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# Studies on structural, morphological, electrical and gas sensing properties of the polyaniline/tungsten oxide (PANI/WO3) composites

**B T Vijaykumar[1], B Manjunatha[2], Ramabai Narasimhachar[1], Mahadevi[1], Raghavendra Naidu S[3], Bharati[1], Reshma1, Basavaraja Sannakki[1*]**

*[1,] Department of Physics, Gulbarga University, Kalaburagi-585106, Karnataka, India.*
*2Department of Physics Govt Women First Grade College Jewargi Colony Kalaburagi 585102*
*[3] Department of Aerospace Engineering, Indian Institute of Technology Kanpur, Kanpur-208 016.*
*Author for correspondences Email: sannakki.phy@gmailcom*

The unadulterated PANI and PANI/WO3 composites were prepared from the reaction of aniline monomer polymerization with tungsten oxide (WO3) particles; APS were used as an oxidant. Tungsten oxide has been added in PANI in five different weight percentages (wt%) i.e. 5, 10, 15, 20 and 25 wt % Analytical techniques such as SEM and X-ray diffraction (XRD) was studied to describe the morphological and structural particulars of the prepared samples. The temperature dependencies of DC conductivity of samples were studied in the temperature between $30^0$C to $200^0$C. The results of the composites suggest the strong cooperation of PANI with tungsten oxide in the composite. The investigation of dc conductivity shows a witness for transport property of the composites. The frequency sensitive of ac conductivity is studied. On exposure to LPG gas, variation in resistance and response of the PANI/WO3 composites recognized.

***Keywords:*** *Tungsten oxide, Polyaniline, Electrical properties, LPG.*

## 1. Introduction

Study on polymeric compound constituent mixes the discipline and equipment of polymer resources. Polymers having metallic oxide establish polymeric mixtures are well deliberate for its assets conductive polymer materials possess a diversity of application in the medical, industrial and science field. Appliance like static coating electromagnetic shielding, anticorrosion etc, which comes under the first generation [1].The first generation application like EMS, anticorrosion and second group application like LED, solar cell, transistor. Control conductivity, high resistance temperature, less rate with simplicity of substance preparations cause the materials gorgeous work and in the technical world [2-3]. Polymer composites containing metal oxides are extensively researched due to their unique and desirable properties [4].The significant uses of conductive polymer such as reversibility's, which can be easiness to use for layering, form; good atmosphere loyalty improves their latent use for practical applications. The primary reading the conductive polymer; PANI gains the electrochemical direct. Polymer obligates turn out to be a part of enlarging consideration in examine due to the detail that those material have huge possible to the solid state method [5-7]. PAni is generally, found in 3 oxidation states namely, leucoemeraldine, pernigraniline and emeraldine. Out of those the most attractive is emeraldine which is owing to its tunable states [8]. The PAni can be synthesized by various routes such as dispersion technique, in- situ polymerization and enzymatic polymerization or by solution blending [9]. Here in existing effort noticed the synthesis of PANI-$WO_3$ composites by in-situ polymerisation method. Then, Structural property of PAni and its composites were characterized using X-ray diffraction. The transport properties being AC and DC conductivity of PAni with its composites by varying $WO_3$ for different weight percentage was studied to understand the transport of the composites. In addition to the composites dielectric constant of different composites were considered [10-13].

## 2. MATERIALS AND METHODS

The material which is used to compose Polyaniline are Aniline, HCL and (NH4)2S2O8 of investigative grades are used for combining of PANI and tungsten oxide was used to equip composites through the insitu chemical oxidative polymerization method.

## 3. PREPARATION OF PANI

All the samples are prepared at normal temperature (RT). The aniline Solution of about 0.2M was processed and 1N of solution of hydrochloric acid is mixed at RT. The above aniline and HCL blend was gently stirred for a 3 hours using magnetic stirrer. Further the mixture of Ammonium persulfate (NH4)2S2O8 of about 0.25M was assemble and added to above mixture drop wise using pipette. Then the mixture is stirred for 8 hours at RT. The hasten formed was removed out by filtering and washed with demineralized water using acetone. The procure concluding interruption was dry with help of oven at 50° C for one day. The yields were grinded into soft powder.

### Preparation of PANI/WO3 composite:

The entire specimen is processed at normal temperature (RT). The aniline Solution of about 0.2M was processed and 1N of solution of hcl is mixed at RT. The above aniline and HCL blend was gently stirred for 3 hours using magnetic stirrer. Further, the Ammonium persulfate (NH4)2S2O8 solution of about 0.25M was prepared and added to above mixture drop wise using pipette. Tungsten oxide (WO3) powder of different weight percentage (5wt%, 10wt%, 15wt%, 20wt%, 25wt%) is break down to the mass fraction of the surpassing solution with effective gently stirring to maintain the WO3 steady and the results are obtained at normal temp. The discharged formed was removed out by filtering and cleaned with demineralised water and with acetone. Procure concluding suspension was dried by using the oven which is maintained the temperature at 50° C

for one day. The final yield was crushed into the soft powder.

## 4. RESULTS AND DISCUSSION

### *X-ray diffraction:*

X-ray diffraction (XRD) is a central approach for the determination of the morphology and composition of obtained composites. The XRD results the confirmation of the crystal phases of polyaniline (PANI) and WO3/PANI composite samples depicted in figure 1 (a) and (b) respectively. The large diffraction peak was recognized between diffracted angle 2θ ranges from $26^0$-$30^0$ which is unique peak polyaniline recommend of the amorphous nature in PANI. The broad diffraction peak with d spacing d=3.29 corresponds to the reflection (200) due to perpendicular and parallel periodicity of the polyaniline (PANI) and no extra diffraction peaks are observed. The XRD peaks captured in the spectra of WO3/PANI composite are in logical with the WO3 structure JCPDS 01- 072-0677. All remarkable diffraction peaks corresponding to (002), (200), (120), (112), (002), (202),(222), (400), (420), (340) are diffraction planes of WO3 logical with the monoclinic structure and are in accordance with JCPDS 01-072-0677. The XRD spectra of the composites confirm the presence of WO3 with specific peaks with small shift when comparable to the standard peaks (JCPDS 01-072-0677). The shift in the XRD peaks of WO3 composite may due occurrence of the PAni matrix. No peaks belonging to PANI were observed being of amorphous nature in the composite. Related results were described by other PANI-based composites [14]. The crystallite size can be computed using Debye–Scherrer’s formula and the doping concentration of the metal oxide was a significant parameter impacting the composite crystallinity of the compound (Gomathi et al. 2018). The average crystalline size of the PANI which is approximately 5nm (D) are

estimated by adopting Debye-Scherrer formula,

$D = K\text{l} / \text{b}Cos\text{q}$

Where D Average crystalline size, λ is wavelength of the X-ray, K is crystallite shape factor a goodapproximation is 0.9,

**β** Full width at half maximum (FWHM) of the X-ray diffraction peak 2θ is the Braggs' angle (deg.) [15-18].

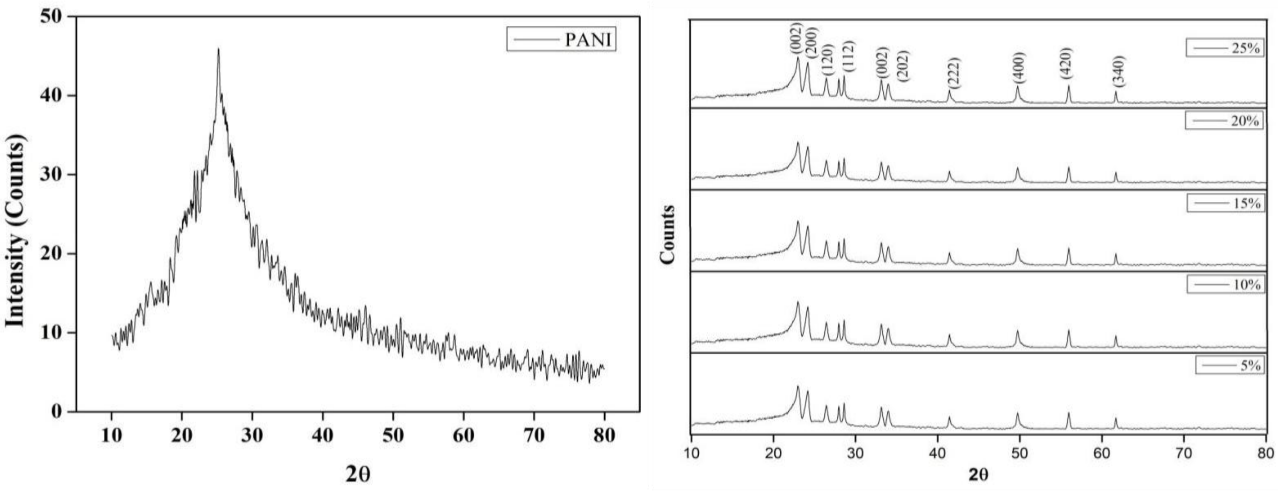

**Figure 1: XRD patterns of (a) PANI and (b) PANI/WO3 composites.**

**Scanning electron microscopy (SEM):**

The synthesized PANI and PANI/WO3 composite of the SEM Micrographs represented in Figure 2. As prepared sample showed morphology with randomly distributed micro-sized round shaped particles with uniformity on the surface and also the few agglomerations. The composite micrograph appeared slightly different morphology from that of the pure PANI suggesting the possible presence of WO3 distributed in polyaniline matrix. The PANI SEM image shows uniform morphological with semi-crystalline like structure and an ample intra-granular distance between the grains. The composite of SEM micrographs clearly, shows that the high degree agglomerated and irregular settled granular in shape, beneath different magnification. The grains are formed which is strong connected which recommend the higher binding energy between the grains. It is observable that the SEM micrograph of PANI/WO3 compound shows distinct morphology as in comparison with the PANI [19].

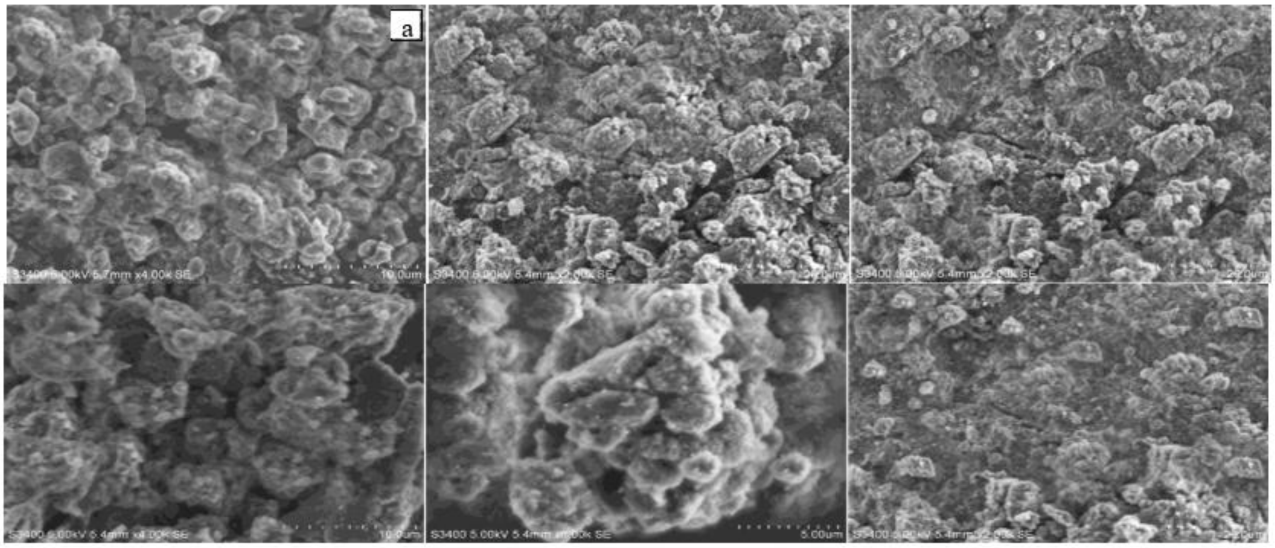

**Figure 2: SEM micrographs of (a) pure PANI and (b)-(f) PANI/WO3 composites.**

**AC conductivity**:

At room temperature, the Ac conductivity of pure PAni and PAni/WO3 composites as concern of frequency showed in Fig 3.It clears that, ac conductivity is increased with increase in frequency. Based on their slopes, two regions I and II are identified. It was around 0.6MHz the AC conductivity almost remained as constant and higher than 0.6 MHz it is observed that increased nearly exponentially to enrichment in the AC conductivity of PANI-WO3 composites over pure PANI ensues to be due to the active spreading of WO3 particles in the PANI matrix, which is favorable to the improved the conductivity due to the well electric transport. The dependent frequency of AC conductivity indicates that transported nearby the charge carriers by hopping over the defect sites of the polymer group. It is generally known that the conductivity of a composite depends on factors such as protonation state of polymer and also the crystallinity percentage, in addition to frequency and temperature. Some composites have shown higher conductivity rather than polyaniline and the highest conductivity are seen in the 20% nanocomposites with a value of $5.0*10^{-2}$ S/cm. The frequency dependency of AC conductivity is the result of interface charge polarization and intrinsic electric dipolar polarization. In heterogeneous systems like polymer – semiconductor composites, the charges accumulate at the interfaces and the large dipole will be formed on semiconductor particles [20]

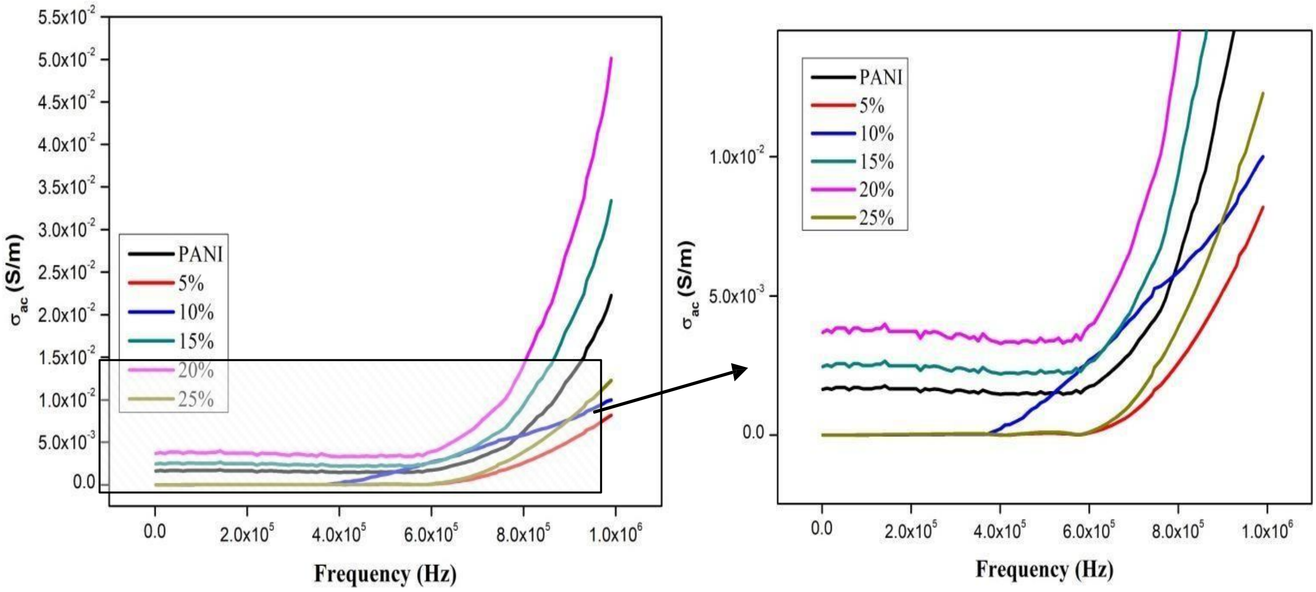

**Figure 3: AC conductivity of (a) pure PANI and (b) PANI/WO3 composites**

**DC conductivity**:

The charge transport mechanism in the natural PANI and PANI/WO3 composite, for the temperature as behavior of electrical conductivity is examined. As the temperature increases the dc electrical conductivity increases exponentially this is suggesting the presence of the semiconducting nature. The DC electrical conductivity increases as the content of WO3 was increased in the polyaniline pattern. The nature of DC conductivity composites dependent on temperature indicates that at higher temperature, due to the excited to the conduction band, the charge carriers gain higher energy, which is a thermal process best so called by the Arrhenius equation given as equation no (1) where $\sigma 0$ is the constant depending on the material, Ea is the activation energy, kB is the Boltzmann constant and T is the absolute temperature [21-22].

$$\sigma = \boldsymbol{\sigma o}\ \boldsymbol{exp}\ \left(-\frac{\boldsymbol{Ea}}{\boldsymbol{kBT}}\right)$$

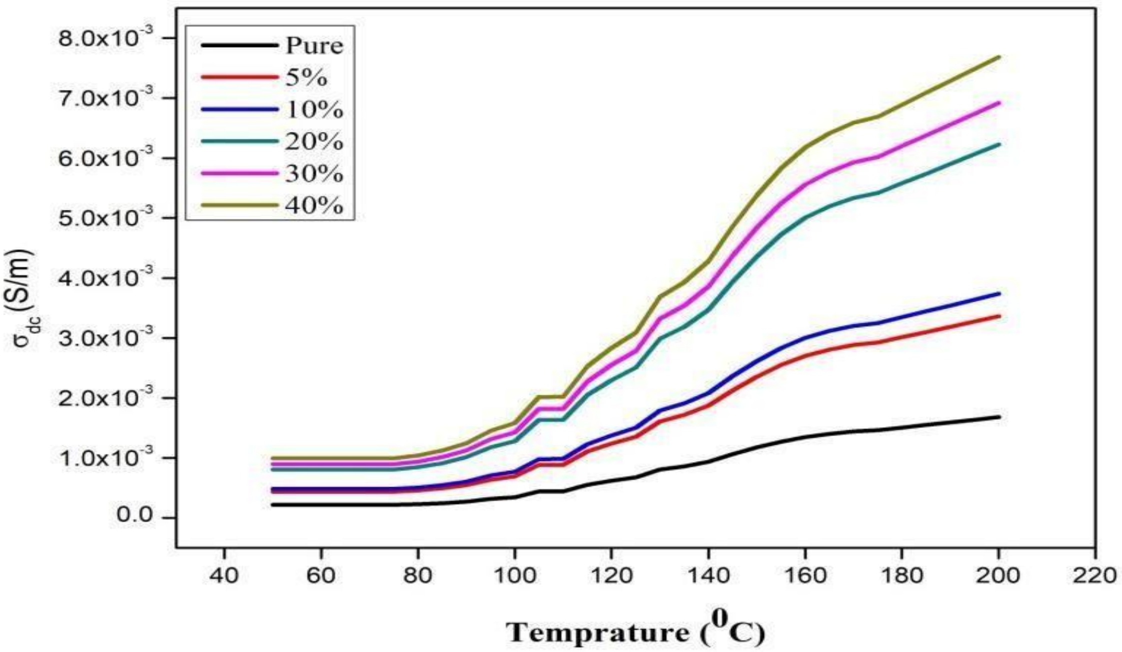

**Figure 4: DC conductivity of (a) pure PANI and (b) PANI/WO3 composites**

**Sensor property**:

The sensors are established on the gas-sensitive properties of semiconducting metal-oxide layer which is usually polycrystalline, and whose conductivity is modulated by the oxygen adsorbed at the surface and at grain boundaries [23]. These metal oxides change their conductivity in the habitation of reducing or oxidizing gases, such as O2, H2, CO, NO3, C2H5OH and hydrocarbons[24]. The gas sensing behavior of natural PANI and PANI/WO3 composite was examined by calculating transformation in the surface resistance of sensing samples with time concerning of LPG exposure which is maintained at room temperature. to evaluate the pacific gas sensing properties of composites, the measured electrical resistance by the help of two probe method. The electrical resistances were measured in a glass chamber with a volume of 1500 cm$^3$. 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 electrical resistance were noted. The change electrical resistance of the PANI and PANI/WO3 composite was shown in figure-5. The electrical resistance found to be decreasesas function of time and then stabilizes. The LPG gas introduced toward the injected composite electrons to the pallet, and thus significantly increased the number of charge carriers in the pellet. As a result, more electrons flowed in the film and concurrent reduced in the resistance of the pallet. The sensor response was monitored in terms of the normalized resistance calculated by Response = R0/Rg and the Rg is the sensor resistance in presence of LPG gas and R0 is the initial stabilized resistance of the pallet. The change in response of the PANI and PANI/WO3 composite was as function of time is shown in figure-6. In comparison to pure PAni Sensor, the composites showed a higher and faster response. So, both the figures disclose that PAni and composite PAni Inflation rapidly due to introduction of LPG gas and become steady within few seconds [25-26]. Hence below figures expose that the response of Pn and all composite rises quickly upon outline of LPG gas and become steady within few seconds [27].

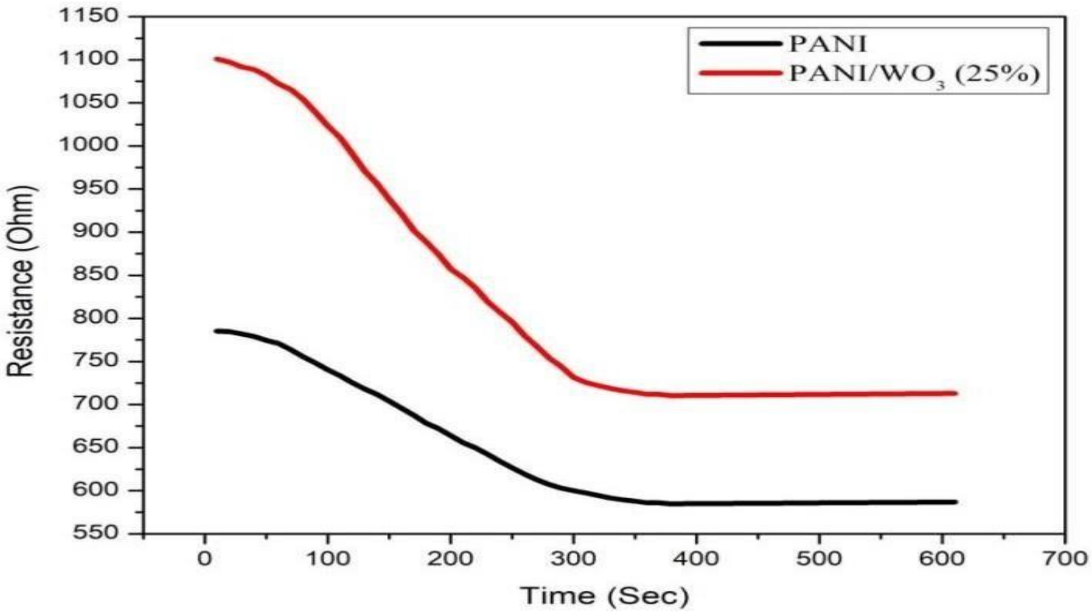

**Figure 5: Change in resistance of (a) PANI and (b) PANI/WO3 composite.**

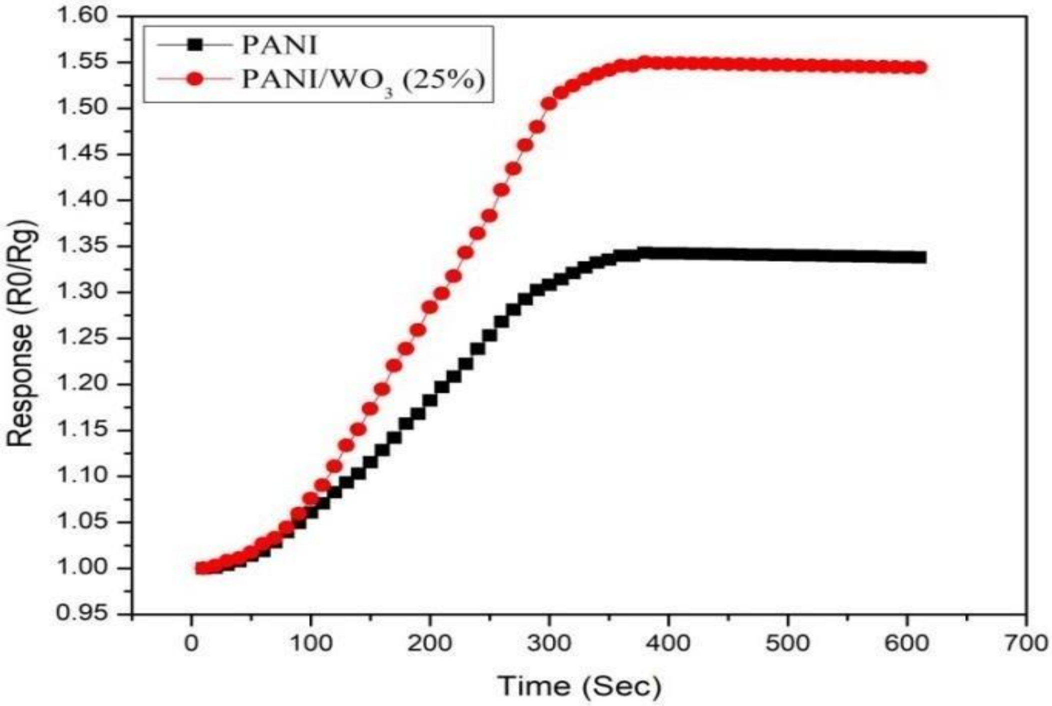

**Figure 6: Response curve of (a) PANI and (b) PANI/WO3 composite.**

## 5. CONCLUSION

Pure PANI and PANI/WO3 composites were synthesized by chemical oxidative route and the mixtures of PANI/WO3 nanoparticles in different weight percentage during polymerization of aniline and using ammonium persulphate as oxidizing agent in aqueous medium. The XRD analysis of pure PANI and PANI/WO3 confirms the successful formation composite and expo the increase in crystallinity with increasing concentration of oxide. SEM analysis polyaniline composites exhibits the transition in the surface morphology of PANI doped with WO3 at different weight percent. The DC conductivity investigation reveals that increase in temperature, the composite conductivity increases and WO3 concentration in PANI up to the magnitude of three orders and confirmed semi-conducting nature of the samples. It may be suggested that conduction takesplace because of present of large range of localized state in polymer composites PANI/WO3. As a function of frequency, The AC conductivity increases at room temperature and was highest for 40% composite and resistance of the sensing material decline with increase in LPG in the chamber as activity of time. The composites particles exhibit a better sensitivity to LPG compared with PANI. The synthesized reveals the faster and higher response in analogy to pure PANI sensor.

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