

Study of LPG Gas Sensing on PANI/TiO₂ Nanocomposite

Shubhra Mathur^{1*}, Rohit Jain²

¹Department of Physics, Jagannath Gupta Institute of Engineering & Technology, Sitapura Industrial Area, Tonk Road, Jaipur, 302022, Rajasthan, India

²Department of Physics, Lachoo Memorial college of Science & Technology, Sector- A, Shastri Nagar Jodhpur, 342001, Rajasthan, India

Date of Submission: 25-11-2021

Date of Acceptance: 11-12-2021

ABSTRACT: Sol-gel method is employed to prepare TiO₂ nanopowder using titanium isopropoxide (TTIP) and methanol as starting materials. The obtained TiO₂ specimen is annealed at 500°C for 1 hour in air. Polyaniline doped with TiO₂ is obtained by adding 0.2 g of TiO₂ nanopowder annealed at 500°C during the preparation of polyaniline by oxidative polymerization. Therefore polyaniline (PANI)/TiO₂-500°C nanocomposite is obtained. The prepared TiO₂ nanopowder is in the form of pure anatase phase as revealed by X-ray diffraction pattern. The formation of PANI/TiO₂ nanocomposite is confirmed by the presence of TiO₂ peaks in polyaniline. Energy band gap value is calculated using UV spectrum. Hence the energy band gap value of PANI/TiO₂-500°C nanocomposite is 2.70 eV. Surface morphology of the specimen is studied by Scanning electron microscopy (SEM) and the bonds present in PANI/TiO₂-500°C nanocomposite are depicted by Raman spectroscopy. LPG gas sensing of PANI/TiO₂-500°C nanocomposite is studied. The gas sensing studies shows that PANI/TiO₂-500°C nanocomposite exhibits sensitivity towards LPG gas at room temperature and its sensitivity increases with increase in temperature. PANI/TiO₂-500°C nanocomposite also shows sensitivity towards LPG gas in the presence of other gases at room temperature and at 200°C. Therefore PANI/TiO₂-500°C nanocomposite may play an important role for industrial applications.

KEYWORDS: Polyaniline, LPG, Gas Sensing, Band Gap, Titanium Dioxide

I. INTRODUCTION

Polyaniline (PANI) is considered as an important polymer because its electrical and optical properties can be changed by oxidation and protonation of the amine nitrogen atoms. Polyaniline is widely used in batteries, sensors, electronic devices, supercapacitors and corrosion protection. The properties of hybrid material become more

pronounced when at least one of the fractions corresponds to nanometric scale [1-5]. Recently nano form of polyaniline also attracted considerable interest due to its enhanced performance in the field of gas sensing, chemical analysis and light emitting diode [6-7].

The doping of metal oxides in organic polymer is a great deal of interest for researchers due to its wide range of applications in the field of gas sensing, solar cell, optical devices and oxidation catalysts [5]. It was reported that doping of TiO₂ in polyaniline improves its structural, electrical and optical properties which enhances its application in gas sensing [3, 8-9].

Liquefied petroleum gas (LPG) is used both for domestic and industrial purpose. The gas is highly inflammable in nature and its leakage can cause major accidents. Several researchers work in the field of LPG gas sensor but to achieve low operating temperature of sensor is still an investigating task [1, 10]. Therefore it will be interesting to prepare a polyaniline nanocomposite doped with TiO₂ which works at room or low operating temperature.

II. EXPERIMENTAL

Titanium isopropoxide and methanol are used as starting material to prepare TiO₂ nanopowder by sol-gel method. PANI/TiO₂ nanocomposite is prepared by adding 0.2 g of TiO₂ nanopowder annealed at 500°C during the formation of polyaniline by oxidative polymerization method. In the preparation of polyaniline the molar ratio of ammonium per sulphate and aniline is kept 1.2:1 in 3M HNO₃ aqueous medium. 0.2 g of TiO₂ nanopowder annealed at 500°C is mixed in the solution of ammonium per sulphate [3]. This solution is added dropwise in the aniline solution during stirring by magnetic stirrer at room temperature. The polymerized sample is washed with deionized water and filtered. Hence the obtained PANI/TiO₂-500°C nanocomposite is dried on hot plate.

III. RESULTS

X-ray diffraction pattern (XRD) of PANI/TiO₂-500^o C is recorded using CuK_α radiation as shown in Fig.1. The crystallite size of PANI and TiO₂ in PANI/TiO₂-500^o C nanocomposite is calculated using Debye Scherrer's formula [11]

$$D = 0.89 \lambda / \beta \cos \theta \quad (1)$$

where D is crystallite size in nanometer, β is the full width at half maximum (FWHM) in radian, λ is the wavelength of the X-ray which is 0.15406 nm for Cu target K α radiation and θ is the Bragg angle.

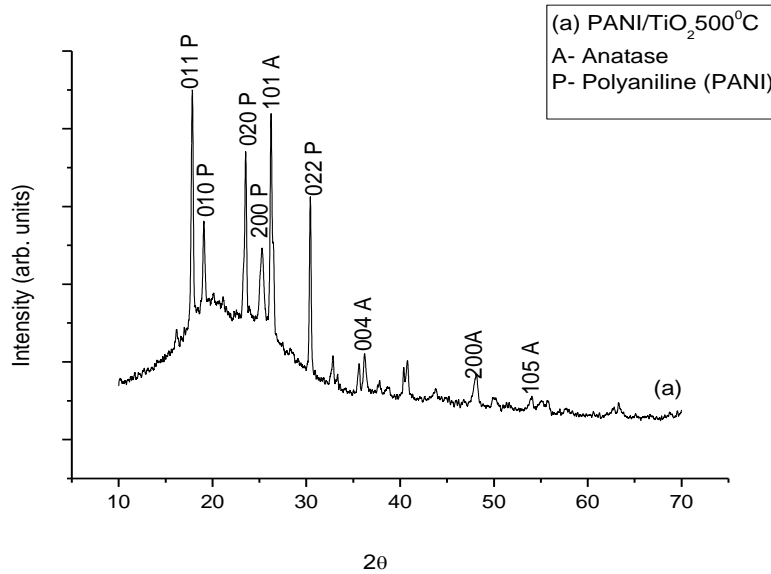


Fig. 1: X-ray diffraction pattern of PANI/TiO₂-500^o C nanocomposite.

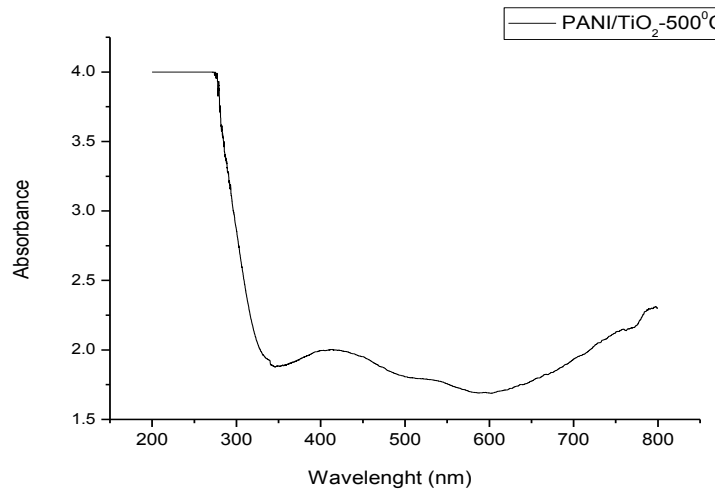


Fig. 2 (a)

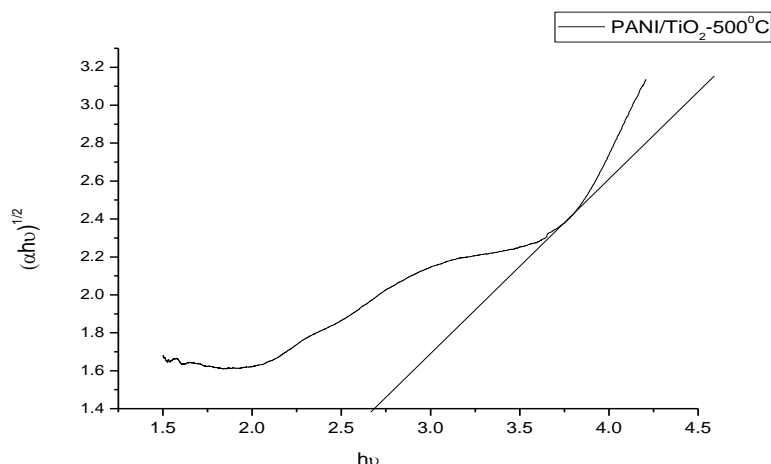


Fig. 2 (b)

Fig. 2: PANI/TiO₂-500⁰C nanocomposite (a) UV spectrum and (b) Tauc plot.

Fig.2 (a) and Fig.2 (b) shows UV spectrum recorded using Shimadzu UV-1800 and Tauc plot of PANI/TiO₂ nanocomposite. The energy band gap is calculated by extrapolating linear region of Tauc plot to X- axis [3]. The crystallite size of PANI and TiO₂ in PANI/TiO₂ nanocomposite and its energy band gap value is mentioned in Table 1.

Fig. 3 (a) and Fig. 3(b) show scanning electron microscopy (SEM) image and Raman spectrum of

PANI/TiO₂ nanocomposite. The SEM image depicts cylindrical form of TiO₂ in PANI matrix. In Raman spectrum the band located at 1360 cm⁻¹ corresponds to the C-N+ bond which confirm the conducting nature of PANI and the band located near 1580 cm⁻¹ indicates C-N stretching from quinoid (Q) structure [3].

Table 1: Crystallite size and energy band gap value of PANI/TiO₂ specimen

Specimen	Crystallite Size	Energy band gap
PANI/TiO ₂ -500 ⁰ C nanocomposite	PANI-25±5 nm TiO ₂ - 15±5 nm	2.70 eV

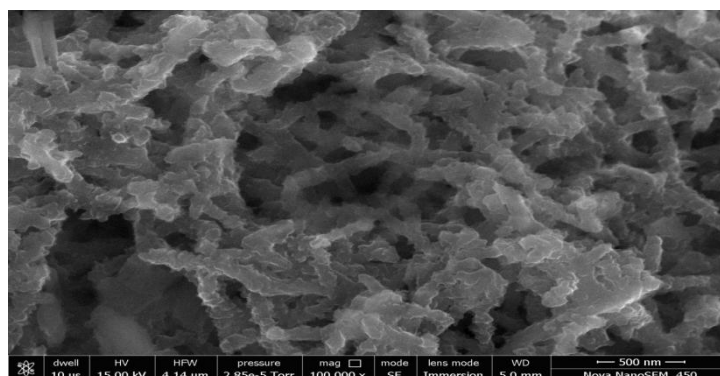


Fig. 3 (a)

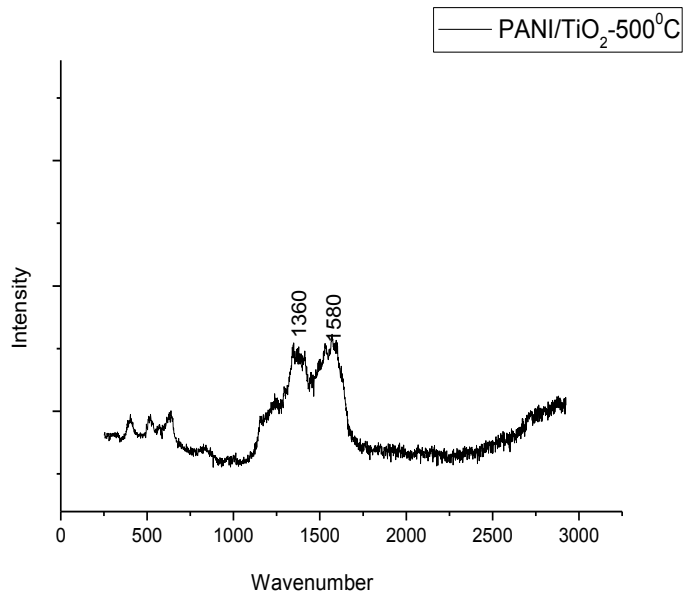


Fig. 3 (b)

Fig. 3: (a) SEM image and (b) Raman spectrum of PANI/TiO₂ nanocomposite prepared by adding TiO₂ nanopowder annealed at 500°C.

Gas sensing measurement is performed on PANI/TiO₂-500°C nanocomposite for LPG as shown in Fig. 4 (a). The sensor response of the gas sensor can be calculated using formula [12]

$$\text{Sensor Response (S.R.)} = (R_a - R_g / R_a) \quad (2)$$

where R_a and R_g represents the resistance of the sensor in air and in the sample gas respectively. Fig. 4 (b) shows the sensitivity of PANI/TiO₂-500°C nanocomposite for LPG in the presence of other gases at room temperature and at 200°C.

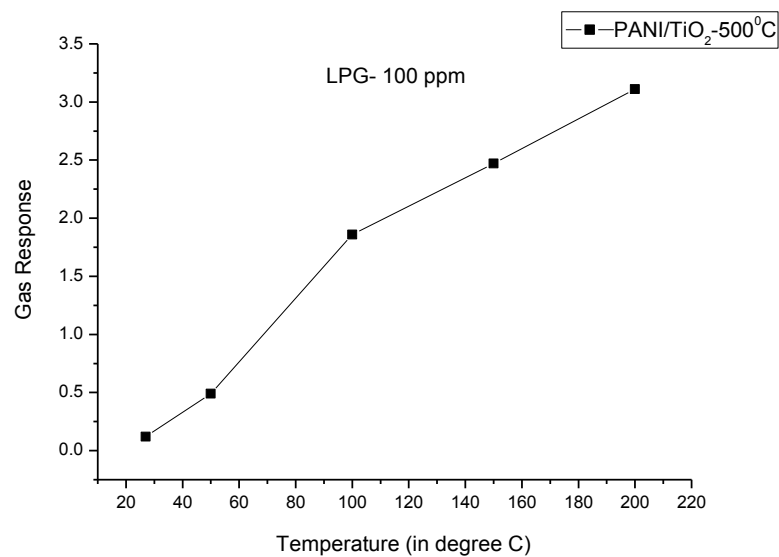


Fig. 4 (a)

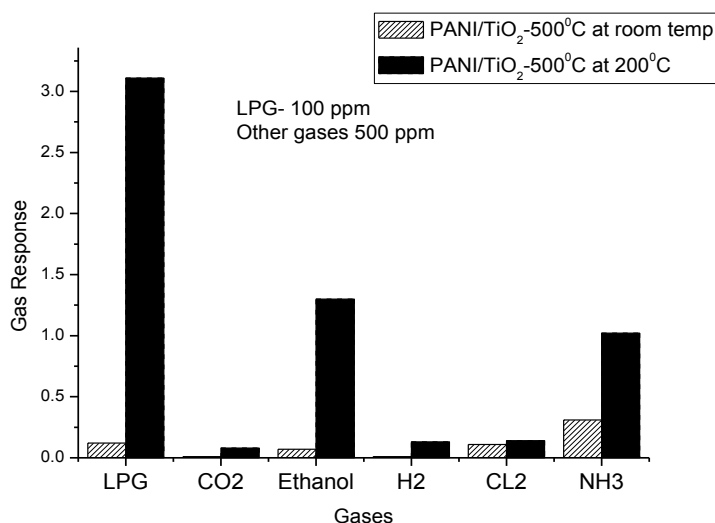


Fig. 4 (b)

Fig. 4: PANI/TiO₂-500°C nanocomposite showing (a) sensitivity (b) selectivity towards LPG

IV. DISCUSSION

X-ray diffraction pattern (XRD) of PANI/TiO₂- 500°C nanocomposite shows anatase phase of TiO₂. The presence of TiO₂ peaks in polyaniline confirms the formation of PANI/TiO₂ nanocomposite. It is observed from Table 1 that crystallite size of PANI and TiO₂ in PANI/TiO₂-500°C specimen corresponds to nanometer range. The nano form of polyaniline gain considerable attention in recent years due to its enhanced performance in gas sensing. The doping of TiO₂ in PANI reduces energy band gap value of PANI/TiO₂-500°C nanocomposite as compared to pure TiO₂ [13-15].

PANI/TiO₂-500°C nanocomposite shows sensitivity towards LPG at room temperature and sensitivity increases with increase in temperature. It may occur due to the fact that increase in operating temperature increases the rate of surface reaction of the target gas and therefore sensitivity increases [16]. PANI/TiO₂-500°C nanocomposite also shows sensitivity towards LPG in the presence of other gases at room temperature and at 200°C. Further the increase in sensitivity and selectivity of PANI/TiO₂-500°C nanocomposite occurs due to trapping of LPG molecules and surface reaction on nanostructured TiO₂. Hence commercial LPG sensor using this nanocomposite material may work at low operating temperature which may increase the life time of sensor element [5].

V. CONCLUSION

1. PANI/TiO₂-500°C nanocomposite exhibits sensitivity towards LPG gas at low operating temperature and in the presence of other gases.
2. Doping of TiO₂-500°C nanopowder in PANI reduces energy band value to 2.70eV.

ACKNOWLEDGEMENT

Authors thank Science and Engineering Research Board (SERB) for providing financial grant vide no SERB/F/5303/2014-15, Dr D. R. Patil, Bulk and Nanomaterials Research Laboratory, Head, Dept. of Physics, Rani Laxmibai Mahavidyalaya Parola, Jalgaon for providing gas sensing facility, CSIR-National Physical Laboratory (NPL) New Delhi for XRD facility and MRC, MNIT, Jaipur for Raman as well as SEM facilities.

REFERENCES

- [1]. Bairi V G, Bourdo S E, Sacre N, Nair D, Berry B C, Biris A S and Viswanathan T, "Ammonia gas sensing behaviour of tanninsulfonic acid doped polyaniline-TiO₂ composite", *Sensors* 2015 (15) 26415-26429.
- [2]. Parveen A and Roy A S, "Effect of morphology on thermal stability of core-shell polyaniline/TiO₂ nanocomposites", *Adv. Mat. Lett.* 2013, 4 (9) 696-701.
- [3]. Mathur S, Arya M, Jain R and Sharma S. K. "A comparative study of structural, optical and electrical properties of PANI and PANI/TiO₂ nanopowder", *Advanced Science, Engineering and Medicine* 2018 (10) 1-3.
- [4]. Tai H, Jiang Y, Xie G, Yu J and Chen X, "Fabrication and gas sensitivity of polyaniline- titanium dioxide nanocomposite thin film", *Sensors and Actuators B* 2007 (125) 644-650.
- [5]. Parveen A, Koppalkar A K and Roy A, "Liquefied petroleum gas sensing of polyaniline-titanium dioxide nanocomposites", *Sensor Letters*, 2012 (10) 1-7.
- [6]. Deshpande N, Chakane S, and Borude R, "Synthesis and Characterization of Polyaniline, using Different Dopant for Sensing Application of Pollutant Gases", *Journal of Atomic, Molecular, Condensate and Nano Physics* 2016 (3) 27-33.
- [7]. Mostafaei A, and Zolriasatein A, "Synthesis and characterization of conducting polyaniline nanocomposites containing ZnO nanorods", *Progress in Natural Science: Materials International*, 2012 (22) 273-280.
- [8]. Zhang L. X, Liu P, and Su Z. X, "Preparation of PANI/TiO₂ nanophotocatalysts and their solid-phase photocatalytic degradation", *Polymer Degradation and Stability* 2006 (91) 2213-2219.
- [9]. Wu Y, Yin Y. D, Zhang X. L, and May S. C, "Preparation of ternary PANI modified TiO₂-HGM nanocomposite and its photocatalytic activity for nitride", *Digest Journal of Nanomaterials and Biostructures*, 2016 (11) 927-933.
- [10]. Sadanand Pandey, "Highly sensitive and selective chemiresistor gas/vapor sensors based on polyaniline nanocomposite: A comprehensive review", *Journal of Science: Advanced Materials and Devices* 2016 (1) 431-453.
- [11]. Dai S, Wu Y, Sakai T, Du Z, Sakai H and Abe M, "Preparation of highly crystalline TiO₂ nanostructures by acid-assisted hydrothermal treatment of hexagonal-structured nanocrystalline titania/cetyltrimethylammonium bromide nanoskeleton", *Nanoscale Research Letters* 2010 (5) 1829-1835.
- [12]. Pandey S, "Highly sensitive and selective chemiresistor gas/vapor sensors based on polyaniline nanocomposite: A comprehensive review", *Journal of Science: Advanced Materials and Devices*, 2016 (1) 431-453.
- [13]. Hanaor D A H and Sorrell C C, "Review of the anatase to rutile phase transformation", *J. Mater Sci.* 2011 (46) 855-874.
- [14]. Pawar S, Chougule M, Patil S, Raut B, Dalvi D, Patil P, Sen S, Joshi P and Patil V, "Fabrication of nanocrystalline TiO₂ thin film ammonia vapor sensor", *Journal of Sensor Technology* 2011 (1) 9-16.
- [15]. Pawar S G, Chougule M A, Godse P R, Jundale D M, Pawar S A, Raut B T and Patil V B, "Effect of annealing on structure, morphology, electrical and optical properties of nanocrystalline TiO₂ thin films", *J. Nano Electron. Phys.* 2011 (3) 185-192.
- [16]. Yousif A A and Hasan M H, "Gas sensitivity and morphologically characterized of nanostructure CdO doped In₂O₃ films deposited by pulsed laser deposition," *J Biosens Bioelectron* 2015, 6 (192) 1-7.