ±10) °C. The combustion is self-propagating and within a few minutes the reaction is completed and fluffy powder is obtained. After completion of the process, the product obtained is grinded well using mortar and pestle.

Synthesis of PVA/NiO nanocomposite films

The PVA/NiO nanocomposite films were prepared by solution casting technique. Powdered PVA of about 2.5g is dissolved in 50 ml of double distilled water by stirring thereby forming PVA stock solution. To this solution 1 wt%, 2 wt%, 3 wt% and 4 wt% of nano nickel oxide powder is mixed. This solution is then warmed up to 333 K and thoroughly stirred using a magnetic stirrer. By removing the trapped air bubbles, the solution is poured onto a leveled clean glass plate and left to dry at room temperature for about 48 hr. The dried films were peeled off from the glass plate and cut into suitable pieces for measurements.

III. RESULTS AND DISCUSSION

X–Ray diffraction

In order to investigate the nature of the polymer composite films, X-ray diffraction studies were carried out using Philips X-ray diffractometer with Cu-Kα radiation. The XRD patterns of nano NiO, pure PVA and PVA/NiO nanocomposite films are shown in Figure1. In the XRD pattern, different lines are attributed to the (111), (200), (220), (311), (222), (400), (331) and (420) planes are in good agreement with the data of NiO powder file (JCPDS number 47-1049) which corresponds to the cubic crystalline structure with lattice constants a=b=c=4.1771 Å [11]. By comparing the XRD pattern of the composite and NiO, it is confirmed that NiO has retained its structure even though it is dispersed in PVA during polymerization reaction.

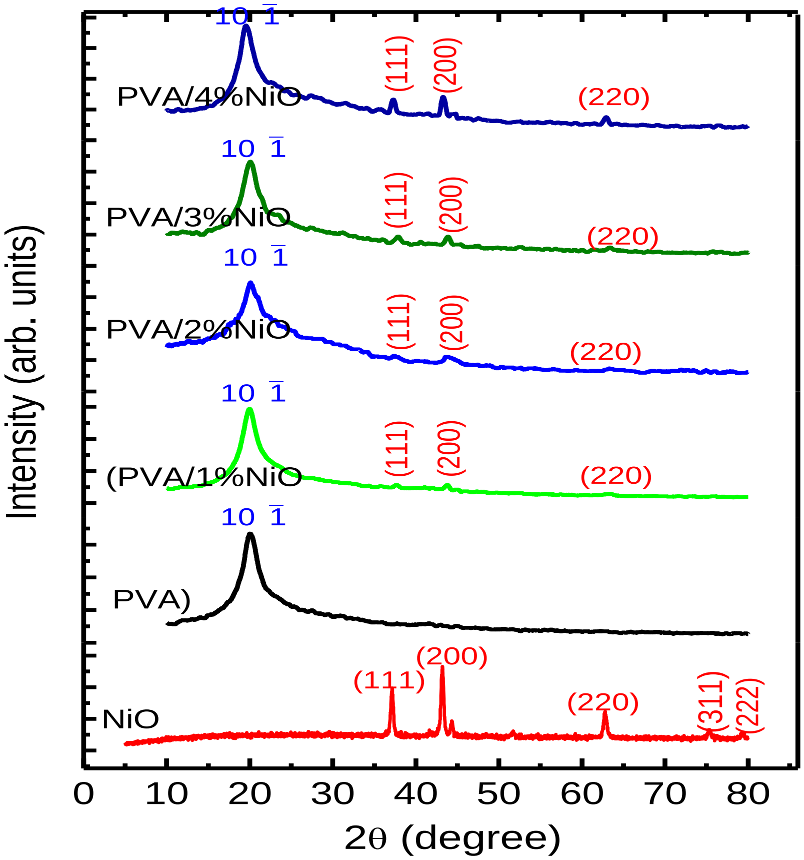

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Figure 1: XRD pattern of pure NiO, pure PVA and PVA/NiO nanocomposite films

FTIR Spectra

The chemical structural analysis of PVA/NiO nanocomposites were carried out using Fourier Transform Infrared (FTIR) spectroscopy (Model: Perkin Elmer 1600) over the wave number range of 400–4000 cm−1 in KBr medium. The FTIR spectra of the PVA, PVA-NiO nanocomposites are shown in Figure 2.

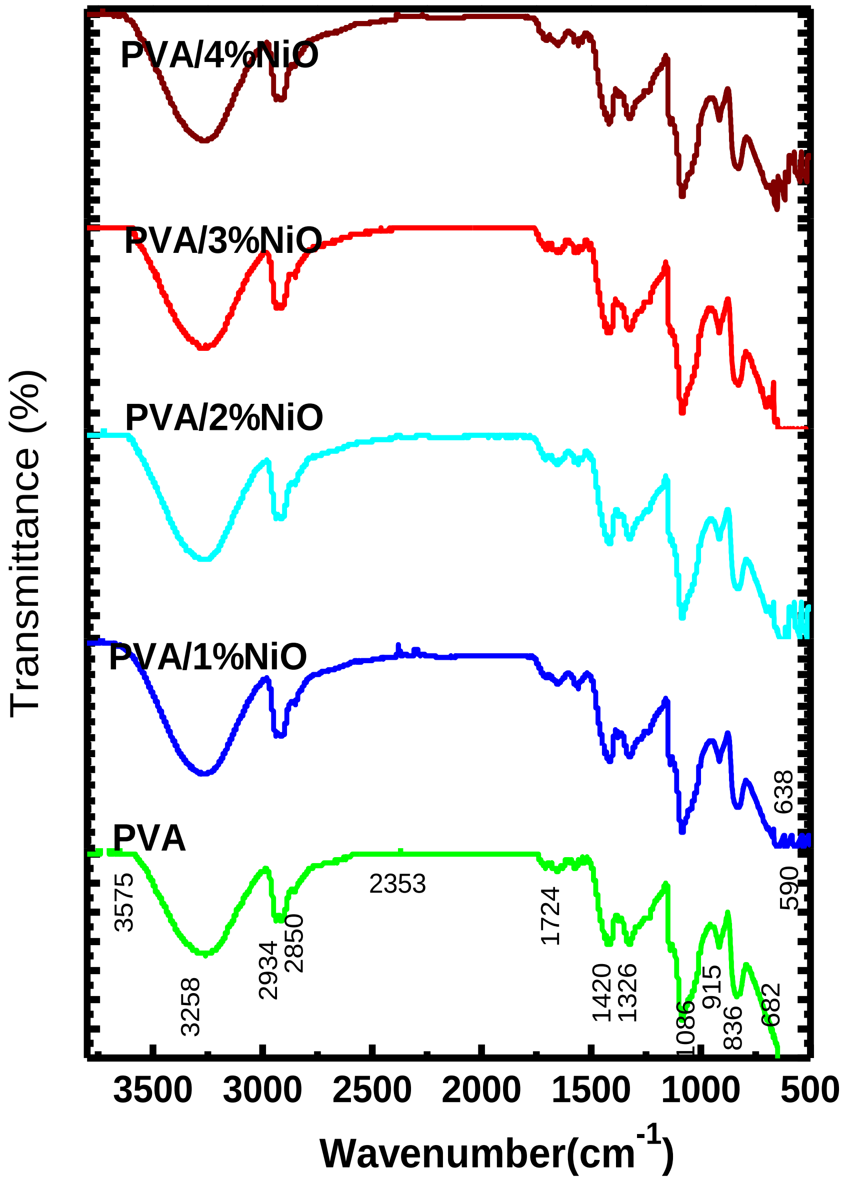

Figure 2: FTIR spectra of PVA and PVA/NiO nanocomposite films

It is interesting to note that the main absorption bands are affected by the presence of NiO in pure PVA. This change is due to loss in conjugation and molecular order after modification of PVA with NiO. Since the frequency of a vibration is directly proportional to force constant of the bonds which indicates the shortening of N–C bonds suggesting localization of p-orbital electrons on N [12]. However the shift of NiO stretching band at 688cm^{-1} is observed in PVA/NiO hybrid nanocomposite films. The observed shift in stretching vibration of Ni–O is due to binding of organic compound to the NiO [13]. The result indicates strong interaction between PVA and NiO nanoparticles.

IV. SENSOR STUDIES

Room temperature gas sensing studies were carried out for NO_2.On interaction with reducing or oxidizing gases, adsorbed oxygen concentration and thereby conductivity changes. Resistance and dynamic gas response of pure PVA film to 100 ppm of NO_2 is shown in Figure 3.

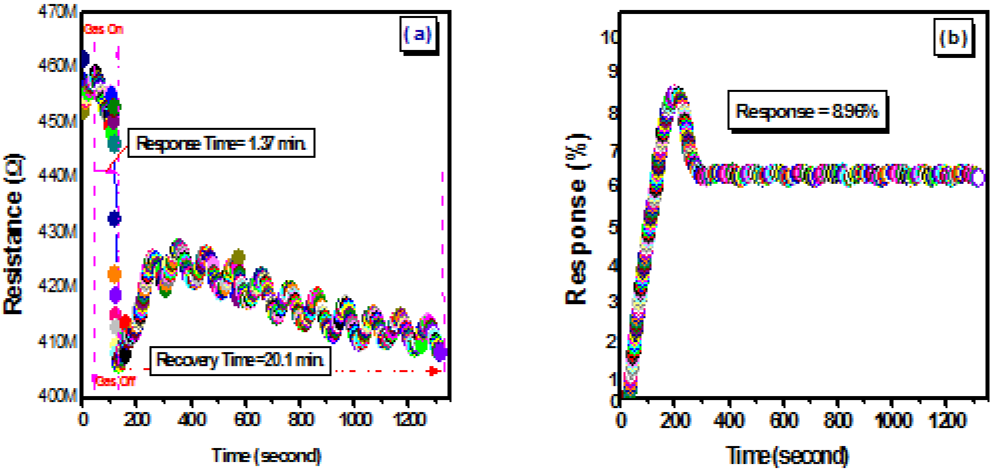

Figure 3: (a) Resistance and (b) Response of pure PVA film to 100 ppm of NO_2

When PVA film sensor is exposed to NO_2 gas, the gas will react with surface-adsorbed oxygen species, thus causing a change in the resistance of the film sensor. The dynamic gas response of PVA is found to be 8.96 %. Resistance of PVA/1% NiO and PVA/4% NiO nanocomposite films to 100 ppm of NO_2 are shown in Figure 4.

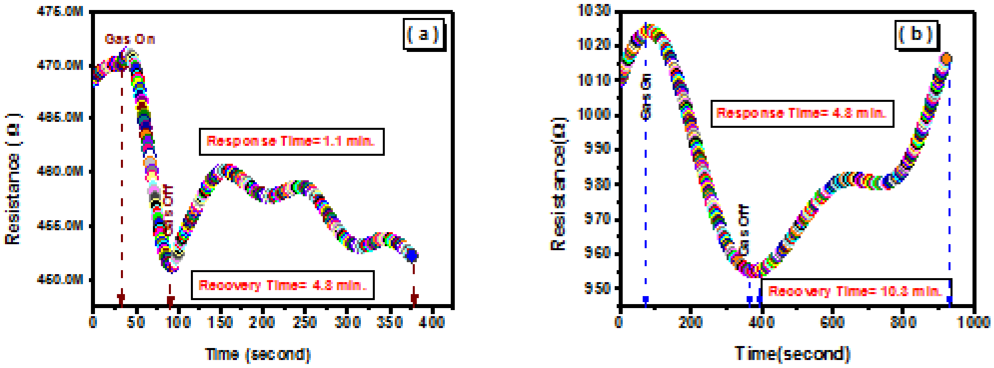

Figure 4: Resistance of (a) PVA/1% NiO and (b) PVA/4% NiO nanocomposite films 100 ppm of NO_2

The gas-sensing mechanism of NiO based sensors belongs to the surface controlled type and the resistance change is controlled by the species and amount of chemisorbed oxygen on the surface. At an operating temperature, in the absence of a target gas, oxygen gets adsorbed on the surface of the sensor and it extracts electrons from the conduction band of the sensor material. Thus, the equilibration of the chemisorption process results in stabilization of surface resistance. Any process that disturbs this equilibrium gives rise to change in the conductance of the semiconductors. The operation of a PVA/NiO nanocomposite sensor is based on dependence of the conductivity to O_2 molecules adsorbed on its surface. When the sensor is exposed to oxidizing gas NO_2, the adsorbed O_2 molecules react with the gas and release the captured electrons, resulting in a significantly decreased sensor resistance. Therefore, the sensor response is remarkably improved as shown in Figure 4 (a) for PVA/1% NiO nanocomposite. Furthermore, the porous structure of NiO may also contribute to the improved sensor response. When the gas is released, for NiO, O_2 molecules capture electrons on the surface or at the grain boundaries resulting in the increase of resistance. Trapped electrons at the grain boundaries also produce potential barriers between grains that impede current flow.

The dynamic gas responses of PVA/1% NiO and PVA/4% NiO nanocomposite films to 100 ppm of NO_2 are shown in Figure 5 and it is found to be 9.6 % and 5.57 % respectively.

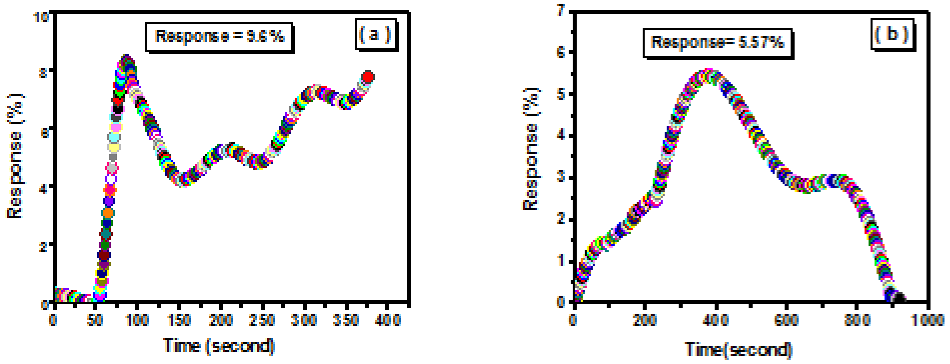

Figure 5 : Response of (a) PVA/1% NiO and (b) PVA/4% NiO nanocomposite films to100 ppm of NO_2

The response histogram of PVA, PVA/1% NiO and PVA/4% NiO nanocomposites to 100 ppm of NO_2 at room temperature is shown in Figure 6.

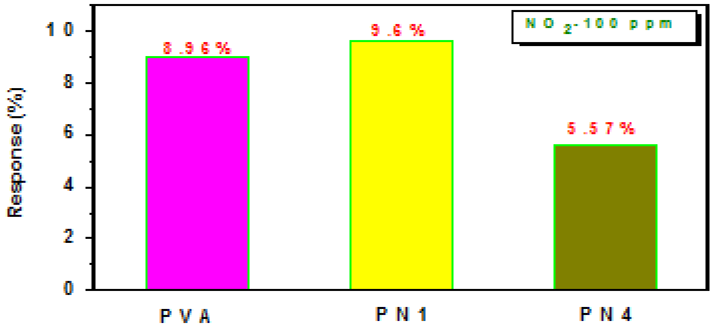

Figure 6: Response histogram of PVA, PVA/1% NiO and PVA/4% NiO nanocomposite films to 100 ppm of NO_2 at room temperature

It is observed that the PVA/1%NiO nanocomposite sensor shows the highest response of 9.60% towards NO_2. This increased response of PVA/1%NiO nanocomposite ascribed due to polyvinyl alcohol gets changed from reduced state to oxidized state due to addition of NiO *i.e.* PVA/1%NiO nanocomposite becomes resistive. It is well known that resistive films gives better response.

V. CONCLUSION

The XRD pattern of pure PVA shows a characteristic peak for an orthorhombic lattice centered at 20° indicating its semi-crystalline nature. The XRD pattern of the synthesized NiO nanoparticles shows good crystallinity. The XRD pattern of PVA/NiO nanocomposites confirmed that NiO has retained its structure even though it is dispersed in PVA. The FTIR spectrum of pure PVA exhibits a peak around 3290 cm^{-1} is due to –OH group in the polymer backbone and 1326 cm^{-1} is due to $–CH_2$ stretching. The FTIR spectrum of pure NiO reveals that the peaks at 1380cm^{-1} is due to C-H in plane bending modes and the peaks at 414cm^{-1} to 590cm^{-1} are assigned to nickel oxide groups. The shift of NiO stretching band at 688cm^{-1} is observed in PVA/NiO nanocomposite films which indicates strong interaction between PVA and NiO nanoparticles. The dynamic gas response of PVA for 100 ppm of NO_2 is found to be 8.96 %. The dynamic gas response of PVA/1%NiO and PVA/4%NiO nanocomposites for 100 ppm of NO_2 at room temperature is found to be 9.6 % and 5.57 % respectively.

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REFERENCES

1. *K A Abdelkader and Z Anwar: J. Appl. Polym. Sci. 2, 2006,1146..*
2. *E M Kim, M Han, Y J Lee and D Song: J. Appl. Polym.Sci. 106, 2007,3259.*
3. *I S Elashmawi and E M Abdelrazek: J. Appl. Polym. Sci. 115, 2010,2691.*
4. *H Sato, T Minami, S Takata and T Yamada: Thin Solid Films 236,1993,27.*
5. *B Sasi, K G Gopchandran, P K Manoj, P Koshy, P Prabhakara Rao and V Vaidyan : Vaccum, 68, 2003,149.*
6. *S Y Wang,W Wang,W Z Wang and Y W Du: Preparation and characterization of highly oriented NiO (200) films by a pulse ultrasonic spray pyrolysis method, Mater. Sci. Eng. B 90, 2002,PP.133–137.*
7. *A K Roslik, V N Konev and A M Maltsev: Oxidation of Metals 43, 1995,1.*
8. *K S Ahn, Y C Nah and Y E Sung: Applied Surface Science 199,2002,259.*
9. *X Chen, N J Wu, L Smith and A Ignatiev : Applied Physical Letters, 84, 2004,2700,*
10. *I Fasaki, A Giannoudakos, M Stamataki, M Kompitsas, E György, I N Mihailescu, F Roubani Kalantzopoulou, A Lagoyannis and Harissopulos : Applied Physics A 91,2008,487.*
11. *K Martin and G Mc Carthy : North Dakota State Univ. Fargo, ND, USA, ICDD GrantinAid,1991.*
12. *M A Chougule, S Sen and V B Patil: Facile and efficient route for preparation of Polypyrrole– ZnO nanocomposites: microstructural, optical, and charge transport properties, J. Appl. Polym. Sci. 125, 2012,pp.1418–1424.*
13. *A C Sonavane, A I Inamdar, D S Dalavi, H P Deshmukh and P S Patil: Simpleand rapid synthesis of NiO /PPy thin films with improved electrochromic performance, Electrochim. Acta. 55, 2010,pp.2344..*