

# Electrical, Structural and Gas Sensing Properties of Polyaniline/DBSA-Fullerene Nanocomposite

M. Nagaraja, Sushma Prashanth, Jayadev Pattar, H.M. Mahesh

**Abstract:** By employing chemical route PANI/DBSA-C<sub>60</sub> (Polyaniline/Dodecyl benzene sulfonic acid -Fullerene) nanocomposite is synthesized by using ammonium persulfate and DBSA as oxidizing agent and acid dopant respectively. Synthesized samples are characterized for FTIR (Fourier Transform Infrared Spectroscopy), SEM (Scanning Electron Microscope), XRD (X-ray diffraction), electrical conductivity using standard four probe method and methanol gas sensing properties. The FTIR spectrum illustrates the existence of interaction between polyaniline and fullerene. XRD spectra prove the formation of PANI/DBSA-C<sub>60</sub>. In collaboration with these, SEM images also indicate the highly branched chain structure of the PANI in the presence of C<sub>60</sub>. The PANI/DBSA-C<sub>60</sub> showed the electrical conductivity more than over pure PANI/DBSA. The gas response of the PANI/DBSA-C<sub>60</sub> nanocomposite towards different concentration of methanol was examined and compared with that of the pure PANI/DBSA. The PANI/DBSA-C<sub>60</sub> was observed higher methanol gas sensing capacity compared to pure PANI/DBSA.

**Keywords:** Conductivity, Nanocomposite, Polyaniline, Sensor

## I. INTRODUCTION

In recent years conducting polymer nanocomposite materials are very useful in the applications of Microelectronics, Biosensors, Actuators, Supercapacitors, Microwave absorbing materials and Light emitting diodes due to various advantages [1]. Amongst researchers polyaniline is having much interest because it encompasses of diverse structure, doping mechanism, environmental stability, processability and high in conductivity. It also gives important interesting properties such as chemical sensitivity and multicolor electrochromism that are essential characteristics required for electronic devices [2]. The conducting polymer nanocomposite with the inclusion of fullerene (C<sub>60</sub>) has attracted considerable scientific and technological attention because it exhibits a novel combination of electrical, optical and mechanical properties [3-11]. These properties play important role in designing and fabrication of organic electronic device such as solar cells and sensor devices etc. Also, the incorporation of C<sub>60</sub> in the conducting polymer chain, polymers undergo an ultrafast electron transfer and fullerene molecules may serve as electron-acceptors in conducting polymer based electronic

devices [12]. This paper presents systematic studies on effect of C<sub>60</sub> on electrical, structural and methanol gas sensing properties of PANI/DBSA.

## II. EXPERIMENTAL

### A. Materials

The monomer aniline (C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>) and APS (ammonium persulfate) (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> are purchased from Merck. Aniline is purified by distillation and APS (oxidizing agent) is used as received. DBSA (Dodecylbenzene Sulfonic Acid) C<sub>12</sub>H<sub>25</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H (purchased from Sigma Aldrich) was used as dopant. High purity (99.99%) C<sub>60</sub> was obtained from SES Research.

### B. Preparation of PANI/DBSA-C<sub>60</sub> Nanocomposite

A blend of aniline-DBSA was obtained by mixing of aniline of weight 0.4g and DBSA of 1.44g in 30 ml of water and stirred for nearly 30 min until obtaining the aniline-DBSA emulsion. This solution is pre-cooled at 0 °C and the 20 wt% C<sub>60</sub> (with respect to aniline) was added to reaction chamber and this mixture was stirred thoroughly for about 2hrs. Later APS of 0.98g dissolved in 5ml of water. This APS solution is slowly added drop wise to reaction beaker and left it to polymerize at 0-10 °C for 5 hrs. Lastly, the obtained solution is filtered and washed with methanol and dried in oven at 80 °C for 4hrs. To obtain pure PANI/DBSA above procedure is followed with the exception of C<sub>60</sub> particles.

### C. Instrumentation

FTIR spectra are obtained by using the instrument Nicolet-FTIR-IMPACT- 420-DSP in the spectral range of 4000-400 cm<sup>-1</sup>. XRD-Patterns are obtained by using PHILIPS-JW-3710 X-Ray-Diffractometer with Ni-Filtered Cu-K $\alpha$  radiation. By using the instrument of JOEL-JSM-35-LF SEM micrographs are recorded. In order to measure the electrical conductivity, powder samples are made into pellets. Then, by employing standard 4-probe method electrical conductivity of the samples are measured.

Revised Manuscript Received on June 22, 2020.

\* Correspondence Author

M. Nagaraja\*, Dept. of Physics, Sri Siddhartha Institute of Technology, Tumakuru-572105, India. Email: madihally.nagaraja@gmail.com

Sushma Prashanth, Dept. of Physics, Sri Siddhartha Institute of Technology, Tumakuru-572105, India.

Jayadev Pattar, School of Physics, REVA University, Bengaluru-560064, India.

H.M. Mahesh, Dept. of Electronic Science, Bangalore University, Bangalore-560056, India.

D. Gas Sensor Measurements

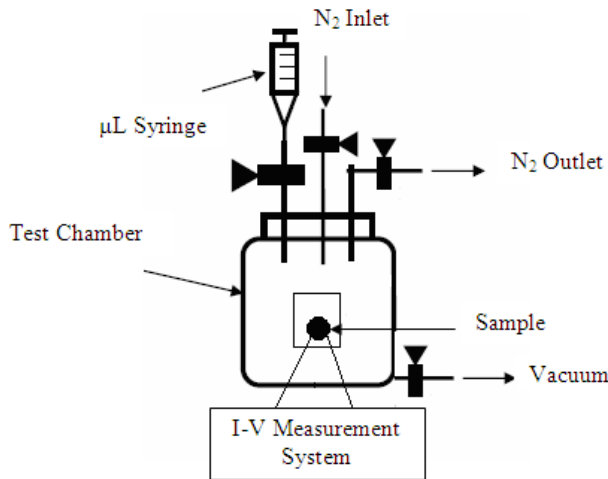


Fig. 1. Experimental setup for gas sensor measurements

The Figure-1 illustrates the experimental method [13] for methanol gas sensor studies. This method comprises of an air-tight chamber and 2-contact wires are taken out in order to connect it to the I-V Measurement unit. Humidity and temperature were maintained at room level. Sensor (Pellet-which acts as a sensor, it is also called as Chemi-Resistor where in which resistance of the sensor is varied in accordance with concentration gas vapors) is placed inside chamber and then closed. Sensor current is measured at 10V. The sensor of PANI/DBSA and PANI/DBSA-C<sub>60</sub> nanocomposite were exposed to methanol gas vapors. A known volume of methanol was injected into the gas chamber using micro-syringe. The droplets of methanol evaporated in 5-10 seconds. After the methanol droplets evaporated completely, the current of a sensor is measured at 10V continuously for every 30 seconds upto 10-15 minutes. Later, the gas-chamber is cleaned by using nitrogen and vented. For next round of testing the samples, chamber is closed and the above procedure is repeated to detect vapors of different concentration (in ppm) of methanol gas vapors.

Response of the sensor measured using following equation,

$$S = \frac{R_g}{R_a}, \text{ for } R_g < R_a$$

&

$$S = \frac{R_a}{R_g}, \text{ for } R_g > R_a$$

Where,

S- is the response,

R<sub>a</sub>- Resistance measured at air,

R<sub>g</sub>-Resistance measured in the presence of methanol gas

III. RESULTS AND DISCUSSION

A. FTIR Spectra

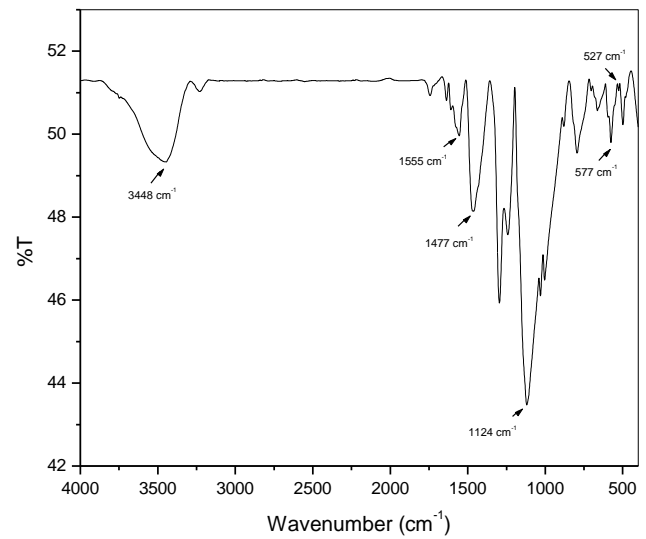


Fig. 2. FTIR Spectra of PANI/DBSA-C<sub>60</sub> nanocomposite

The FTIR-Spectra of PANI/DBSA-C<sub>60</sub> nanocomposite is as shown in Figure-2. Prominent peaks of PANI are assigned as C=N and C=C stretching-modes of for Quinoid-Benzoid units occurs at 1555 cm<sup>-1</sup> and 1477 cm<sup>-1</sup>. These peaks confirm the oxidation-state of Emeraldine-Salt form of polyaniline. The peaks at 527 cm<sup>-1</sup> and 599 cm<sup>-1</sup> indicated the peaks of C<sub>60</sub> in the nanocomposite [14]. Further, the main strong characteristic band appearing around 1124 cm<sup>-1</sup> is described as “*electronic-like band*”, this indicates the delocalization of electrons in the polymer chain. It is also a characteristic peak of PANI/DBSA electrical conductivity [15, 16]. FTIR spectrum of PANI/DBSA-C<sub>60</sub> is almost same as pure PANI/DBSA; which has been published in our earlier research paper [17] but there is change in intensities of all peaks. Therefore, this change in intensity confirms some interaction may exist between polyaniline and C<sub>60</sub>.

B. SEM and XRD spectra

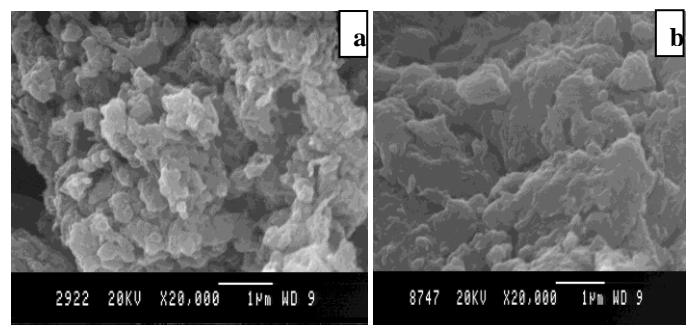


Fig. 3. SEM images of a) PANI/DBSA and b) PANI/DBSA-C<sub>60</sub> nanocomposite

The SEM-images of PANI/DBSA and PANI/DBSA-C<sub>60</sub> Nanocomposite are shown in Figure-3. The SEM image of PANI/DBSA presents agglomerated like structure whereas PANI/DBSA-C<sub>60</sub> nanocomposite illustrates highly branched chain like structure due to presence of C<sub>60</sub>.



Figure-4 depicts the X-ray diffraction pattern of PANI/DBSA and PANI/DBSA-C<sub>60</sub>. The XRD patterns of C<sub>60</sub> powder exhibits number of strong reflections in the range of the scattering angles 2θ=10-35°, which corresponds to a cubic-lattice crystalline symmetry [18]. The PANI/DBSA-C<sub>60</sub> XRD-Spectra showed all the characteristic peaks at 2θ values of fullerene are in kept- intact, even its peaks are difficult to differentiate between pure-C<sub>60</sub> and PANI/DBSA-C<sub>60</sub>. Therefore, these XRD results represent the strong formation of PANI/DBSA-C<sub>60</sub> complex. The XRD patterns of PANI/DBSA showed 2-broad peaks at 2θ angles around 21° and 26°. The XRD pattern of this sample is already published in our earlier paper [17].

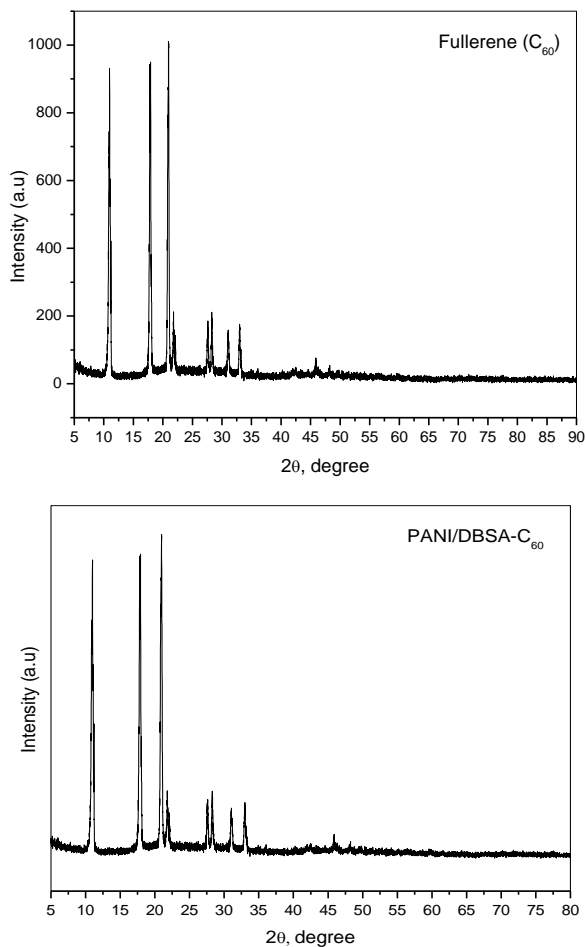


Fig. 4. X-ray diffraction patterns of Fullerene and PANI/DBSA-C<sub>60</sub> nanocomposite

### C. Electrical Conductivity

The values of electrical conductivity of PANI/DBSA and PANI/DBSA-C<sub>60</sub> Nanocomposite were found to be 0.02 S/m and 0.277 S/cm respectively. Therefore PANI/DBSA-C<sub>60</sub> Nanocomposite conductivity is almost fourteen times more than pure PANI/DBSA. As referred previous research works it is found that electrical conductivity of the polymer nanocomposites depends on various parameters such as doping level, conjugation length, and chain length also external factors like compactness and orientation of microparticles [19]. Generally, fullerenes are good electron-acceptors [20, 21] whereas polyaniline can be treated as a good electron-donor, hence increase in conductivity of the nanocomposite is due to the dopant effect or charge transfer from the quinoid unit of polyaniline to the fullerenes. This behavior may be due to the fact that, the large

surface area of C<sub>60</sub> able to act as conducting-bridges of PANI/DBSA conducting domains [22].

### D. Methanol Gas Sensor Properties

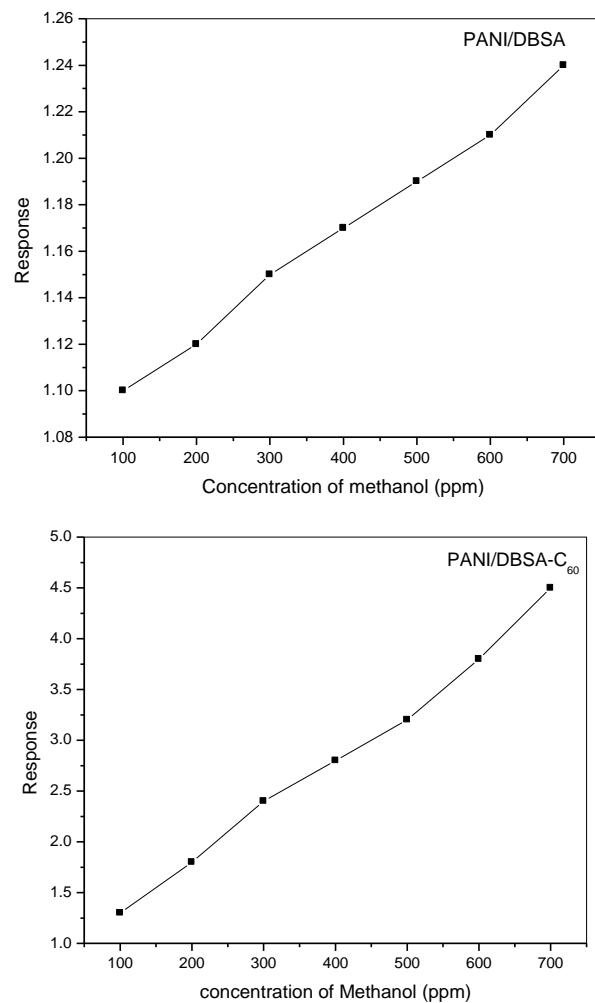


Fig. 5. Response of PANI/DBSA and PANI/DBSA-C<sub>60</sub> Nanocomposite with methanol concentration

Figure-5 illustrates the methanol gas response PANI/DBSA and PANI/DBSA-C<sub>60</sub>. When PANI/DBSA and PANI/DBSA-C<sub>60</sub> nanocomposite sensors are subjected to different concentration of methanol vapors, the resistance is increased for all the concentration. This behavior of increase in resistance of the sensor upon exposure to the methanol vapor may be due to polymer-swelling [23, 24] or may be decrease in the carrier concentration on the polymer backbone of the DBSA doped PANI [25].

The variation of response of PANI/DBSA-C<sub>60</sub> Nanocomposite with the methanol concentration and response of composite increased linearly with the increase of concentration of methanol vapors is presented in Figure-5. The PANI/DBSA-C<sub>60</sub> Nanocomposite serves as an efficient sensor compared to blank PANI/DBSA which can be accounted in terms of the enhanced degree of interactions between the composite and the vapors due to the larger surface area provided by the C<sub>60</sub> nanoparticles present in the composite. The incorporated C<sub>60</sub> nanoparticles play a significant role due to their surface activities.



The response time, i.e., the time required to reach 90% total resistance change of the prepared sensors upon exposed to methanol. The response time of the sensor for all the concentration of methanol was few minute only.

## IV. CONCLUSION

PANI/DBSA-C<sub>60</sub> Nanocomposite prepared by *insitu* oxidative chemical polymerization of PANI with the presence of C<sub>60</sub> and ammonium persulphate and DBSA used as oxidant and dopant respectively. From the FTIR spectra there an interaction exists between the PANI and C<sub>60</sub>. XRD patterns reveals the crystalline nature of C<sub>60</sub> even presence of the PANI. Measured electrical conductivity of PANI/DBSA-C<sub>60</sub> Nanocomposite was higher than the pure PANI/DBSA. PANI/DBSA-C<sub>60</sub> showed improved gas sensing response over PANI/DBSA.

## ACKNOWLEDGMENT

Authors are thankful to Dr.K.Rajanna, Professor, Department of Instrumentation and Applied Physics, Indian Institute of Science, Bangalore for providing gas sensing lab facility and useful discussion.

## REFERENCES

- R.P. Tandon, M.R. Tripathi, K.A. Arora, S. Hotchandani, Gas and humidity response of iron oxide-Polypyrrole nanocomposites, *Sens. Actuators B*, 114 (2006) 768-773.
- W.S. Huang, A.G. MacDiarmid, Optical properties of polyaniline, *Polymer*, 34 (1993)1833-1845.
- N.S. Sariciftci, L. Smilowitz, A.J. Heeger, F. Wudl, Photoinduced electron transfer from a conducting polymer to buckminsterfullerene. *Science*, 258 (1992) 1474-1476.
- N.S. Sariciftci, A.J. Heeger, *Handbook of Organic Conductive Molecules and Polymers* (S. Halwa, H, ed.), vol. 1, Wiley, New York, 1997, p. 437
- N.S. Sariciftci, D. Braun, C. Zhang, V. Srdanov, A.J. Heeger, G. Stucky, F. Wudl, Semiconducting polymer-buckminsterfullerene heterojunctions - Diodes, photodiodes, and photovoltaic cells, *Appl. Phys. Lett.* 62 (1992) 585-587.
- F.L. Zhang, M. Johansson, M.R. Andersson, J.C. Hummelen, O. Inganas, Polymer solar cells based on MEH-PPV and PCBM, *Syn. Met.* 137 (2003) 1401-1402.
- T. Fromherz, F. Padinger, D. Gebeyehu, C. Brabec, J.C. Hummelen, N.S. Sariciftci, Comparison of photovoltaic devices containing various blends of polymer and fullerene derivatives, *Solar Energ. Mater. Solar Cells*, 63 (2000) 61-68.
- D. Mendoza, G. Gonzalez, R. Escudero, Clusters of C<sub>60</sub> Molecules, *Adv. Mater.*, 11 (1999) 31-33.
- P. Topart, P. Hourquebie, Infrared switching electroemissive devices based on highly conducting polymers, *Thin Solid Films*, 352 (1999) 243-248.
- S.A. Chen, K.R. Chuang, C.I. Chao, H.T. Lee, White-light emission from electroluminescence diode with polyaniline as the emitting layer, *Synth. Met.* 82 (1996) 207-210.
- G. Gustafsson, Y. Cao, G.M. Treacy, F. Klavetter, N. Colaneri, A.J. Heeger, Flexible light-emitting diodes made from soluble conducting polymers, *Nature*, 357 (1992) 477-479.
- N.S. Sariciftci, Role of Buckminsterfullerene C<sub>60</sub> in organic photoelectric devices, *J. Prog. Quant. Electr.* 19 (1995) 131-159.
- L. Cheng, A. Chakraborty, Effects of dimensions on the sensitivity of a conducting polymer microwire sensor, *Microelectronics Journal*, 40 (2009) 912-920.
- T. Kazuyoshi, M. Yukihiro, O. Yoshiaki, Y. Tokio, Doping effect of C<sub>60</sub> on soluble polyaniline, *Synthetic Metals*, 66 (1994) 193-196.
- J. McElvain, M. Keshavarz, H. Wang, F. Wudi, A.J. Heeger, "Fullerene-based polymer grid triodes, *J. Appl. Phys.* 81 (1997) 6468.
- L.I. Ming, W. Meixiang, Doped polyaniline with C<sub>60</sub>, *Sol. Stat. Comm.* 93 (1995) 681-684.
- M. Nagaraja, H.M. Mahesh, J. Manjanna, K. Rajanna, M.Z. Kurian, S.V. Lokesh, Effect of multiwall carbon nanotubes on electrical and structural properties of polyaniline, *J. Electr. Mater.* 41 (2012) 1882-1885.
- K. Tanigaki, H.S. Nalwa, *Handbook of organic conductive molecules and polymers*, vol. 1. New York: Wiley, 1997, p. 298
- W. Feng, X.D. Bai, Y.Q. Lian, J. Liang, X.G. Wang, K. Yoshino, Well-Aligned Polyaniline/CarbonNanotube Composite Films Grown by in-Situ Aniline Polymerization, *Carbon*, 41 (2003) 1551-1557.
- N. Serdar Sariciftci, Role of buckminsterfullerene C<sub>60</sub> in organic photoelectric devices, *Prog. Quant. Electr.* 19 (1995) 131-159.
- H.Y. Lim, S.K. Jeong, J.S. Suh, E.J. Oh, Y.W. Park, K.S. Ryu, C.H. Yo, Preparation and properties of fullerene doped polyaniline, *Synth. Met.* 70 (1995) 1463-1464.
- Z. Huseyin, Z. Wensheng, J. Jianyong, C. Richard, D.W. Smith, L. Echegoyen, D.L. Carroll, S.H. Foulger, J. Ballato, *Adv. Mat.* 14 (2000) 1480
- B. Lundberg, B. Sundqvist, Resistivity of a composite conducting polymer as a function of temperature, pressure, and environment: Applications as a pressure and gas concentration transducer. *J. Appl. Phys.* 60 (1986) 1074.
- M.F. Mabrook, C. Pearson, M.C. Petty, An inkjet-printed chemical fuse, *Appl. Phys. Lett.* 86 (2005) 013507.
- J. Jang, M. Chang, H. Yoon, Chemical sensors based on highly conductive Poly(3,4-ethylenedioxythiophene) nanorods, *Adv. Mater.* 17 (2005) 1616-1620.

## AUTHORS PROFILE



**Dr. M. Nagaraja** completed h M.Sc. and Ph.D degree from Kuvempu University. Also, he has cleared UGC-NET and KSET exams. He is having 15 years of teaching and research experience. Presently, serving as an Associate Professor in the Department of Physics, Sri Siddhartha Institute of Technology, Tumakuru. He has published more than 40 research papers in National and International journals and conferences.



**Mrs. Sushma Prashanth** completed M.Sc in Physics from Karnataka University, Dharwad. She has 9-years of teaching experience. Presently she is pursuing Ph.D in Sri Siddhartha Academy of Higher Education, Tumakuru, Karnataka



**Dr. Jayadev Pattar** did his M.Sc. and Ph.D degree in Kuvempu University. Presently, he is working as an Associate Professor in the department of Physics, Reva University, Bengaluru. He has 15 Years of teaching and research experience. He has published various research papers in National and International journals and conferences. Also, he is a Gold medal student in Bachelor and Masters degree.



**Dr. H. M Mahesh** presently working as a Professor in the department of Electronic Science, Bangalore University, Bengaluru. He has 25 Years of teaching and research experience and published more than 100 research papers in National and International Journals and Conferences.