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## Enhanced room temperature sulphur dioxide sensing behaviour of in-situ polymerized polyaniline-tungsten oxide nanocomposite possessing honeycomb morphology

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### Abstract

Polyaniline-tungsten oxide hybrid nanocomposite with honeycomb type morphology was synthesized by in-situ one pot chemical oxidative method and used for sulphur dioxide (SO<sub>2</sub>) monitoring application for the first time. The sensing device was fabricated using cost effective spin coating technique for the monitoring of SO<sub>2</sub> at the level as low as 5 ppm. The fabricated sensing device works at room temperature, which reduces its power consumption, cost and complex circuitry. It was found that the sensing response of nanocomposite based sensing device (~10.6%) is much more enhanced as compared to that of its individual parent devices (~4% for polyaniline nanofibres and is negligible for tungsten oxide nanostructures) for 10ppm SO<sub>2</sub> at room temperature. The reason for this remarkable response has been discussed in light of several factors like optimum porosity, branched structure and formation of heterojunctions. Also, the fabricated nanocomposite based sensor was found to be reliable in terms of stability, selectivity, response and recovery time, detection range and reproducibility. The mechanism of SO<sub>2</sub> sensing in the said composite is proposed and discussed in terms of formation of heterojunctions by energy band diagram.

**Keywords:** Nanocomposite, heterojunctions, sulphur dioxide, tungsten dioxide, optimum porosity.

## Introduction

The growing concern about environmental imbalance has led to incessant expansion in sensor development. Although numerous variety of sensors are well established in diverse fields such as agriculture, industries and medicines, still the research on development of sensing devices with enhanced sensing characteristics is growing on vast scale. From the last few decades, many organic and inorganic materials have been widely researched as sensing materials due to their particular advantages<sup>1</sup>. Inorganic materials such as metal oxide nanostructures like tungsten oxide  $\text{WO}_3$ <sup>2-6</sup>, tin oxide  $\text{SnO}_2$ <sup>7-10</sup>, zinc oxide  $\text{ZnO}$ <sup>11</sup> based gas sensing devices have been extensively used for detection of various hazardous environmental contaminates (such as ammonia  $\text{NH}_3$ , sulphur dioxide  $\text{SO}_2$ , Nitrous oxide  $\text{NO}$ ). These sensing devices possess good sensitivity, high thermal and electrical stability and high carrier motilities. On the other hand, these devices require higher temperature for their optimum operation. The operation of these devices at elevated temperature causes gradual change in properties of metal oxide nanostructures. The high temperature operation can cause fusion of grain boundaries, which can avert the stability of nanostructure and makes life time of sensing device shorter. Also, operation of such devices at elevated temperature requires a distinct temperature controlled complex heating assembly and needs extra power consumption for heating purpose. The need of such micro-heating assemblage adds to cost of such sensing devices and complexity in the circuitry<sup>12</sup>. Thus, it is extremely essential to have sensing devices, which can operate at room temperature and have comparable sensing properties. This brought researcher's quest to organic materials for the gas sensing applications. Organic materials such as conducting polymers (CP) based gas sensing devices possess characteristics like room temperature operation, which are contrary to most of the conventional metal oxides based sensors<sup>13-15</sup>. Though rapid progress has been made in the field of gas sensing at room temperature using inorganic materials based gas sensors<sup>16-19</sup>. Out

of all CPs, polyaniline (PAN) has shown very promising results for sensing applications in terms of rapid response, ease of synthesis and fast recovery<sup>20</sup>. But these devices to certain extent lack environmental stability and selectivity<sup>21</sup>. PAN is a versatile sensor for various analytes and degrades in environment with time, which restricts their commercial development. Thus, both types of materials (organic and inorganic) possess merits and demerits contrary to each other. This brought the interest of researchers towards the fabrication of organic-inorganic nanocomposite based sensing devices. Such composites possess merits of both the parent materials, which results in improved hybrid system with enhanced optical and electrical properties<sup>22-23</sup>. In the past decade, PAN has been hybridized with different metal oxides such as ZnO, SnO<sub>2</sub>, WO<sub>3</sub> and iron oxide nanoparticles (Fe<sub>2</sub>O<sub>3</sub>) for gas sensing applications<sup>24-27</sup>. The addition of these metal oxide nanoparticles enhances both porosity and effective surface area of PAN as well as its environmental stability and selectivity towards particular analyte. Though PAN is easy to synthesize by simple chemical oxidative polymerization<sup>28</sup>, but it is very difficult to embed inorganic material nanoparticles uniformly into the PAN matrix by simply mixing or blending in solution form. Thus, both the materials must be synthesized together for the formation of a uniform nanocomposite. One of the techniques is the one pot synthesis or in-situ synthesis method for synthesis of nanocomposite. It is a cost effective approach, which leads to formation of heterojunctions amongst the parent materials within the nanocomposite, which enhances the sensing characteristics of monitoring devices. With this motivation, we have prepared an inorganic – organic hybrid nanocomposite with n type WO<sub>3</sub> as inorganic phase dispersed in p-polyaniline as organic matrix using one pot self-assembly.

Out of all contaminants, sulphur dioxide is a poisonous gas having exposure limit of 5 ppm<sup>29</sup>. It attacks human respiratory system<sup>30</sup> and is the major reason for acid rain<sup>31</sup>. Thus, its monitoring is critically required. There are very few reports in literature about sulphur

dioxide sensing by individual PAN<sup>32-37</sup> and WO<sub>3</sub><sup>2-6</sup> based sensing devices, but they too lack in justifying the essential parameters required for reliable SO<sub>2</sub> monitoring. To the best of our knowledge, this is first attempt to use PAN/WO<sub>3</sub> hybrid nanocomposite for the SO<sub>2</sub> monitoring. In this communication, we have used template less one pot synthesis method to synthesize PAN/WO<sub>3</sub> hybrid nanocomposite and explored its application for SO<sub>2</sub> monitoring. We have tried to optimize all essential characteristics of a reliable sensor such as simple circuitry, ease of fabrication, cost effectiveness, rapid response, fast recovery, selectivity, stability and reproducibility.

## Experimental Details

### Synthesis and sensor fabrication

The samples were synthesized using bottom up chemical approach. Polyaniline nanofibres were prepared using template free chemical oxidative polymerization of monomer, aniline by oxidant ammonium peroxodisulphate (APS)<sup>28</sup>. Tungsten dioxide (WO<sub>3</sub>) nanoparticles were prepared by solvothermal approach. In typical synthesis, 0.1M solution of tungsten hexachloride (WCl<sub>6</sub>) was stirred in 200ml of ethanol for 4 hours at 180°C. The resultant was precipitated and kept in vacuum oven for overnight at 200°C. For the synthesis of polyaniline – tungsten oxide nanocomposite (PW), in-situ one pot self assembly technique was used rather than mixing individually synthesized parent materials (PAN and WO<sub>3</sub>) as to obtain uniform dispersion. In a typical synthesis, 0.1 M solution of WCl<sub>6</sub> was preheated at 80°C for two hours. Meanwhile, a separate solution of 0.1 M aniline was continuously stirred at 5°C for 30 min. Both the solutions were mixed rapidly and stirred at 5°C. After 30 minutes, a precooled 0.1 M solution of APS was added dropwise to the above solution. The reaction was carried out for 6 hours at 5°C in nitrogen environment under constant stirring. The reaction

was stopped by adding 5mM methanol and precipitate was collected by centrifugation. After repeated washing of precipitate with double distilled water and methanol, it was dried in oven at 60°C for 48 hours. For the fabrication of sensing devices, 0.2g of synthesized materials were dispersed in 25 ml of m-cresol and ultrasonicated for 24h. Then, the solutions were filtered and films were spin casted on pre-cleaned glass slides. The films were allowed to dry at 60°C in vacuum oven for 12 hours. Afterwards, parallel conducting electrodes were thermally deposited on these films.

### **Characterizations and sensing apparatus**

The prepared sensing devices were characterized for their optical, electrical, morphological and sensing characteristics using UV- visible spectroscopy (UV-Vis), field effect scanning electron microscopy (FE-SEM), High resolution X-ray diffraction study (HR-XRD), Fourier transform infrared spectroscopy (FTIR), High resolution transmission electron microscope (HR-TEM), Brunaur-Emmett-Teller (BET) and indigenously designed fully automated gas sensing setup. The HR-XRD measurements of fabricated sensing devices were achieved with Bruker D8 Discover diffractometer system having Cu radiation source (3KW) of wavelength around 1.540 Å. The diffraction patterns of scattered radiations were recorded in the  $2\theta$  range of  $10^0$  to  $60^0$  with scanning rate  $2^0$  per minute. The surface morphology of fabricated sensing devices was analysed with Tescan MIRA3 FE-SEM system in secondary emission mode. Furthermore, the crystal structure and morphology of prepared samples is confirmed using HR-TEM, FEI-Tecnai G2. The porosity and specific surface area of the prepared samples was analysed under BET studies by a Quantachrome Autosorb automated gas sorption analyser at 77K under vacuum conditions. The optical absorption spectra were recorded with in a wavelength range of 250-1000 nm using a Hitachi-330 UV-visible spectrometer, with glass substrate as reference. The IR spectra of fabricated sensing devices were recorded with FTIR spectrum RX1 spectrometer by Perkins-Elmer in the wavenumber range of 500-4000

cm<sup>-1</sup> at 64 scans per spectrum at 2 cm<sup>-1</sup> resolution. The spectra were recorded in transmission mode and were corrected for moisture and carbon dioxide presence in the optical path. The electrical gas sensing analysis were recorded by self-made assembly of Keithley's 6487 picoammeter, Eurotherm 2408i temperature controller, Allicat mass flow controller and gas sensing chamber connected by GPIB (KUSB-488.2), and programmed by LAB View and Flow vision software (Fig. 1). The measurements were taken by loading sensing devices into sensing chamber and placing conducting probes on contact parallel electrodes. The sensing devices were analysed for different exposure cycles of SO<sub>2</sub>. The SO<sub>2</sub> sensing response was measured in terms of change in surface resistance and calculated by formula:

$$\text{Response (\%)} = \frac{R_{\text{air}} - R_{\text{analyte}}}{R_{\text{air}}} * 100$$

Where,  $R_{\text{analyte}}$  and  $R_{\text{air}}$  are the surface resistance of sensing device for the insertion and evacuation of SO<sub>2</sub>, respectively.

## Results and discussions

### Structural and morphological characteristics of sensing devices

#### FTIR study: Chemical structure

The molecular structures of prepared samples were characterized by FTIR spectroscopy. Fig.2 presents the FTIR spectra of WO<sub>3</sub>, PAN and PW hybrid nanocomposite, respectively. For WO<sub>3</sub>, the peaks located at 730 cm<sup>-1</sup> and 890 cm<sup>-1</sup> are attributed to stretching vibrations of (O - W<sup>6+</sup> - O) bonds<sup>38</sup>. The sharp band around 980 cm<sup>-1</sup> is contributed from asymmetric stretching vibrations of (W=O) bonds<sup>39</sup>. The peak at 1590 cm<sup>-1</sup> is due to (O-H) bending mode. A minute peak around 2932 cm<sup>-1</sup> corresponds to (-OH) group of WO<sub>3</sub><sup>40-41</sup>. For

pristine PAN, the peak around  $1122\text{ cm}^{-1}$  is assigned to  $\text{Q}=\text{NH}^+\text{-B}$  (where, Q and B denotes quinoid and benzenoid rings, respectively) bending vibrations. The peak at  $1294\text{ cm}^{-1}$  corresponds to C-N tertiary aromatic stretching mode, which is considered as characteristic peak of proton doped PAN. The peaks around  $1486\text{ cm}^{-1}$  and  $1568\text{ cm}^{-1}$  are due to C=C stretching vibrations of benzenoid and quinoid rings, respectively. The peaks at  $780\text{ cm}^{-1}$  and  $876\text{ cm}^{-1}$  are attributed to C-H in and out of plane stretching of para substituted aromatic ring. The peak at  $2380\text{ cm}^{-1}$  is due to N-H stretching vibrations<sup>28, 42</sup>. The FTIR spectra of PW hybrid nanocomposite possess all the prominent peaks, which confirm the presence of both PAN and  $\text{WO}_3$  in the hybrid structure. It exhibits significant shift of various prominent peaks towards lower wavenumber side, which signifies strong interaction between  $\text{WO}_3$  and PAN. The shift in (W=O) stretching mode (from  $980\text{ cm}^{-1}$  to  $934\text{ cm}^{-1}$ ) signifies a strong modification in  $\text{WO}_3$  surroundings due to its dispersion in PAN matrix, where it is surrounded by more polarized sites ( $\text{Q}=\text{NH}^+\text{-B}$ ). The enhancement in quinoid to benzenoid ratio suggests a strong interaction between  $\pi$ -bonded surface of  $\text{WO}_3$  and conjugated PAN, which stabilizes the quinoid ring structure and alters the molecular order along with conjugation. As tungsten is a transition metal, it forms coordination compound with ( $\text{N}^+$ ) atom in PAN, which is also confirmed in UV-Vis study. Thus, it may results in formation of heterojunctions between p-PAN and n- $\text{WO}_3$ . A petite peak observed around  $670\text{ cm}^{-1}$  corresponds to 1, 3-coupling of aromatic rings, which suggests presence of branched chain structure<sup>28, 43</sup>. This kind of structure helps in fast charge transport during interaction with analyte and enhances sensing response. Thus, the FTIR confirms the formation of PW hybrid nanocomposite with branched chain structure.

**FE-SEM study: Morphological characteristics**

Fig. 3 (a-c) presents FE-SEM micrographs of prepared pristine PAN, WO<sub>3</sub> and PW hybrid nanocomposite, respectively. Fig. 3 (a) reveals the formation of PAN nanofibres with average diameter around 50nm and length around few microns. This nanofibillar morphology is inherent to polyaniline in the vicinity of temperate directed synthesis. These initially formed nanofibres serves as seeds during the whole course of polymerisation and leads to nanofibillar morphology<sup>44-45</sup>. Fig. 3 (b) depicts the formation of WO<sub>3</sub> nanoparticles with average diameter around 50nm. It is well known that during template free synthesis aggregation is energetically more favourable due to high surface energy. Thus, it may be the plausible reason for the formation of quasi-spherical nano aggregations of WO<sub>3</sub>. Fig. 3 (c) shows the formation of honeycomb type morphology of PW hybrid nanocomposite. The absence of solitary fibillar or quasi-spherical morphology overrules the probability of co-existence of both components. Thus, it reveals the formation of nanocomposite of honeycomb type morphology. This kind of morphology exhibits optimum porosity, which would help to reach the analyte molecules into interstitial sites on exposure. This morphology also possesses increased effective surface area which in turn enhances the sensing response towards analytes.

**BET: Porosity and specific surface area**

The porosity and the specific surface area of the prepared samples were investigated using BET analysis<sup>46-48</sup>. Fig. 4 shows the BET adsorption isotherm between the relative pressure of nitrogen and quantity of gas adsorbed for PW, WO<sub>3</sub> and PAN, respectively. The specific surface area, S<sub>B</sub> was evaluated using linear part of isotherm (called as B point). The S<sub>B</sub> is defined as:

$$S_{BET} = Q_m A_m N$$

Here,  $Q_m$  symbolizes the volume of analyte adsorbed as a monolayer on 1g of sample,  $A_m$  symbolizes the molecular cross sectional area of analyte ( $A_m = 0.162 \text{ nm}^2$  for nitrogen) and  $N$  is the Avogadro number. The  $Q_m$  value for each sample was calculated using BET equation:

$$\frac{\frac{P}{P_0}}{Q * \left(1 - \frac{P}{P_0}\right)} = \frac{1}{Q_m * C} + \frac{C - 1}{Q_m * C} * \frac{P}{P_0} = (i + kx)$$

In BET equation,  $Q$  symbolizes the volume of analyte adsorbed at temperature  $T$  and pressure  $P$ ;  $P_0$  is the saturated vapour pressure of the analyte at  $T$ ;  $C$  is the constant term associated to heats of adsorption and liquefaction of analyte at  $B$  point of relative pressure ( $P/P_0$ ).

Using these equations, the value of specific surface area was found to be around  $511 \text{ m}^2/\text{g}$ ,  $96 \text{ m}^2/\text{g}$  and  $52 \text{ m}^2/\text{g}$  for PW,  $\text{WO}_3$  and PAN, respectively. Thus, PW nanocomposite possesses higher specific surface area for larger adsorption of analyte molecules as compared to  $\text{WO}_3$  and PAN samples. Moreover, the pore volume was evaluated using BET isotherm and found to be around  $9.332\text{E-}01 \text{ cc/g}$ ,  $2.854\text{E-}01 \text{ cc/g}$  and  $1.038\text{E-}01 \text{ cc/g}$  for PW,  $\text{WO}_3$  and PAN, respectively. Thus, the optimum porosity and larger surface area of PW nanocomposite attributes to larger sensing response towards  $\text{SO}_2$  as compared to that of  $\text{WO}_3$  and PAN samples.

### HR-XRD: Ordering

The HR-XRD patterns of  $\text{WO}_3$ , PAN and PW films recorded in the  $2\theta$  range of  $10^\circ$  to  $60^\circ$  are shown in Fig. 5. The diffraction pattern of  $\text{WO}_3$  film shows the presence of hexagonal phase of  $\text{WO}_3$  (JCPDS 85-2460) whereas, pristine PAN film doesn't reveal any traces of crystalline behaviour. A broad hump in the region  $2\theta = 20^\circ\text{-}30^\circ$  was caused by an amorphous glass substrate<sup>49</sup>. The HR-XRD pattern of PW composite shows a similar profile with  $\text{WO}_3$  film with surge in intensity. This surge in intensity suggests that  $\text{WO}_3$  nanoparticles are highly

dispersed in PAN matrix. The pattern exhibits three prominent peaks, which corresponds to ( 0 0 2 ), ( 2 0 0 ) and ( 2 0 2 ) planes of  $\text{WO}_3$ <sup>39</sup>. The peak positions observed in XRD pattern of PW composite reveals that there is mere change in crystalline structure of  $\text{WO}_3$  while prepared by in-situ polymerisation inside PAN matrix (which is consistent with results obtained in FTIR spectroscopy).

### **HR-TEM: Diffraction pattern**

The crystal structure and morphologies of the  $\text{WO}_3$  and PW hybrid nanocomposite are further characterized by using HR-TEM technique. From fig. 6 (a) it can be seen that  $\text{WO}_3$  nanoparticles are of quasi-spherical shape with average diameter less than 50nm. Fig. 6 (b) illustrates the honeycomb type morphology of PW hybrid nanocomposite. The selected area diffraction (SAED) pattern of PW hybrid nanocomposite has same characteristic rings as that of  $\text{WO}_3$  but accompanied with clouding from amorphous PAN. The interplanar spacing was calculated to be 0.383nm for both the samples, which consists with the ( 0 0 2 ) plane of the hexagonal phase of  $\text{WO}_3$  (JCPDS 85-2460), which is also confirmed by XRD studies.

### **UV-Visible study: Band gap**

The absorbance spectrum of PAN and PW hybrid composite is shown in Fig. 7. The band around 313 nm is assigned to  $\pi$ - $\pi^*$  electron transitions of benzenoid segments. The bands around 449 nm and 890 nm are attributed as polaron absorption band (due to radical cation formation) and bipolaron absorption band (due to dication formation), respectively. A shift of band from 890nm to 553 nm is observed in spectra of PW hybrid composite. This blue shift is attributed to charge compensation of positive charge on  $\text{WO}_3$  surface during insitu polymerization<sup>50</sup>. Such charge compensation leads to formation of n-type  $\text{WO}_3$ / p-type PAN heterojunctions. The optical band gap ( $E_g$ , in eV) was calculated using absorption edge values ( $\lambda$  edge, in nm) from absorption spectra by using<sup>51</sup>:

$$E_g = \frac{1240}{\lambda_{edge}}$$

The estimated values of  $E_g$  are 2.7 eV and 2.2 eV, for PAN and PW hybrid composites, respectively. It can also be observed from PAN spectra that leucoemeraldine part of PAN exhibit larger (higher than 3 eV) band gap whereas pernigraniline part possess lower (less than 2 eV) band gap<sup>52</sup>, whereas optical band gap of composite lies between them.

### Electrical Sensing Response

A reliable sensor is defined in terms of 3-S's, which are sensitivity, selectivity and stability. Thus, we have tried to optimize all 3-S in our sensing studies along with essential 5-R's i.e. recovery, repeatability, range, room temperature operation and reproducibility. The dynamic electrical sensing behaviours of fabricated sensing devices were recorded at room temperature in SO<sub>2</sub> environment. Fig.8 shows electrical sensing response of prepared PAN, WO<sub>3</sub> and PW hybrid nanocomposite based sensing devices towards 10 ppm of SO<sub>2</sub> as function of time at room temperature. It is observed that sensing response of PW hybrid nanocomposite based sensing devices (~10.6 %) is much higher than that of PAN based device (~4%), whereas negligible sensing response was observed for WO<sub>3</sub> based device at room temperature. The response time, which is defined as the 90% of dynamic response before saturation<sup>28</sup> is found to be around 160s for PAN and 180s for PW hybrid based sensing devices, respectively. It is also observed that the PAN sensor leads to saturation before 200s, whereas PW hybrid based sensor response sensor leads to saturation after 200s. The reason for this is can be attributed to lower conductivity of PW hybrid nanocomposite due to inclusion of WO<sub>3</sub> nanoparticles as compared to that of PAN sample. Thus, the PW hybrid sample contributes larger number of active sites having higher probability of oxidation. Thus, it gives better for SO<sub>2</sub> sensing. The response was found to be reversible (by purging in dry nitrogen gas) for both the cases with recovery time around 320s for PAN and

180s for PW based sensing devices, respectively. Though some fluctuations in recovery period for higher concentration  $\text{SO}_2$  were observed, but they corresponds to accumulation of desorbed  $\text{SO}_2$  ions near sensor surface due to limitation of sensing apparatus. This shows there is a weak interaction between analyte and sensing layers, as for stronger interactions reversible behaviour is not observed due to nucleophilic chemical reactions. Thus, the PW hybrid based gas sensing device shows high response, fast recovery and delayed saturation as compared to PAN based device. The reasons for such enhanced sensing behaviour of PW hybrid nanocomposite based sensing device are ascribed to the formation of heterojunctions within the nanocomposite (as confirmed from FTIR, HR-XRD, HR-TEM, UV-Vis and FE-SEM studies), to its honeycomb type morphology with optimum porosity (as observed from FE-SEM, BET and HR-TEM studies) and its branched chained structure (as observed from FTIR spectra). The sensing response for fabricated PAN and  $\text{WO}_3$  based sensing device at room temperature are found to be in accordance or rather improved as compared to that reported in the literature<sup>2-6, 32-37, 53-54</sup>. However, to the best of our knowledge, no reports on  $\text{SO}_2$  sensing using PW nanocomposite are found to be in literature. Also, the sensing parameters of PW hybrid nanocomposite based sensing device is found to be enhanced as compared to PAN/ $\text{WO}_3$  based sensors reported earlier<sup>2-11, 32-37, 53-54</sup>. It is further illustrated by a comparative analysis of present work with previously reported work in literature on  $\text{SO}_2$  sensing in table 1.

To further ensure its reliability for  $\text{SO}_2$  monitoring, the fabricated PW hybrid based sensing device was tested for different concentrations of  $\text{SO}_2$  (in ppm) at room temperature as shown in Fig. 9. The sensing response was found to be around 4.3%, 10.6%, 24%, 36%, 51.5% and 69.4% for 5ppm, 10ppm, 25ppm, 40ppm, 60ppm and 80ppm, respectively. It can be seen that the results were found to be repeatable at all ppm levels of  $\text{SO}_2$  (as observed for many consecutive cycles). This kind of reproducible sensing behaviour also indicates a weaker

interaction between analyte and sensing layer rather than any chemical reaction or strong bonding. From Fig. 10 it is observed that a surge in concentration (in ppm) of SO<sub>2</sub> gas leads to increase in sensing response of fabricated sensing device. This is due to the reason that at high concentration of analyte, its molecules cover more surface area of sensing layer. Due to this, the probability of adsorption of analyte molecules at active sites of sensing layer increases, which in turn increases the response of sensing device. This up surge in response with increase in concentration is found to be linear, which suggest that the fabricated sensor is reliable for SO<sub>2</sub> sensing in this dynamic range. Selectivity towards particular analyte molecules is one of the significant parameter of a sensing device to characterize it in terms of reliability. The selectivity of fabricated PW hybrid based sensing device (for different samples) was tested by subjecting it to various toxic analyte vapours such as ethanol, methanol, ammonia and hydrogen sulphide (10 ppm) at room temperature. It was found that the sensing device shows highest sensing response to SO<sub>2</sub> as compared to other analytes (Fig. 11). The reason can be ascribed to the characteristic of adsorbed analyte molecules and sensing layer. The PW –based sensor also showed significant response towards 10ppm of reducing analyte like ammonia. But in case of reducing analyte the surface resistance of PW hybrid increases due to the transfer of protons from –NH– ring of PAN to the analyte molecule<sup>28</sup>. Thus, the sensing operation of PW hybrid based sensor varies for oxidising (SO<sub>2</sub>)<sup>54</sup> and reducing (NH<sub>3</sub>) analytes, which can be taken care by electronic circuitry.

The fabricated sensor was also tested for its stability in ambient conditions. To test its stability and reproducibility, the sensing device was kept in atmospheric conditions for consecutive four weeks and its sensing response was recorded every week (at 10 ppm of SO<sub>2</sub>). A very less decent in sensing response was observed as shown in Fig. 12. This may be due to the presence of WO<sub>3</sub> in PW hybrid composites. Since polymers like PAN is reasonably sensitive to humidity due to adsorption of water molecule and interaction with

polymer backbone itself or with the donor molecule<sup>55</sup>. Thus, the study of influence of humidity on the prepared sensor is very necessary. To analyse the effect of humidity on PW sensor, we have recorded the value of surface resistance of the fabricated PW sensor as a function of relative humidity. It was perceived that as the value of humidity increases, the surface resistance decreases monotonously (Fig. 13). However, this decent is of negligible order. The reason for this can be ascribed to inclusion of  $\text{WO}_3$  into the polymer matrix, thereby reducing bare PAN sites for humidity adsorption. So, the PW sensor could be useful for environmental application at room temperature. Thus, fabricated sensing device was found to be reliable in terms of selectivity and stability.

### Gas Sensing Mechanism

The gas sensing mechanism in p-type conducting polymers (like PAN) is quite different as compared to that in inorganic semiconductors (like n- $\text{WO}_3$ ). It is observed that the resistance of PAN decreases on exposure to  $\text{SO}_2$  at room temperature. But  $\text{WO}_3$  nanoparticles show negligible response to  $\text{SO}_2$  up to  $200^\circ\text{C}$  within range of our experimental setup. However, as reported in literature  $\text{WO}_3$  nanoparticles sense  $\text{SO}_2$  in range of  $150^\circ\text{C}$ - $250^\circ\text{C}$  and resistance of  $\text{WO}_3$  increases on exposure to  $\text{SO}_2$ . In PAN, the mechanism of  $\text{SO}_2$  sensing may be explained in terms of charge compensation between p-PAN and electron acceptor  $\text{SO}_2$  as proposed in Fig.14. On interaction of PAN with  $\text{SO}_2$ , there may be transfer of electrons from p-PAN to electron accepting  $\text{SO}_2$ , which may results in decrease of resistance of PAN<sup>54</sup>. On the other hand, in semiconductor metal oxides like  $\text{WO}_3$ , grains are always covered with adsorbed oxygen ( $\text{O}_2$ ) molecules<sup>56</sup>. These adsorbed  $\text{O}_2$  molecules capture electrons from conduction band of metal oxide, which results in formation of chemisorbed oxygen species ( $\text{O}_2^-$ ,  $\text{O}^-$  and  $\text{O}^{2-}$ ) depending upon sensor's operating temperature (Fig. 15b: R1). For operating temperature less than  $100^\circ\text{C}$ , the oxygen ions exist in  $\text{O}_2^-$  form, whereas  $\text{O}^-$  and  $\text{O}^{2-}$  ions are produced for temperature more than  $100^\circ\text{C}$ . After adequate adsorption of oxygen

species, either depletion or inversion layer is formed on surface region of the grains (Fig.15a-b) <sup>57-58</sup>. When this system is exposed to sulphur dioxide gas, the SO<sub>2</sub> molecules extract electrons from conduction band of WO<sub>3</sub>, as well as react with the O<sub>2</sub>. This can be illustrated in terms of chemical reactions as:



This results in increase of width of depletion layer and decrease in conductivity of sensor device (Fig.15b), which is contrary to PAN case. When SO<sub>2</sub> molecules are flushed out, SO<sub>2</sub><sup>-</sup> got desorbed and sensing system recovers to its initial state. But the sensing mechanism is more complicated in hybrid nanocomposite systems due to presence of both p and n-type materials. The sensing mechanism of such systems may be explained in terms of formation of heterojunctions by band theory. In our case, it was observed that the resistance of PW hybrid nanocomposite decreases on exposure to SO<sub>2</sub>. Thus, it indicates that p-polyaniline dominates the charge transport during sensing mechanism. This can be explained in terms of energy band diagram constructed by using experimental values of band gap estimated by UV-Vis study. The schematic of energy band diagram for p-PAN (with Fermi level adjacent to valence band) and n-WO<sub>3</sub> (Fermi level adjacent to conduction band) and PW hybrid nanocomposite are shown in Fig. 16. It depicts the formation of depletion region in case of PW hybrid nanocomposite due to interaction of WO<sub>3</sub> nanoparticles with polymer matrix. On exposure to electron acceptor SO<sub>2</sub> molecules, the depletion region width decreases due to reduction in electrons. This decreases the resistance of the PW hybrid nanocomposite and increases its conductivity. This modulation in space charge region at the proposed heterojunction interface leads to enhanced sensing response of PW hybrid nanocomposite based sensing devices.

## Conclusions

The PW hybrid nanocomposite (possessing honeycomb type morphology) based sensing device was fabricated by insitu one pot assembly oxidative polymerization followed by spin coating technique. It was found that PW hybrid based sensing device shows enhanced SO<sub>2</sub> sensing characteristics than that of individual PAN nanofibres/WO<sub>3</sub> nanoparticles based devices. Based on FTIR and UV-vis investigations the plausible reason for enhanced sensing response is discussed in terms of formation of heterojunctions and energy band diagram. The modulation of modulation in space charge region at the proposed heterojunction interface leads to enhanced sensing response of PW hybrid nanocomposite. To the best of our knowledge, this is the first attempt to use PW hybrid nanocomposite for SO<sub>2</sub> monitoring application. The fabricated sensor works at room temperature (unlike WO<sub>3</sub> based devices) and possesses environmental stability (unlike PAN based devices). Thus, fabricated PW hybrid based sensing device is cost effective, consumes low power, easy to fabricate and operate, selective and possesses all the essential characteristics of reliable sensing device.

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Figure captions:

Fig. 1: Schematic of indigenously designed gas sensing setup.

Fig. 2: FTIR spectra of polyaniline (PAN), tungsten oxide ( $\text{WO}_3$ ) and polyaniline-tungsten oxide (PW) hybrid nanocomposite.

Fig. 3: SEM micrographs of fabricated (a) PAN (b)  $\text{WO}_3$  and (c) PW hybrid based sensing device.

Fig. 4: BET isotherm of prepared samples.

Fig. 5: XRD pattern of fabricated (a) PAN (b)  $\text{WO}_3$  and (c) PW hybrid based sensing device.

Fig. 6: HR-TEM images of (a)  $\text{WO}_3$  and (b) PW hybrid along with SAED patterns.

Fig. 7: Absorbance spectra of polyaniline (PAN), tungsten oxide ( $\text{WO}_3$ ) and polyaniline-tungsten oxide (PW) hybrid nanocomposite.

Fig. 8: Dynamic electrical gas sensing response of fabricated (a) PAN (b)  $\text{WO}_3$  and (c) PW hybrid based sensing device at 10 ppm of sulphur dioxide.

Fig. 9: Gas sensing response of fabricated PW hybrid based sensing devices for 10ppm, 25ppm, 40ppm, 60ppm and 80ppm of  $\text{SO}_2$ .

Fig. 10: Dynamic range of fabricated PW hybrid based gas sensing device.

Fig. 11: Selectivity of fabricated PW hybrid based gas sensing device.

Fig. 12: Stability of fabricated PW hybrid based gas sensing device.

Fig. 13: Response of PW sensor towards humidity.

Fig. 14: Sensing mechanism in Polyaniline nanofibres.

Fig. 15: (a) Effect of oxygen traps on  $\text{WO}_3$  surface. (b) Interaction of  $\text{SO}_2$  with  $\text{WO}_3$  nanoparticles.

Fig. 16: Energy band diagram for polyaniline (PAN), tungsten oxide ( $\text{WO}_3$ ) and polyaniline-tungsten oxide (PW) hybrid nanocomposite.

Table 1

S.No.	Sensing Material	Sensing Response (%)	Lowest Detection Limit	Operating Temperature (°C)	Reference
1.	WO <sub>3</sub> Nanoplates	1.25%	5 ppm	220	[2]
2.	SnO <sub>2</sub> thin film	1%	1 ppm	268	[6]
3.	ZnO tetrapods	0.2%	100 ppm	30	[7]
4.	DMEDA copolymer	6.6%	50 ppm	30	[28]
5.	PAN-CSA	1%	200 ppm	30	[29]
6.	PAN nanofibres	60%	100 ppm	30	[54]
7.	PAN nanoneedles	4.2%	10 ppm	30	[55]
8.	PAN nanofibres	3%	10 ppm	30	[55]
9.	PW nanocomposite	4.3%	5 ppm	30	Present work
10.	PAN nanofibres	4%	10 ppm	30	Present work

Table 1: A comparative analysis of present work with previously reported work in literature on SO<sub>2</sub> sensing.

Figures:











