



# Optical, morphological and thermal studies of polyaniline (PANI)-ZnS composites and their sensitivity performance towards ammonia

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## Abstract

*In the present study, optical, morphological and thermal studies of polyaniline (PANI)-ZnS composite are carried out and are tested for NH<sub>3</sub> sensing. The composites are prepared by chemical co-dispersion by preparing ZnS nanoparticles (NPs) in the same bath of PANI synthesis. The as prepared composite materials are studied for optical, morphological and thermal properties through UV-Visible, photoluminescence (PL), FTIR, FESEM and TGA. The sensitivity towards ammonia is measured through the measurement of the change in electrical resistance of the material on NH<sub>3</sub> intake. UV-Visible spectra show bands in the composite slightly red shifted compared to PANI. PL spectra shows some voids/defects related luminescence peaks which might act as site are to be suitable for gas sensing. FTIR spectra confirms the cross linking between PANI and ZnS. The FESEM study also confirms formation of nanocomposites. Addition of ZnS NPs effectively reduces the agglomeration of PANI and makes the composites more uniform and compact. PANI-ZnS composites show better thermal stability and follows three-dimensional diffusion mechanisms. The gas (NH<sub>3</sub>) sensing is due to exchange of electron at the surface and is dependent on the gas concentration.*

**Keywords:** Polyaniline, ZnS, Thermal studies, Nanocomposites, Ammonia, Sensitivity.

## Introduction

Conducting polymers (CPs) have attracted significant attention in the field of fundamental and technical research because of their unique features, such as simple method of preparation<sup>1,2</sup>, environmental stability, tuneable conductivity through reversible doping / dedoping, and ability of fast charging–discharging capacitance etc. The development of nano composites based on the combination of inorganic semiconducting and conducting polymer materials have been receiving significant research interest among the research communities due to wide range of potential applications of these composite materials in optoelectronic devices, gas sensors and electromagnetic interference (EMI) shielding<sup>3-9</sup>. Also, these show a synergetic behaviour between the two components<sup>10,11</sup>.

At nano scale, the large surface to volume ratio of this type of semiconducting nanomaterial is expected to modify the electrical and optical properties of the CP by a significant amount<sup>9</sup>. Among the family of conducting polymers, polyaniline (PANI) is one of most studied one due to its numerous optical applications in the visible region<sup>12</sup>.

Zinc sulphide (ZnS) is wide band gap II-VI semiconductor with wide range of applications in diverse fields, such as light emitting diodes, sensors, lasers and photocatalysis<sup>13-16</sup>. Also, the study of ZnS is very important as the properties like optical absorption and luminescence can be tuned by controlling the grain size of the material<sup>16</sup>.

The nanocomposites of PANI and ZnS have covered a great range of applications including light emitting diodes and gas sensors<sup>17-18</sup>. In the present articles, studies on optical, morphological, thermal and sensitivity performance towards ammonia of the as prepared PANI-ZnS composites are reported.

## Methodology

**Materials:** Materials utilized in the composite preparation are Aniline (0.1M), HCl(1M), Ammonium Persulphate (APS); Zinc Acetate dihydrate (Zn (CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>.2H<sub>2</sub>O) and Sodium sulphide (Na<sub>2</sub>S). Aniline is purchased from SD Fine Chemicals limited, APS from Fisher Scientific (India), Zinc acetate and sodium sulphide from Merck (India). Double distilled Aniline and deionised water are used in the synthesis process.

**Synthesis technique: Synthesis of ZnS:** For the synthesis of ZnS nanoparticles, 0.2M of Zn (CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>.2H<sub>2</sub>O is dissolved in 50ml of deionised water and stirred for 1 hr. NH<sub>4</sub>OH solution is added in the above solution to adjust pH value 7. Then, as the sulphur source (0.1M Na<sub>2</sub>S) in 50ml deionised water is dissolved and added to the earlier solution and stirred for another 4 hrs. The resultant solution is kept overnight for the growth of ZnS nanoparticles. The precipitates are collected after filtration and repeatedly washed with deionised water and acetone. The obtained ZnS is dried at room temperature to be used for further characterizations.

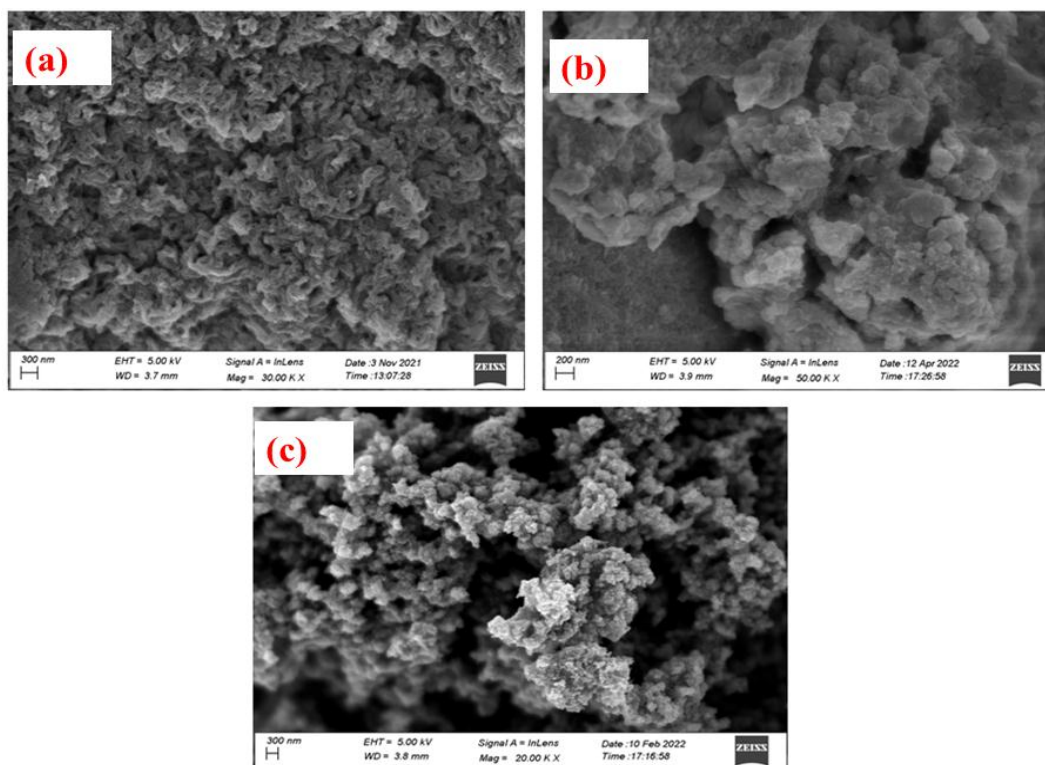
**Synthesis of PANI-ZnS nanocomposites:** Typically, 0.08g ZnS nano powder is dissolved in 10ml aq. Solution of HCl (1M) and ultrasonicated it for 1 hr. Then 0.1M Aniline in 10ml aq. HCl (1M) is added to the above solution and the solution is stirred for another 2 hrs under ice bath (0-5<sup>o</sup>C). The oxidizing agents, ammonium persulphate (APS) (0.25M) is dissolved in 10ml aqueous HCl(1M) solution and added drop wise to the above solution under vigorous stirring and kept stirred for another 3 hr to progress the polymerization reaction. The resultant solution is kept overnight at room temperature to complete the polymerization process. The precipitates obtained are collected after filtration and repeatedly washed with deionised water and acetone. The obtained nanocomposite is dried at room temperature and kept under vacuum to complete further characterization.

**Characterization techniques:** As-synthesized samples are characterized for morphological study by field emission secondary electron microscopy (FESEM Model: Zeiss sigma 300). The chemical structure and bonding characteristics are investigated through FTIR by Perkin Elmer Spectrum 1000. The UV-Visible absorption spectroscopic measurements are performed by employing UV-1900I. The TGA analysis for thermal studies is done by Mettler Toledo; TGA 2. The PL measurements are carried out using F-2700 FL Spectrophotometer. The gas sensing measurements are carried out by measuring the change in electrical resistance on gas exposure using computer interfaced Keithley 2400 Source meter.

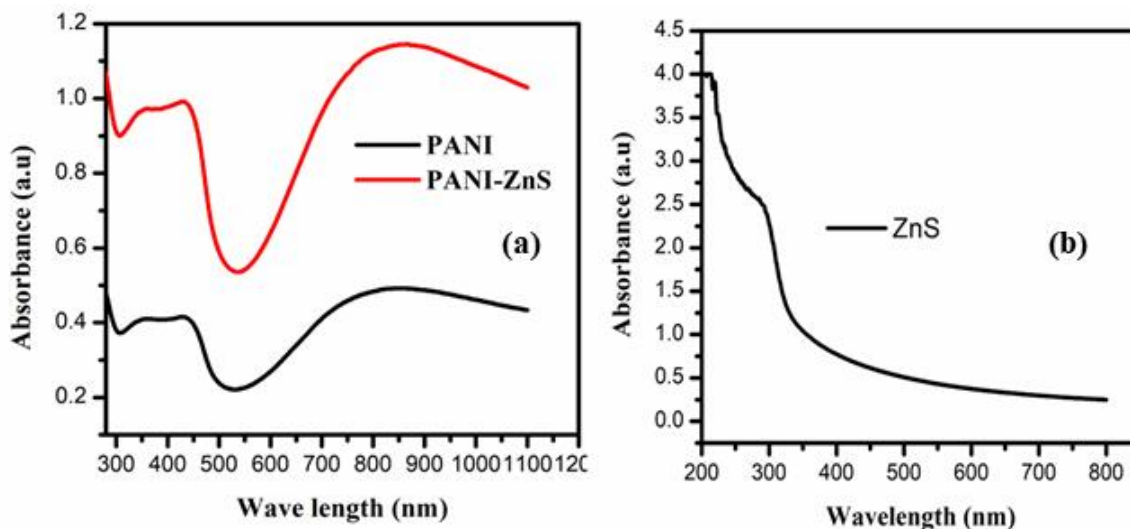
## Results and discussion

**FESEM Studies:** The FESEM images of the bare PANI, bare ZnS and PANI-ZnS composites are shown in Figure-1 (a), (b), (c). Bare PANI synthesized in the HCl medium shows some collection of a flake-like morphology and is shown in Figure-1 (a). Pure ZnS reveal nanosphere morphology, which are agglomerated as seen from Figure-1 (b) and the one for the composite in Figure-1 (c). This shows ZnS nanospheres attached to the surface of PANI matrix confirming successful penetration of the ZnS NPs into the PANI matrix. Moreover, the incorporation of ZnS NPs have effectively reduced the agglomeration of PANI, which is clear from the comparison of the images of Figure-1 (b) and (c), making the composite more uniform and compact.

**UV-Visible Studies:** The absorption spectra of bare PANI, bare ZnS and PANI-ZnS composites are shown in Figure-2 (a) and (b), Figure-2 (a) shows the spectra for PANI and the composite whereas Figure-2 (b) shows that of ZnS NP. From the Figure it is clear that bare PANI exhibits three main characteristic absorption peaks at 345 nm, 430nm and 850nm. These peaks are assigned to  $\pi$  to  $\pi^*$ , polaron to  $\pi^*$  band and  $\pi$  to localized polaronic band transitions of PANI respectively<sup>19,20</sup>. The absorption band edge near 326nm (Figure-2(b)) corresponds to the ZnS NPs<sup>21</sup>. The UV absorption peaks for the PANI-ZnS composite are slightly red shifted on incorporation of ZnS into the PANI matrix. This red shift suggests a decrease in the energy band gap<sup>17</sup>.



**Figure-1:** FESEM images of (a) bare PANI (b) bare ZnS and (c) PANI-ZnS composites.



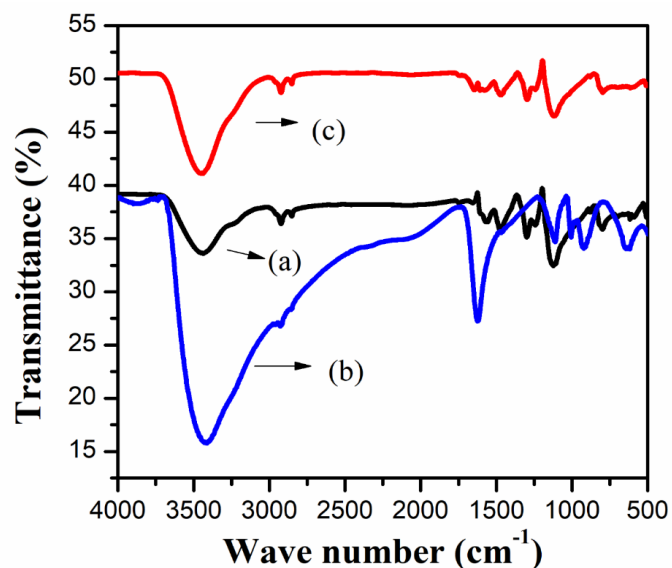
**Figure-2:** UV-Visible absorption spectra of (a) bare PANI and PANI-ZnS and (b) ZnS NP.

**FTIR studies:** Figure-3 shows FTIR spectra of bare PANI, ZnS and PANI-ZnS composite. The characteristic peaks near 1568, 1480, 1296, 1128 and 800 $\text{cm}^{-1}$  reveal the signature of doped PANI<sup>17</sup>. The transmittance bands near 1568 $\text{cm}^{-1}$  are assigned to both for C=N and C=C stretching modes of vibration at the quinonoid (Q) segments<sup>17</sup>. The band at 1480 $\text{cm}^{-1}$  is responsible for the stretching vibration of the aromatic ring at the benzenoid (B) segments of PANI<sup>17</sup>. The characteristic transmittance bands near 1296 $\text{cm}^{-1}$  attribute to the vibration of C-N of secondary aromatic amine and band at 1128 $\text{cm}^{-1}$  might be due to formation of polaronic band on doping of PANI<sup>17,22</sup>. In ZnS, the absorption peak at 1624 $\text{cm}^{-1}$  may be due to adsorbed CO<sub>2</sub> on ZnS surface<sup>23</sup>. The characteristic broad band's at 3440 $\text{cm}^{-1}$  for PANI is due to N-H stretching vibrations of amino groups in PANI and for ZnS the bands at 3420 $\text{cm}^{-1}$  due to O-H stretching vibrations<sup>24,25</sup>. Moreover, it is also observed that all the significant bands of PANI and ZnS are present in the PANI-ZnS composites with little shift in peak position. Hence, one can conclude that there is a crosslink between PANI and ZnS.

**PL studies:** The PL spectra of bare ZnS and polyaniline (PANI)-ZnS composites are shown in Figure-4(a). The PL studies are done by dispersing the sample in ethanol exciting with wavelength of 290 nm. Pure ZnS shows one strong luminescence peak at 327nm and another small hump at 410 nm. The peak at 327nm is due to band-to-band transition<sup>26</sup>. The weak hump might be due to interstitial zinc and sulphur vacancies<sup>27</sup>. These defects are usually present at the surface of ZnS nanomaterials prepared by chemical methods. The schematics of electronic transitions are shown in Figure-4(b).

**Thermal studies:** Thermal studies are done through thermo gravimetric analysis (TGA) of the samples. The TGA results of bare PANI and PANI-ZnS composites are depicted in Figure-5. Bare PANI suffers three steps of weight losses. The first step of temperature ranges from 30 $^{\circ}\text{C}$ -150 $^{\circ}\text{C}$  due to elimination of impurities, moisture content in the polymer matrix. The second

one in the range of 150 $^{\circ}\text{C}$ -330 $^{\circ}\text{C}$  might be due to removal of the dopant molecules from the polymer structure<sup>28,29</sup>. Weight loss beyond 440 $^{\circ}\text{C}$  due to structural decomposition of PANI backbone. TGA graph shows weight loss beyond 330 $^{\circ}\text{C}$  is slowed down in case of PANI-ZnS compared to bare PANI. This might be due to interlink age between PANI and ZnS to stabilize the polymer.



**Figure-3:** FTIR spectra of (a) bare PANI (b) bare ZnS and (c) PANI-ZnS composites.

**Kinetic analysis of TGA data:** Determination of the thermal activation energy, pre-exponential factor and order of reaction are considered as most essential parameters to get an insights of a reaction mechanisms in solid phases. The decomposition reaction of solid under non isothermal condition is described in equation<sup>30</sup>

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(\frac{-E}{RT}\right) f(\alpha) \quad (1)$$

Where  $\beta$  is linear constant heating rate;  $\alpha$  is degree of conversion;  $f(\alpha)$  differential conversion function;  $A$  is pre-exponential factor;  $E$  is the activation energy and  $T$  is the reaction temperature.

In the present study, modified Coats-Redfern equation<sup>31</sup> is used to evaluate kinetic parameters for degradation of synthesized PANI and PANI-ZnS composites using the equation

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad (2)$$

The conversion rate and the dependency of  $g(\alpha)$  for 1-D diffusion mechanism (D1),  $g(\alpha) = \alpha^2$ , for 2-D diffusion mechanism (D2),  $g(\alpha) = (1 - \alpha) \ln(1 - \alpha) + \alpha$  and for 3-D diffusion mechanism (D3),  $g(\alpha) = [1 - (1 - \alpha)^{1/3}]^2$ .  $\ln g(\alpha)/T^2$  vs  $1/T$  plots are shown in Figure-6,7,8 for 1, 2 and 3-D diffusions respectively. One can calculate apparent activation energy from the slope of the plots using all the three-diffusion mechanism for bare PANI and PANI-ZnS composites. The apparent activation energy is found to increase from 3.97 kJ/mol to 4.10kJ/mol in case of bare PANI and for PANI-ZnS composites 21.8kJ/mol to 25.22kJ/mol respectively. Also, it is observed that the 3-D diffusion model fits best in the present system and apparent activation energy also increases from D1 model to D3.

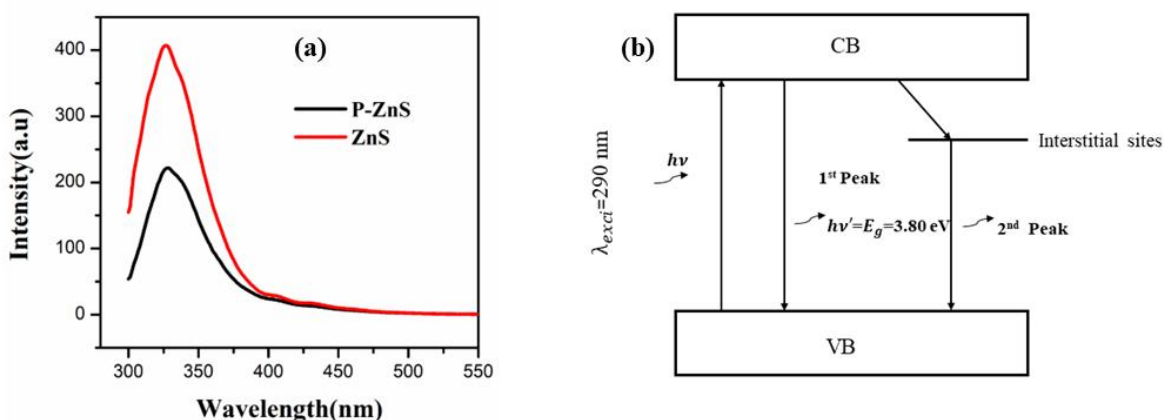


Figure-4: (a) PL Spectra of ZnS and PANI-ZnS composites and (b) Electronic transitions of ZnS NPs.

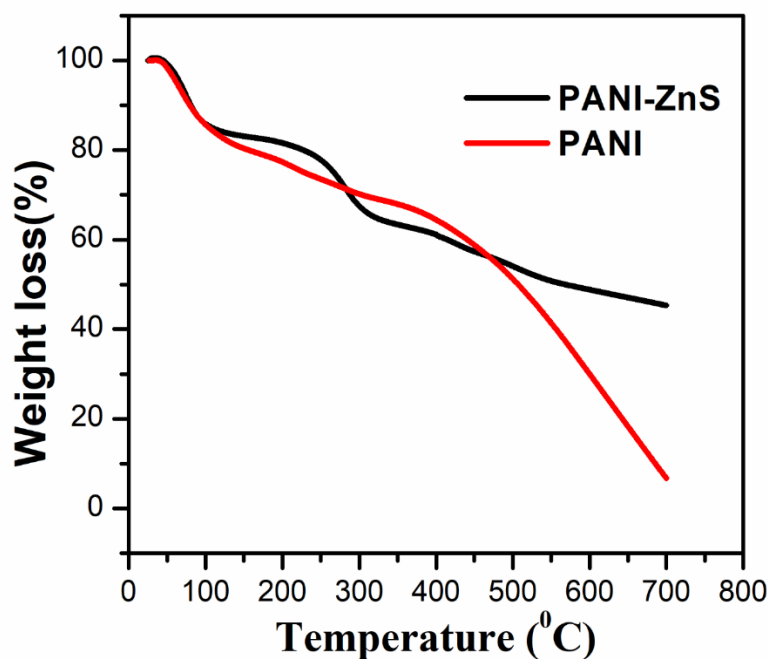


Figure-5: TGA thermograph of PANI and PANI-ZnS composites.

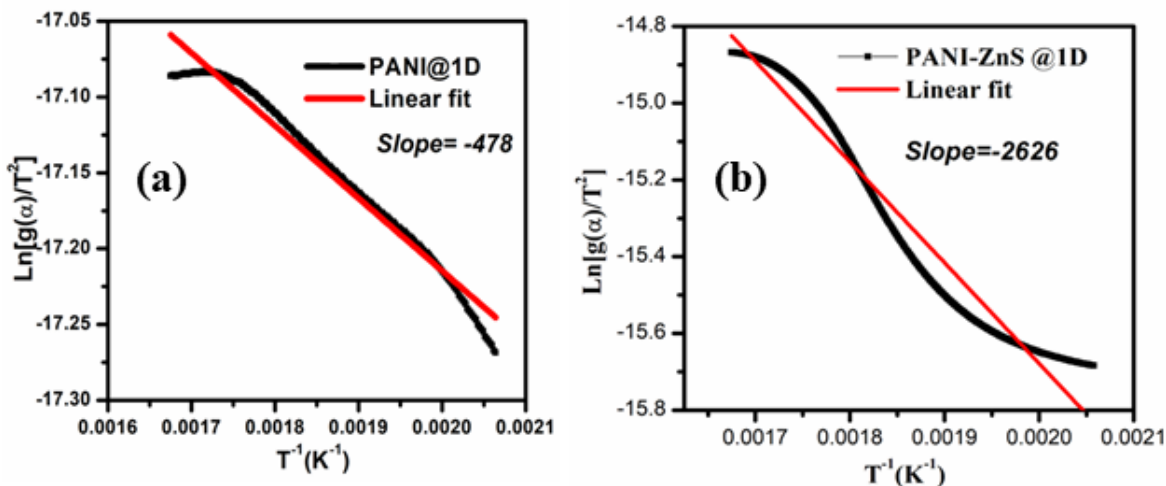


Figure-6: 1-D diffusion model (D1) for (a) bare PANI and (b) PANI-ZnS composites.

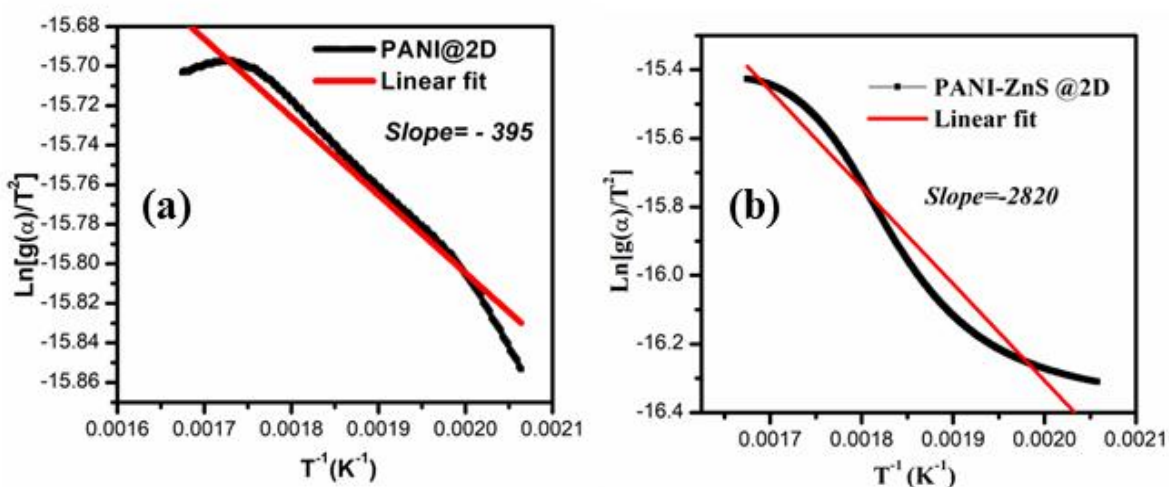


Figure-7: 2-D diffusion model (D2) for (a) bare PANI and (b) PANI-ZnS composite.

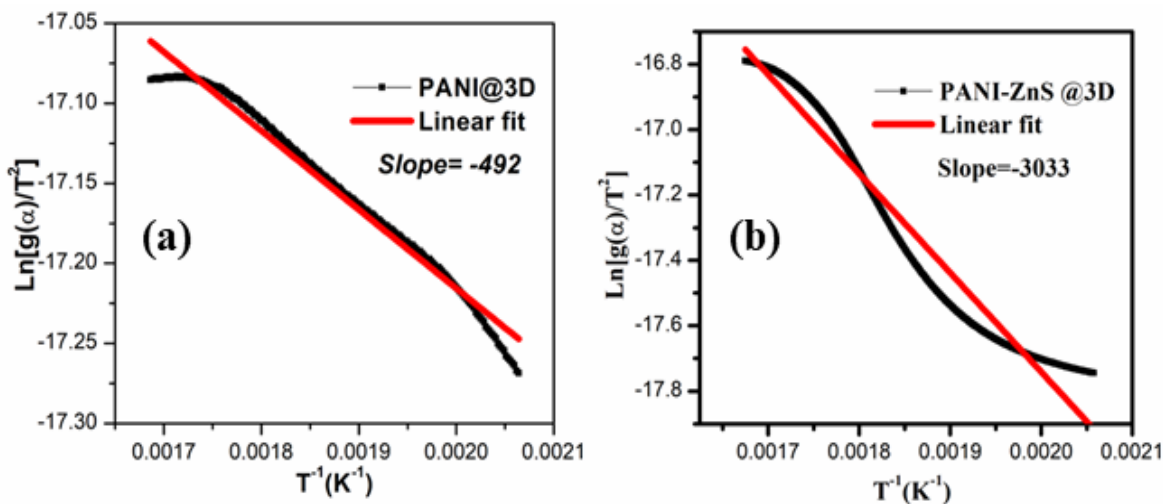
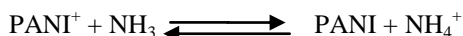


Figure-8: 3-D diffusion model (D3) for (a) bare PANI and (b) PANI-ZnS composite.

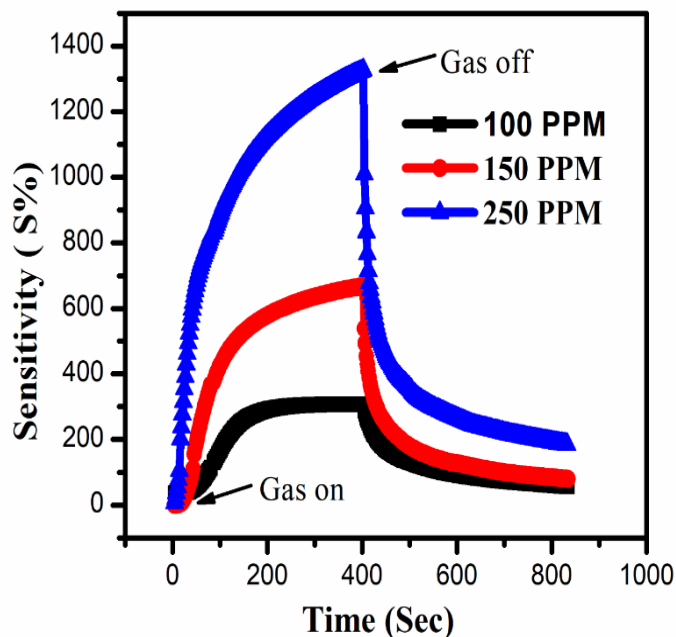
**Sensing performance of PANI-ZnS composite upon exposure of ammonia (NH<sub>3</sub>):** The gas sensing study of the present report is done in terms of change of electrical resistance on intake of a target gas. This may be due to exchange of electron at the surface of the sensing materials. In bare PANI sensor, the gas response is believed to be mainly due to protonation/deprotonation on absorption and desorption of the gas molecules<sup>32</sup>. PANI exists in two most common states i.e., emeraldine salt (conducting) and emeraldine base (insulator). As NH<sub>3</sub> behaves as an electron donor<sup>33</sup> so, on exposure to NH<sub>3</sub> conducting states of PANI converts to insulating states and so increase in the electrical resistance. The reaction mechanism can be described as<sup>34</sup>



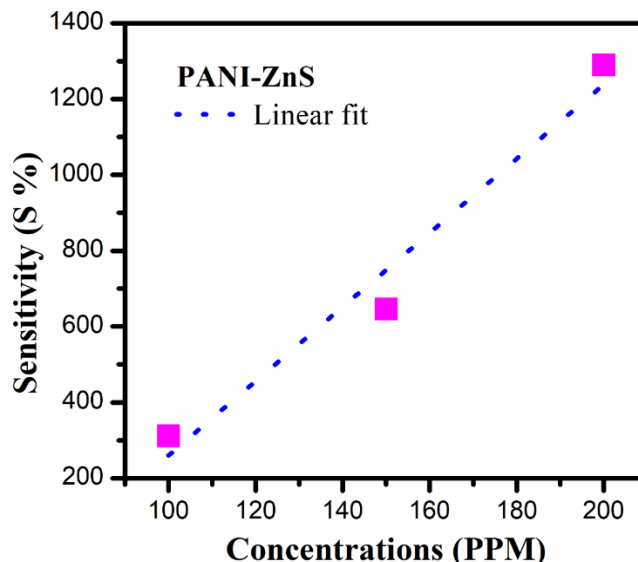
The sensitivity (S%) of a sensor is measured in terms of electrical resistance in presence of target gas and in air using eq.<sup>32</sup>

$$\text{Sensitivity (S\%)} = \frac{R_g - R_a}{R_a} \times 100\%$$

Where: R<sub>g</sub> and R<sub>a</sub> represents electrical resistances on gas intake and in ambient air respectively. The sensitivity performance of the PANI-ZnS sensor for different concentrations of NH<sub>3</sub> is shown Figure-9. From the sensitivity plot, it is observed that the response of the sensor film increases continuously on exposure to NH<sub>3</sub> within a few minutes. The sensor response (S%) is found to increase with increase in NH<sub>3</sub> concentration, which is shown in Figure-10.



**Figure-9:** Gas responses of PANI-ZnS towards various ammonia concentrations.



**Figure-10:** Sensitivity vs concentration plot of the composite film.

### Conclusion

In the present study, the PANI-ZnS composite is successfully synthesized by chemical polymerization technique. Optical and morphological study reveals the successful composition of ZnS with the polymer matrix. Thermal studies explain better stability of PANI-ZnS composite compared to the bare PANI. Kinetic studies on degradation of PANI and PANI-ZnS composite showed good thermal stability and follows three-dimensional diffusion mechanisms (D3). Also, NH<sub>3</sub> sensitivity performance of the PANI-ZnS composite showed increase in sensitivity with ammonia concentration.

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