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Studies on Structural, Morphological, Electrical and Gas Sensing Properties of the Polyaniline/Bismuth Oxide (PANI/Bi_2O_3) Composites.

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Abstract:

By adding bismuth oxide to the polymerization mixture of aniline hydrochloride and ammonium persulphate using chemical oxidation polymerization, conducting polyaniline/bismuth oxide (PANI/Bi_2O_3) composite was prepared. The effect of adding Bismuth oxide powder, during polymerization process, on the time and temperature of reaction has been studied. The structural and morphology of the composite were distinguished by X-ray diffraction pattern (XRD) and scanning electron microscope (SEM) micrographs. The dc electrical transport property of PANI/Bi_2O_3 composites has been investigated within temperature range 30-200^{0}C and ac electrical property of PANI/Bi_2O_3 composites has been studied as function of frequency. The gas-sensing performance of the PANI/Bi_2O_3 composites was studied at room temperature for Liquified Petroleum Gas (LPG). The change in resistance of the composites as function of time towards LPG was investigated.

Key words: Bismuth oxide, Polyaniline, Electrical properties, LPG.

Introduction:

Polymers were generally considered to be electrically non-conducting; however, the discovery of certain class of polymers called conjugated polymers with electrical conductivity comparable to that of metals opened a new field for the development of materials technology. The characteristic features of conducting polymers such as environmental and thermal stability, facile synthesis, electrochemical properties, bio-compatibility, significant electrical conductivity, reversibility, switching capability between conducting-oxidized and insulating-reduced state is the basis for various technological and commercial applications [1–3].

Metal-like conductivity is expected in an ideal conducting polymer with a highly organized p-conjugated structure. In order to produce these kinds of highly ordered structures, additional filler materials must be added in order to create a new class of materials known as conducting polymer composites. Conducting polymer composites are thought of as hybrid materials made up of distinct metal salts or organic and inorganic oxides combining in a unique way to provide interfacial mechanisms that change the composite's characteristics. A new area of study called "nanostructures of conducting polymers and their composites" has evolved to support the creation of new materials for usage in current and emerging technologies [4-9].

Polyaniline (PANI), a type of conductive polymer, was chosen as an interesting material for this study due to its versatile properties, making it one of the most promising candidates for applications such as corrosion resistance, rechargeable batteries, and sensors. . Electromagnetic shielding, light emitting diodes, solar cells, switches, etc .

Bismuth typically occurs as bismite (bismuth oxide [Bi_2O_3]), bismuthite (bismuth carbonate), and bismuthinite (bismuth sulfide). In medicine, bismuth is used as an antidiarrheal agent to treat vomiting, abdominal pain, and nausea. Bi_2O_3 exhibits significant polymorphism, including solid phases of α-Bi_2O_3, β-Bi_2O_3, γ-Bi_2O_3, δ-Bi_2O_3, and the recently characterized ε-Bi2O3. α-Bi_2O_3 is the thermodynamically most stable phase at room temperature and pressure [10]. Under standard reaction conditions in aqueous solution, α-Bi_2O_3, a poorly water-soluble species with surface hydroxyl groups, is formed. α-Bi_2O_3 is a basic oxide, and its Bi-O bonds are primarily ionic. This is a p-type semiconductor material [11]. Bi_2O_3 is a derivative of great technological importance and is used in the production of glass and ceramic products and as a catalyst in the oxidation of hydrocarbons. It is widely used in applications such as microelectronics, sensors, and optical technology [12-14].

2. Materials and Methods:

Aniline, hydrochloric acid (HCL) and ammonium persulfate of analytic grade are used for synthesis of polyaniline and manganese oxide was used to prepare composites via chemical oxidative polymerization method.

i. Preparation of Polyaniline (PANI) All the samples are prepared at room temperature (RT). Solution of aniline of about 0.2M was prepared and mixed with 1N of solution of hydrochloric acid at RT. The above aniline and HCL mixture was stirred for 3 hours using magnetic stirrer. Further the solution of ammonium persulfate of about 0.25M was prepared and added to above mixture drop wise using pipette. Then the mixture is stirred for 8 hours at RT. The precipitate formed and separated out by filtering and washed with deionised water with acetone. The obtained final suspension was dried in oven at 50° C for 24 hrs. The final product was grinded into powder.

ii. Preparation of PANI/Bi_2O_3 composite: All the samples are prepared at room temperature (RT). Solution of aniline of about 0.2M was prepared and mixed with 1N of solution of hydrochloric acid at RT. The above aniline and HCL mixture was stirred for 3 hours using magnetic stirrer. Further the solution of ammonium persulfate of about 0.25M was prepared and added to above mixture drop wise using pipette. Bismuth oxide (Bi_2O_3) powder for different additive weight percentage (5%, 10%, 15%, 20%, 25%) is dissolved in the mass fraction to the above solution with vigorous stirring in order to keep the Bi_2O_3 homogeneously suspended in the solution and stirring of final solution was continued for another 8 hours at room temperature. The precipitate formed and separated out by filtering and washed with deionised water with acetone. The obtained final suspension was dried in oven at 50° C for 24 hrs. The final product was grinded into powder.

3. Results and Discussion

3.1 X-ray diffraction:

XRD patterns provide information in relation to the nature and structure of the samples. XRD pattern of undoped sample of polyaniline shows amorphous nature. XRD patterns of doped samples show semi-crystalline nature. Since the conductivity of polymers depends on various parameters such as doping level (carrier's concentration), formation of polarons and bipolarons (Fink and Leising 1986), the semicrystalline nature of polymers arises owing to the systematic alignment of polymer chain folding or by the formation of single or multiple helices, for part of their length (Kazim et al 2006) [28].

X-ray diffraction is one of the widely used experimental techniques for determining lattice parameters. Figure 1 shows the XRD pattern of the synthesized polyaniline (PANI) scattered by the angle 2θ values as 10^0 to 80^0. From the figure, it can be observed that, broad peak are ascribed to the periodic parallel and perpendicular features of the polymer chains of PANI. They are centered at $2\theta = 26^0$-30^0 corresponding to (200) crystallographic plane reflection, which represents the characteristic peak in the PANI [15-17].

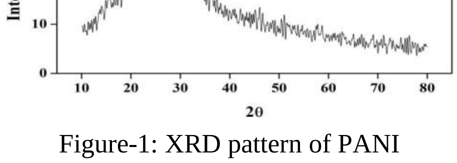

Figure-1: XRD pattern of PANI

The XRD confirmation of the crystal phases of PANI/Bi_2O_3 composite samples depicted in figure 2. The XRD peaks obtained in the spectra of PANI/Bi_2O_3 composite are in consistent with the Bi_2O_3 structure JCPDS card PDF file no. 27-0050. All remarkable diffraction peaks corresponding to (210), (201), (211), (002), (102), (212), (222), (203), (402) are diffraction planes of Bi_2O_3. The XRD spectra of the composites confirm the presence of Bi_2O_3 with specific peaks with small shift compared to the standard peaks (JCPDS card PDF file no. 27-0050). No peaks belonging to PANI were observed because of its amorphous nature in the composite. Analogous results were described for other PANI-based composites [18]

The crystallite size can be computed using Debye–Scherrer's formula and the doping concentration of metal oxide is a significant parameter impacting the composite crystallinity of the composite (Gomathi et al. 2018). The average crystalline size of the PANI are estimated to be approximately 25nm (D) are calculated by using Debye -Scherrer formula,

$$D = \frac{K\lambda}{\beta \cos\theta}$$

Where D is average crystalline size, λ is wavelength of the X-ray, K is crystallite shape factor a good approximation is 0.9, **β** is the full width at half the maximum (FWHM) of the X-ray diffraction peak and 2θ is the Braggs' angle (deg.).

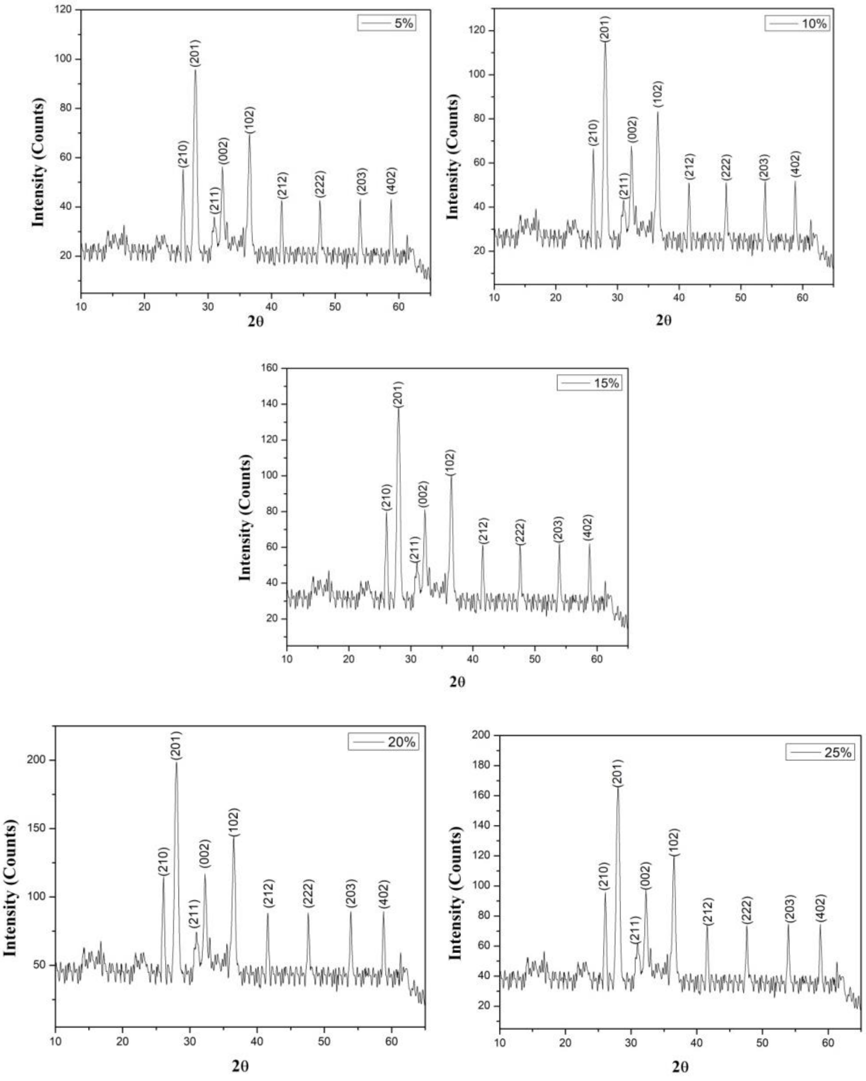

Figure-2: XRD pattern of PANI/Bi_2O_3 composites

3.2 Scanning electron microscopy (SEM):

Figure -3 shows SEM micrograph of pure PANI and PANI/Bi_2O_3 composites. The SEM photograph shows typical features of the polymer where it is mainly composed of irregularly arranged granular and flakes with sharp edges. Moreover, the structure looks non-porous, morphology with randomly distributed micro-sized round shaped particles with uniformity on the surface as well as a few agglomerations. The composite micrograph showed morphology slightly different from that of the micrograph of pure PANI suggesting the possible presence of Bi_2O_3 distributed in the polyaniline matrix. The SEM image of PANI shows uniform morphology with semi-crystalline like structure and has a substantial intra-granular distance between the grains. The SEM micrographs of the composites shows highly agglomerated and irregular arranged granular in shape under different magnification. The grains are found to be well connected which suggests the higher binding energy between the grains [19].

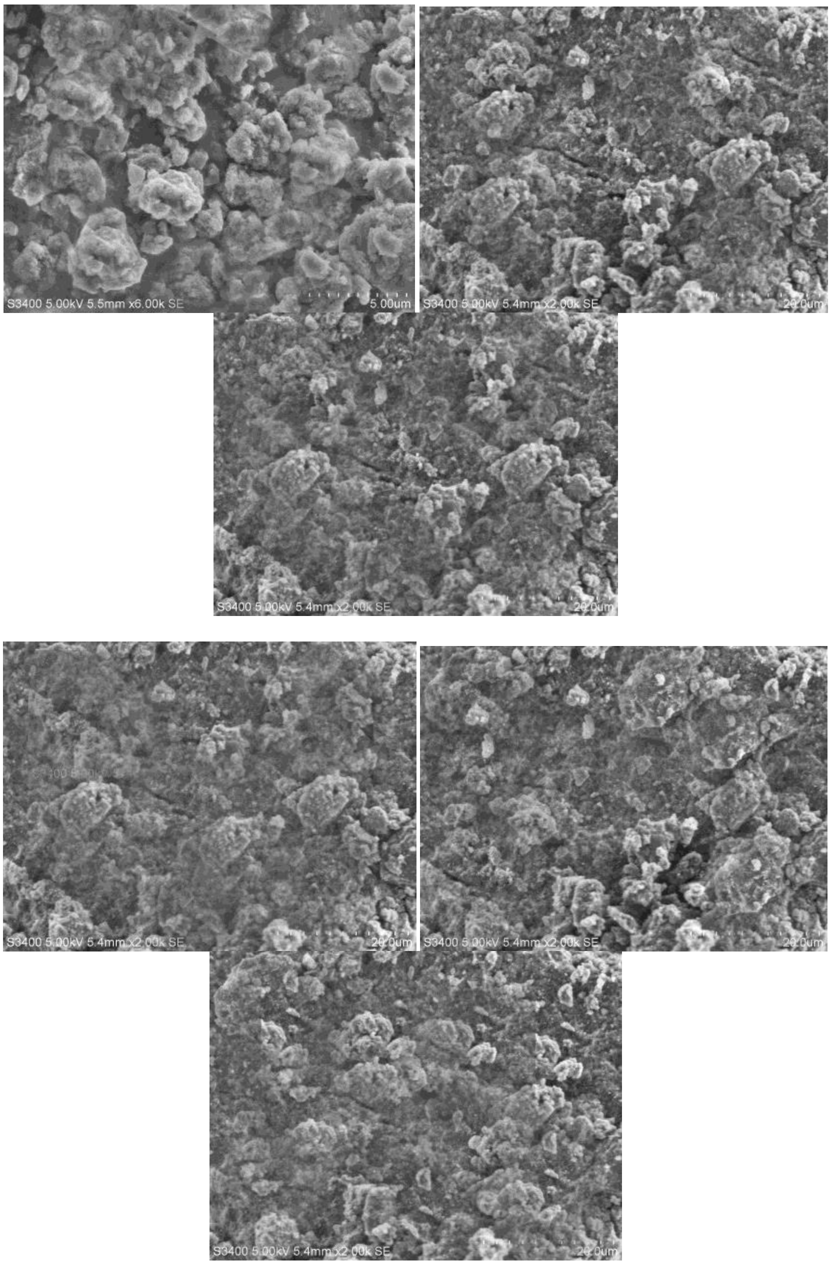

Figure 3: SEM micrographs of pure PANI and PANI/ Bi_2O_3 composites.

3.3 AC conductivity:

The polyaniline powder was thoroughly grounded in a mortar to obtain very fine particles, and then it was compressed under a pressure of (10 tone) in the form of a pellet.

The A.C conductivity for the common polymer is changes with the frequency according to the following formula (Joshi & Sinha, 2007):

$$\sigma_{ac}(\omega) = \sigma_t - \sigma_{d\tau} = A\omega^s$$

Where (A) is a constant independent on temperature, (ω =2*π*f) and (s) is the frequency exponent.

The ac conductivity of the pure PANI and PANI/Bi_2O_3 composite as function of frequency at room temperature is shown in figure-4. It is observed that from the Figure 4, ac conductivity is increased with increase in frequency. Two distinct regions namely region I and region II are identified based on their slopes. Upto around 0.6MHz the AC conductivity almost remained as constant and more than 0.6 MHz it is observed to be increased nearly exponentially. The enrichment in the AC conductivity of PANI/Bi_2O_3 composites over pure PANI happens to be due to the effective dispersion of Bi_2O_3 particles in the PANI matrix, which is favorable to the better electrical conductivity due to the better electric transport. The general values of frequency appear to be consistent with a hopping process of charge carriers (protons) between polymer chains. The ac conductivity of the composites is found to be higher compared with ac conductivity of pure PANI. Also the ac conductivity increases as the content of bismuth oxide increase in PANI matrix. Maximum conductivity is observed for 25 wt% of Bi_2O_3 in PANI composite [20-21].

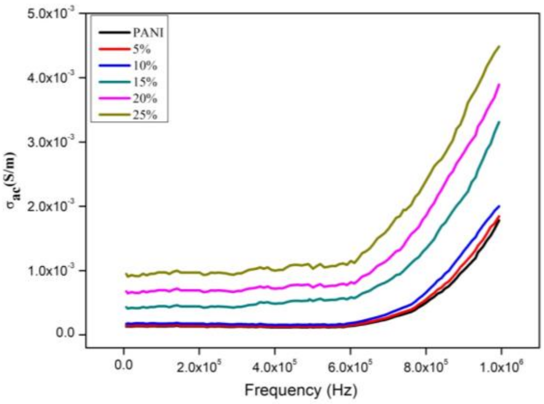

Figure 4: AC conductivity PANI and PANI/Bi_2O_3 composite

3.4 DC conductivity:

D.C. conductivity of pure PANI and PANI/Bi_2O_3 composite pellets (diameter, 0.008m, thickness, 0·00105 m) was measured by using two-probe method in the temperature range 30 – 200^0C. D.C. conductivity of the pellets was measured by mounting them between steel electrodes inside a specially designed sample holder. The temperature was measured with a calibrated copper-constantan thermocouple mounted near the electrodes. The samples were annealed to avoid any effect of moisture absorption. Conductivity was measured by using Ohm's law,

$$V = IR$$

where I is the current (in amperes) through a resistor, R (in ohms) and V the drop in potential (in volts) across it.

In ohmic material, the resistivity measured is proportional to the sample cross-section, A, and inversely proportional to its length, l:

$$R = \frac{\rho l}{A}$$

where ρ is the resistivity. Its inverse $\sigma = \rho^{-1}$ is the conductivity.

Figure 5 shows the temperature dependence of DC-conductivity in the temperature range 30 – 200^0C for undoped PANI and PANI/Bi_2O_3. D.C. conductivity of pure PANI increases exponentially with temperature, exhibiting semiconductor behaviour. The doping of conducting polymers implies charge transfer, the associated insertion of a counter ion and the simultaneous control of Fermi level or chemical potential. The electrical conductivity of conducting polymers results from mobile charge carriers introduced into π-electronic system through doping [28]. Due to the thermally activated behavior of conducting polymers, increase in conductivity is observed in all the composites with increase in temperature. There may be increase in efficiency of charge transfer between polymer chains and Bi_2O_3 with increase in temperature. The dc electrical conductivity also increasing as the content of Bi_2O_3 increased in the polyaniline matrix [22-24].

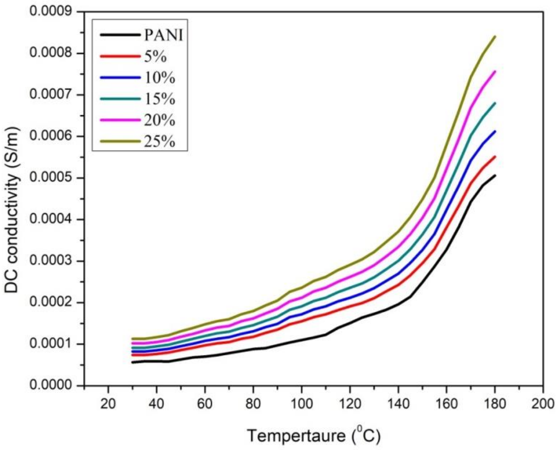

Figure 5: DC conductivity of PANI and PANI/ Bi_2O_3 composites

3.5 Sensor property:

The gas sensing mechanism in PANI/Bi_2O_3 composites is expected mainly because of two reasons. First, the trapping of LPG molecules in between the PANI/ Bi_2O_3 composites islands is by electrostatic forces and second is a surface controlled phenomenon i.e., it is based on the change in surface resistance of the composites at which the LPG adsorb and reacts with pre-adsorbed oxygen molecules [25]. These sensors are based on the gas-sensitive properties of a semiconducting metal-oxide layer which is usually polycrystalline, and whose conductivity is modulated by the oxygen adsorbed at the surface and at grain boundaries [26]. These metal oxides change their conductivity in the presence of reducing or oxidising gases, such as O_2, H_2, CO, NOx, C_2H_5OH and hydrocarbons [27].

The gas sensing behavior of pure PANI and PANI/Bi_2O_3 composite was studied by calculating change in the surface resistance of sensing samples with time toward LPG exposure at room temperature. In order to evaluate the gas sensing properties of composites, the electrical resistance was measured using two probe method. The electrical resistance was measured in a glass chamber with a volume of 1500 cm3. The samples are placed in sample holder of the sensing setup. Initially the air was injected into the glass chamber using flow meter in order to establish the equilibrium between oxygen adsorbed at surface of the samples and atmospheric oxygen. When the resistance of the sensor is stabilized, then the gaseous mixture LPG was injected into the chamber using flow meter and the resultant change in the electrical resistance was noted. The change electrical resistance of the PANI and PANI/Bi_2O_3 composite was shown in figure-6. The electrical resistance found to be decreases as function of time and then stabilizes. The introduction of LPG gas toward the composite injected electrons to the pallet, and thus significantly increased the number of charge carriers in the pallet. As a result, more electrons flowed in the film and at the same time reduced the resistance of the pallet. The response of sensor was monitored in terms of the normalized resistance calculated by Response = R0/Rg and the Rg is the resistance of the sensor in presence of LPG gas and R0 is the initial stabilized resistance of the pallet. The change in response of the PANI and PANI/Bi_2O_3 composite was as function of time is shown in figure-7. The composites show a higher and faster response in comparison to pure PANI sensor. Hence Both these figures reveal that the response of PANI & all composite increases rapidly upon introduction of LPG gas and becomes stable within few seconds.

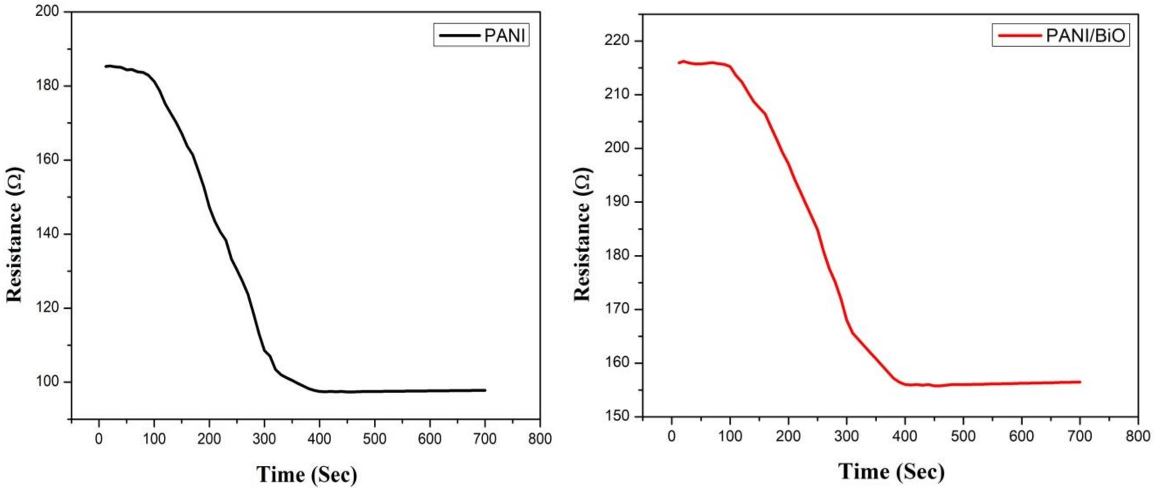

Figure 6: Change in resistance of PANI & PANI/Bi_2O_3 composite

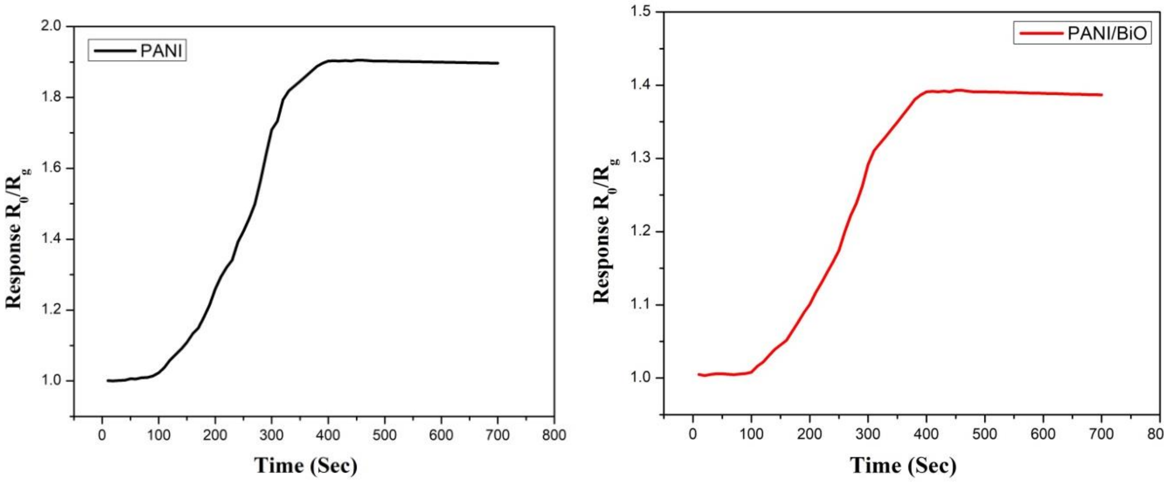

Figure 7: Response curve of PANI & PANI/Bi_2O_3 composite

3.6 Conclusion:

PANI/Bi_2O_3 composite was prepared by chemical oxidative polymerization method and ammonium persulphate as an oxidizing agent. XRD result showed that all the prepared composite samples are semi-crystalline in nature. All the tentative crystalline peaks matches with the JCPDS card. The ac electrical conductivity measurements demonstrate that the conductivity of composites is greater than those of PANI and by increasing Bi_2O_3 particles, value of ac electrical conductivity increased. The temperature dependence of DC-conductivity increases exponentially with increase in temperature which is suggesting the behavior of the semiconducting nature and by increasing Bi_2O_3 particles, value of dc electrical conductivity increased. The composites particles exhibit a better sensitivity to LPG compared with PANI. The composites show a higher and faster response in comparison to pure PANI sensor.

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