

Green Fabrication of Nio Nano Particles Doped PS-PVDF Nanocomposite Films: Structural, Morphology and Electrical Studies

Umme Salma¹, Nayeemuddina²

^{1,2}Department Of Mechanical Engineering, Khaja bandha Nawaz College of Engineering, Kalaburagi, Karnataka, India- 585104

Corresponding author: nayeem499@gmail.com

ARTICLE INFO

Received: 14 Dec 2024

Revised: 30 Jan 2025

Accepted: 18 Feb 2025

ABSTRACT

Solution cast polymerization scheme was used to create PS-PVDF/Nickel oxide (NiO) hybrid nanostructures (NSs) utilizing Nickel nitrate as a metal precursor, PS-PVDF as a polymerizing agent, and Aloe-Vera (A.V.) gel as an organic fuel. In contrast to the unadulterated segments, PS-PVDF and NiO nanoparticles (NPs), due to communication among the PS-PVDF and the NiO NPs, the electrical investigations of PS-PVDF/ NiO hybrid NCs are rather distinct. Dielectric behavior is observed that NCs with dopant of 40 wt.% NiO shows maximum dielectric constant compared with the rest of the composites and at the relaxation point, dielectric loss and the conductivity increases which correspond to fall in the dielectric constant. The results of the gas sensing investigations show that the constructed NCs have an excellent reaction to gas leaking. As the NiO NPs concentration increases from 10% to 50% wt%, AC and DC conductivity in the hybrid NCs increases from 1×10^{-5} to 5×10^{-5} (S/cm)⁻¹ at ambient temperature. The presented sensor system exhibits lower noise, higher resolution and higher sensitivity than electrochemical sensors previously used. PS-PVDF/ NiO NCs sample based on the results of the measurements and data collected, the synthesized hybrid NCs might be employed in optoelectronic device applications and it's a semiconducting material.

Keywords: Polymer, Nickel Oxide (Nio), Nano Composites (Ncs), TEM, Conductivity and Mechanical Parameters.

INTRODUCTION

Hybrid composites comprising polymer and inorganic nano oxides have been widely used in a variety of sectors, including soldierly gear, defensive sartorial, catalysis, automobiles, aircraft, and photosensitive strategies. It comes from the mixing of natural and inorganic hybrid materials, which gives them remarkable characteristics [1-2]. High mechanical characteristics, fire confrontation, chemical and radiation confrontation, environmental constancy, water repellency etc, are all required for usage of these hybrid NCs in a variety of application zones. Further, in polymer and inorganic oxide nano oxide hybrid composites the components and their volume percentages, geometrical construction, incorporations of matrix and filler material, superficial communications between the matrix and inclusions are all significant variables [1-4].

The composites are made of usual foremost polymers such as PS-PVDF [2], and poly-thiophene (PTH). PS-PVDF, amongst the aforementioned polymers, has gotten a lot of attention because of its unique characteristics in comparison to others [5, 6]. Because of their prospective uses and logical interests, Inorganic oxide materials in the nano domain have been thoroughly investigated. These materials have good physical and chemical characteristics due to the influence of their size [7, 8]. NCs made up of PS-PVDF and NiO are being studied more and more because their characteristics differ significantly from those of PS-PVDF and NiO NPs, which can be ascribed to interfacial interactions between the PS-PVDF and NiO NPs [9-14]. Several papers may be reviewed to learn more about an electrochemical characteristic of PS-PVDF and its NCs [15-19].

The current study focuses on dispersing NiO nanoparticles in a PS-PVDF matrix to create hybrid NCs.

Many researchers have established that the PS-PVDF base nano composites can be broadly used as sensors to detect a variety of gases [20]. Srivastava et al. [21] reported multiwall carbon nanotube (MWCNT) doped PS-PVDF(PS-PVDF) composite thin films for hydrogen gas sensing applications. Their results reveal that the MWCNT/PS-PVDF composite film shows a higher sensitivity in comparison to pure PS-PVDF and it decreases with increasing hydrogen gas pressure. Zhang et al. [22] developed a PS-PVDF-SWCNT thin film nano composite based sensor for ammonia (NH_3) gas sensing, and they concluded that the electrochemical fictionalization of SWCNTs provides a promising new method with improved sensitivity, response time, and reproducibility.

The control of the morphology on the gas sensing performance is another important factor, and therefore, should be considered. The literature survey of polymer NCs concerning that the sensors composition is a main factor that affects the surface morphology of sensing materials which depend primarily on the nature of the components and the processing conditions [23]. In the present work, structural, morphology, and H_2S sensing properties of PS-PVDF functionalized NiO NCs prepared by Solution castpolymerization were systematically investigated.

The inorganic oxide NiO NPs were produced using a solution combustion method and then embedded in a PS-PVDF matrix NCs. various characterization techniques were used to examine the produced NCs.

Experimental

All of the chemicals were purchased from commercial foundations and were used exactly as they were.

MATERIALS

Sigma Aldrich provided analar grade chemicals such as cobalt nitrate hexahydrate [$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], Polystyrene (PS) [C_6H_8]_n, Polyvinyl Floride (PVDF) ($\text{C}_2\text{H}_2\text{F}_2$)_n, ammonium per sulphate [$(\text{NH}_4)_2\text{S}_2\text{O}_8$], hydrochloric acid [HCl ; purity 37 percent], and acetone [CH_3COCH_3]. Fresh aloe-vera gel was extracted from the plant.

The Polymer Synthesis

In order to make PS-PVDF an aqueous solution of aniline is combined with ammonium per sulphate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$). A greenish black precipitate was produced, which was filtered out and treated with acetone as a cleaning agent. PS-PVDF powder was formed and then dried for 24 hours in an hot air oven at around 80 °C the chemical structure and resonance structure of PS-PVDF

Green fabrication of NiO nanoparticles

Using Aloe-Vera (A.V.) gel as an organic fuel, a low-temperature Solution combustion method was used to produce NiO NPs. In a ceramic crucible, 2.90 grammes of Nickel nitrate hexahydrate was placed, and 15 ml of A.V. gel was put into the crucible and place on the magnetic stirrer for uniform mixture. The response combination was then placed in a pre-heated muffle furnace at a temperature of 500 degrees Celsius. The metallic nitrates and the fuel undergo a combustion process shown in Fig.1. resulting in nano powders of NiO.

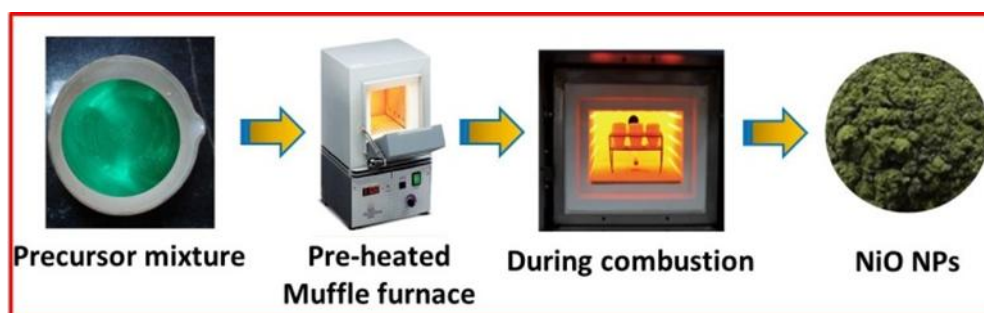


Fig.1. Schematic representation of the combustion synthesis of Nickel Oxide nanoparticles

Synthesis of PS-PVDF/NiO hybrid nanostructures

Solution cast polymerization method was used to combine PS-PVDF with NiO NCs. To achieve homogeneity, 0.1 M aniline was combined with 1M hydrochloric acid (HCl) and agitated for 15 minutes. Nickel oxide (NiO) NPs were added to the aforementioned mixture at the appropriate weight percentage to homogeneously distribute the NiO NPs. The oxidizing agent, 0.2M ammonium per-sulphate, was added to the polymer mixture drop-by-drop with constant stirring and kept at ice temperature for 4 hours to complete polymerization. The precipitate was filtered before being washed in acetone and de-ionized water. To get an uniform mass, it was calcined for 24 hours at 80°C

in a hot air oven. This method was used to make PS-PVDF/ NiO NCs with different percentages of NiO (i.e., 10, 20, 30, 40, and 50wt percent). as shown in Fig.2.

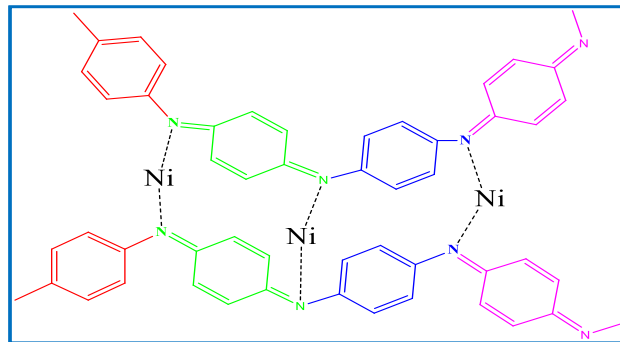


Fig.2.Chemical structure of PS-PVDF/NiO NCs

RESULT AND DISCUSSION

PXRD Analysis

Figure.3. shows the X-ray diffraction patterns of PS-PVDF, NiO NPs, and PS-PVDF/NiO(10-50wt%) NCs (a). PS-PVDF nanoparticles show a broad diffraction peak at 24° Bragg's angle (2θ) [16-19]. In the current matrix, doping with the filler NiO NPs weakens the broad peak of PS-PVDF. In line with the standard ICDD card No. 73-1519 [20], the XRD patterns of Nickel oxide (NiO) demonstrate a simple cubic structure with lattice parameters $a = b = c = 4.1678$. Using established relations, the lattice parameters for the (200) X ray diffraction of cubic structured NiO in PS-PVDF/NiO(10-50 mol percent) polymer NCs were determined to be $a = b = c = 4.183 \text{ \AA}$.

The PS-PVDF/NiO hybrid NCs showed a significant increase in the lattice parameters of NiO..[21-23] the adsorption of PS-PVDF atomic chains on the surface of NiO results in a small extension of the fundamental building block (unit cell) of the crystalline NiO material. The change in crystallite size of the most prominent peaks (200) planes in X-ray diffraction patterns of PS-PVDF/NiO hybrid NCs can also be ascribed to the presence of such interactions. Scherrer's formula (shown below) is used to compute the usual crystallite sizes of NiO and PS-PVDF/NiO hybrid NCs for the (200) visible peaks.

$$D = \frac{0.9\lambda}{\beta \cos \theta} \dots \dots \dots (1)$$

Where D denotes the average crystallite size and β is the peak's full width at half-maxima (FWHM). In PS-PVDF/NiO NCs, the crystallite size of Nickel oxide (NiO) along the (200) plane increases from 22 nm to 37 nm. The fact that the crystallinity of NiO is enlarged by the absorption of PS-PVDF subatomic chains on the surface of NiO in PS-PVDF/NiO NCs demonstrates that the crystallinity of NiO is expanded. [24-27].

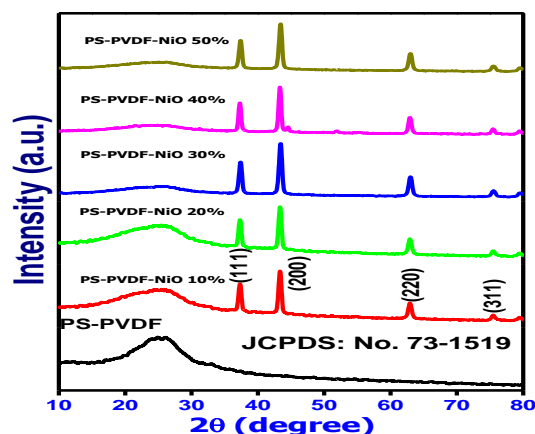


Fig.3. PXRD patterns PS-PVDF/NiO NCs (10- 50 wt %)

Co ₃ O ₄ (wt %)	Crystallite size (nm) by Scherer's method
10	23
20	29
30	30
40	33
50	34

Table.1. The estimated average crystallite size, PS-PVDF/Co₃O₄ (10-50 wt%) NCs.

Organizational and morphological studies

Figure.4. depicts surface morphological investigations of the current polymer/Metal oxide nano composites. [24-25] Surface morphology of pure PS-PVDF shows granular morphology with holes in the centre of spectrograms (Fig. 4a), and nano-crystalline morphology of NiO NPs (Fig. 4b). The morphology of prepared NCs PS-PVDF/NiO (10–50 wt percent) is shown in Figure 4c. The morphology shows congested groups when the NiO content in the PS-PVDF matrix is increased 50% (Fig.6c). Further incorporation of NiO (50 wt%) NCs into the PS-PVDF matrix (Fig.4c) results in permeable linked nanospheres [21-23]. Fig 4(a-g) SEM EDX spectra show the presence of NiO content in the PS-PVDF matrix. The TEM analysis provides further inset over the shape and structure of Pure PS-PVDF, NiO NPs in PS-PVDF/NiO hybrid NCs, as shown in Fig. 5(a) to 5(d) correspondingly. The size of the synthesized PS-PVDF/NiO 50 wt % NCs was in the range of 38 to 40 nm in diameter, as shown in Fig. 5(a-d) [24-28]. These results are in good accord with the acquired results from the PXRD pattern [24]. Figure 5(c-d) shows the inter-planer space of PS-PVDF/NiO50 wt % NCs from 28 to 32 nm. [27-28].

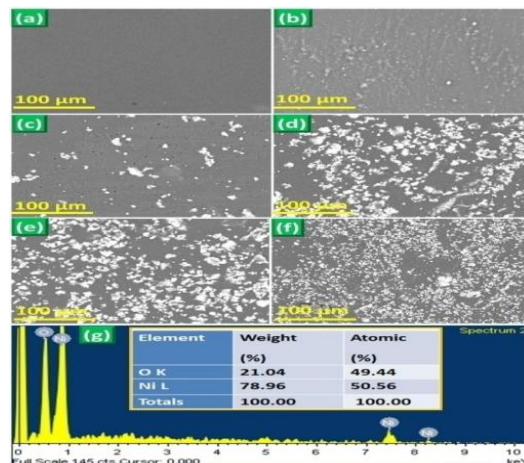


Fig.4. SEM micrographs of (a) pure PS-PVDF, (b) NiO NPs (c) PS-PVDF/NiO NSs and (d-e) EDAX Spectra of PS-PVDF/NiO NSs

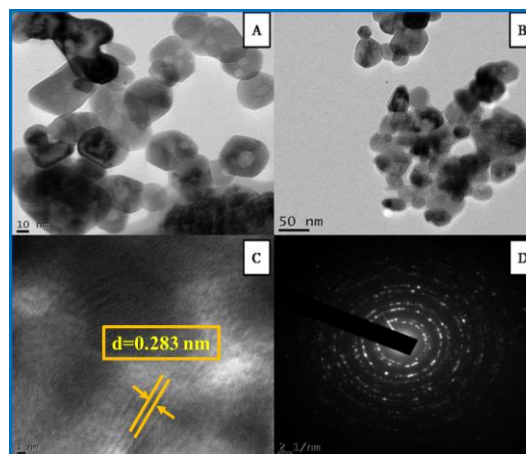


Fig.5. TEM Images of (a) PS-PVDF (b) NiO NPs and (c, d) PS-PVDF/NiO(50 wt %) NSs

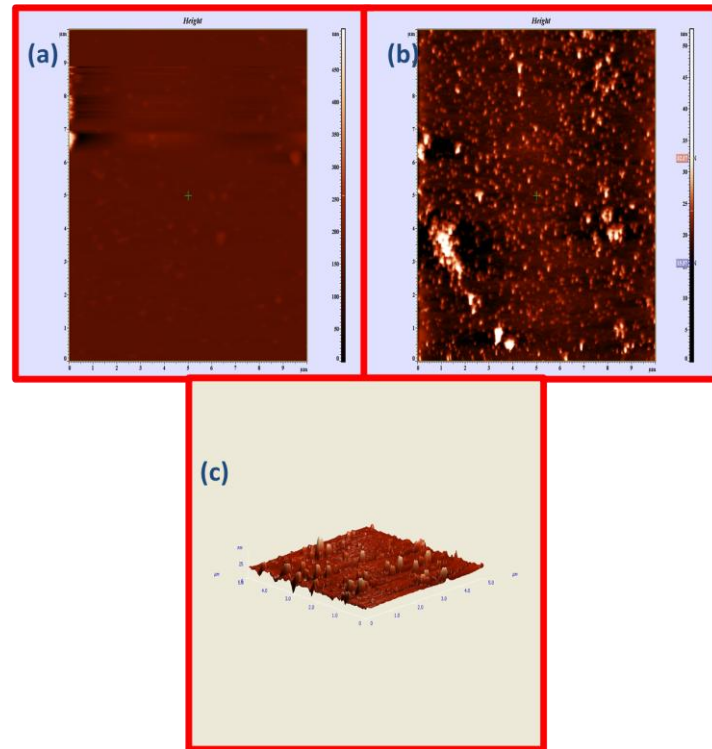


Fig.6. AFM Images of (a) PS-PVDF (b) NiO NPs and (c, d) PS-PVDF/NiO(50 wt %) NSs

Structral studies

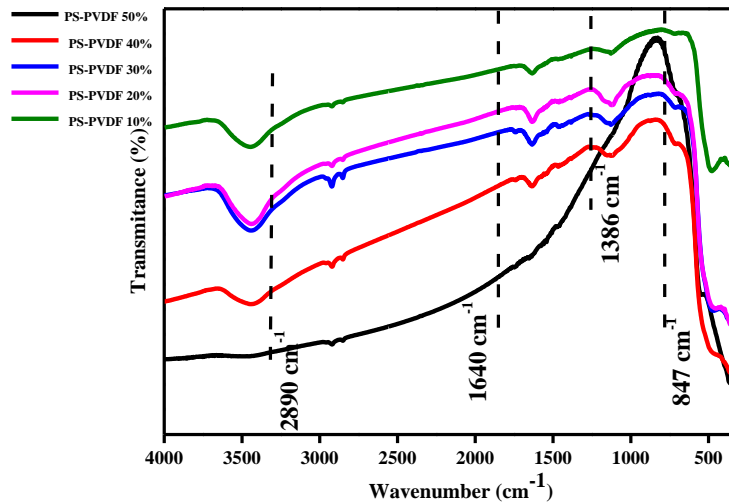


Fig.7. FTIR Spectra of PS-PVDF/NiO (50 wt. %) NSs

AC Conductivity

The frequency-dependent AC conductivity of PS-PVDF/NiO NCs is shown in Fig.10. The conductivity of PS-PVDF/NiO NCs remains constant up to a frequency of 2×10^7 Hz, after which it increases at higher frequencies [21-25]. The maximum conductivity seen in PS-PVDF/NiO (50 wt %) samples might be related to the chain length, as evidenced by the IR graph. Enhanced charge polarization might be the cause of increased conductivity.

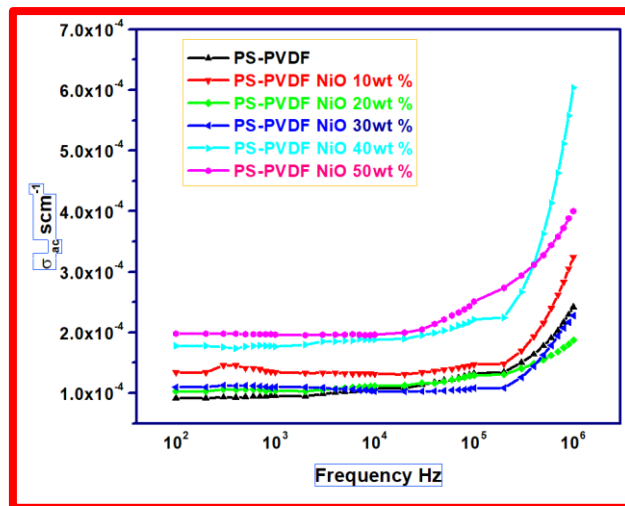


Fig.8. AC conductivity of PS-PVDF/NiO (10-50 wt %) NCs

5. DC conductivity

Figure.11 demonstrates the assortment of dc conductivity as a factor of temperature for (NiO) in PS-PVDF. It is watched so as to the assessment of dc conductivity of these NCs increases exponentially with temperature. Further the shrink in conductivity is watched which might be credited because of the dispersion of (NiO) NPs of larger grain measure which are halfway blocking the hopping of charge carriers [17-20]. The temperature-dependent DC conductivity of PS-PVDF/NiO NCs is shown in Figure 4. The conductivity of PS-PVDF/NiO NCs remains constant up to 110°C, after which it begins to rise at higher temperatures. The extreme conductivity seen in PS PVDF/NiO (30 wt%) samples might be related to the chain length, as evidenced by the IR graph. Enhanced charge polarization might be the cause of amplified conductivity [24-28].

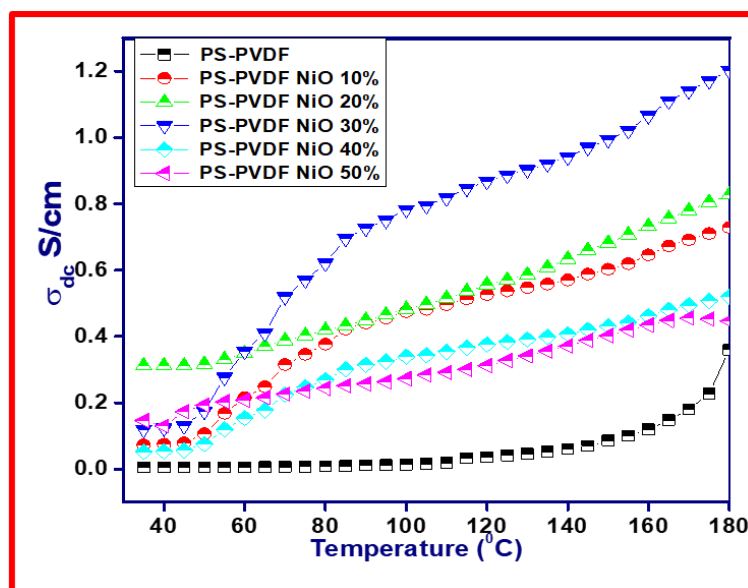


Fig.9. DC Conductivity studies of PS-PVDF/NiO NCs.

CONCLUSION

In conclusion, the PS-PVDF/NiO NCs were successfully produced using an Solution castpolymerization method. The amorphous nature of pure PS-PVDF and the cubic phase of NiO NPs are confirmed by PXRD patterns and also the morphology of pure PS-PVDF and blends was investigated in depth with TEM micrographs. The AC Conductivity of PS-PVDF/NiO (50 wt %) exhibits superior electrical characteristics when compared to the other NCs. samples might be related to the chain length, as evidenced by the IR graph. Enhanced charge polarization might be the cause of increased conductivity. It is observed that NCs with dopant of 40 wt% NiO shows maximum

dielectric constant compared with the rest of the composites and at the relaxation point, dielectric loss and the conductivity increases which corresponds to fall in the dielectric constant. The extreme temperature-dependent DC conductivity seen in PS-PVDF/NiO (50 wt %) samples might be related to the chain length, as evidenced by the IR graph. Enhanced charge polarization might be the cause of amplified conductivity. To summaries, the current PS-PVDF/NiO hybrids NCs are promising materials for fabricating for semiconducting as well as sensing devices, according to the findings and the designed NCs materials belongs to the semiconductor.

REFERENCES:

- [1] L.Y. Wang, E.H. Song, Y.Y. Zhou, T.T. Deng, S. Ye, Q. Y. Zhang, Synthesis and warm-white LED applications of an efficient narrow-band red emitting phosphor, *Rb₂ZrF₆: Mn⁴⁺*. *J. Mater. Chem. C* 5 (2017) 7253-7261.
- [2] H. K Inamdar, M. V. N. Ambika Prasad, R. B. Basavaraj, M.Sasikala, S. C. Sharma, and H.Nagabhushana, *Optical Materials*, 88, 458–465(2018).
- [3] H. K.Inamdar, M.V.N.Ambikaprasad , and H.Nagabhushana , *Composites Communications*, 14, 21–28(2019).
- [4] H. Wei, C. He, J. Liu, H. Gu, Y. Wang, X. Yan, J. Guo, D. Ding, N.Z. Shen, X. Wang, S. Wei, Z. Guo, Electropolymerized PS-PVDF nanocomposites with cobalt oxide coated on carbon paper for electrochemical energy storage, *Polymer*. 67 (2015) 192-199.
- [5] C.Shen, Y. Sun, W. Yao, Y. Lu, Facile synthesis of PS-PVDFnanospheres and their carbonized products for potential application in high-performance supercapacitors, *Polymer*. 55 (2014) 2817-2824.
- [6] A.Kausaite-Minkstiniene,V. Mazeiko, A. Ramanaviciene,A.Ramanavicius, Evaluation of chemical synthesis of PS-PVDF particles, *Colloids and Surfaces A: Physicochem. Eng. Aspects* 483 (2015) 224-231.
- [7] M.R. Mahmoudian, W.J. Basirun, Y. Alias, M. Ebadi, Synthesis and characterization of PS-PVDF/Sn-doped TiO₂nanocomposites (NSs) as a protective pigment, *Appl. Surf. Sci.* 257 (2011) 8317-8325.
- [8] Hajeebaba K Inamdar, R.B. Basavaraj, H. Nagabhushana, MahaleshDevendrappa, SharanabasammaAmbalgi, BasavarajaSannakki, R.D. Mathad, DC Conductivity Study of Polyaniline/Co₃O₄ Nanocomposites prepared through Green Synthesis, *Materials Today: Proceedings* 3 (2016) 3850–3854
- [9] Sharanabasamma M Ambalagi, Hajeebaba K Inamadara and BasavarajaSannakki, Mechanism of DC Conductivity Measurement of Zinc Oxide Doped PS-PVDFNanocomposites, *Materials Today: Proceedings* 3 (2016) 3945–3950
- [10] Hajeebaba K Inamdar, M.V.N.AmbikPrasada, M.Sasikal, Synthesis and characterization of PS-PVDF/Co₃O₄ doped Nanocomposites (NSs) for Dielectric studies, *Materials Today: Proceedings* 5 (2018) 22652-22656
- [11] Z. Wang, P. Xiao, L.Qiao, X.Meng, Y. Zhang, X. Li, F. Yang, PS-PVDF sensitized ZnO nanorod arrays for efficient photo-electrochemical splitting of water, *Physica B*. 419 (2013) 51-56.
- [12] E.R. Macedo, P.S. Oliveira, H.P. de Oliveira, Synthesis and characterization of branched PS-PVDF/titanium dioxide photocatalysts, *J. Photochem. Photobiol. A* 307–308 (2015) 108–114.
- [13] D. Jia, Q. Ren, L. Sheng, F. Li, G. Xie, Y. Miao, Preparation and characterization of multifunctional PS-PVDF–Au coated Co₃O₄ nanocomposites and study of their electrocatalysis toward several important biothiols, *Sens. Actuators, B*. 160 (2011) 168–173.
- [14] P.M. Nia, W.P. Meng, F. Lorestani, M.R. Mahmoudian, Y. Alias, Electrodeposition of Cobalt oxide/PS-PVDF/reduced grapheneoxide as a nonenzymatic glucose biosensor, *Sens. Actuators, B*. 209 (2015) 100–108.
- [15] Hajeebaba K Inamdar, M.Sasikala, DayanandAgsar, M.V.N. Ambika Prasad, Facile green fabrication of ZnO nanopowders: Their antibacterial, antifungal and photoluminescent properties, *Materials Today: Proceedings* 5 (2018) 21263–21270
- [16] D. Das, B.C. Nath, P. Phukon, B.J. Saikia, I.R. Kamrupi, S.K. Dolui, Cobalt oxide/PS-PVDF/silver nanocomposites with core/shell/shellstructure: Synthesis, characterization and their electrochemical behaviour with antimicrobial activities, *Mater. Chem. Phys.* 142 (2013) 61-69.
- [17] G.H. Lee, S. Kang, Studies in crystal structure and luminescence properties of Eu³⁺-doped metal tungstate phosphors for white LEDs, *J. Lumin.* 131 (2011) 2606–2611.
- [18] Publication CIE no 17.4 (1987) International Lighting Vocabulary, Central Bureau of the Commission Internationale de L'Eclairage, Vienna, Austria.
- [19] C.K Jorgensen, R. Reisfeld, Judd-Ofelt parameters and chemical bonding, *J. Less Comm. Met.*, 93 (1983) 107-112.

-
- [20] S. Pandey, Highly sensitive and selective chemiresistor gas/vapor sensors based on PS-PVDFnanocomposite: a comprehensive review, *J. Sci. Adv. Mater.Devices* (2016) 431e453.
- [21] S. Srivastava, S.S. Sharma, S. Kumar, S. Agrawal, M. Singh, Y.K. Vijay, Characterization of gas sensing behavior of multi walled carbon nanotube polyaniline composite films, *Int. J. Hydrogen Energy* 34 (2009) 8444e8450.
- [22] T. Zhang, M.B. Nix, B.Y. Yoo, M.A. Deshusses, N.V. Myung, Electrochemically functionalized single-walled carbon nanotube gas sensor, *Electroanalysis* 18 (2006)1153e1158.
- [23] C. Liu, H. Tai, P. Zhang, Z. Yuan, X. Du, G. Xie, Y. Jiang, A high-performance flexible gas sensor based on self-assembled PS-PVDF-CeO₂ nanocomposite thin film for trace-level NH₃ detection at room temperature, *Sensor. Actuator. B Chem.* 261 (2018) 587e597.
- [24] B. R. Judd, Optical absorption intensities of rare-earth ions, *Phys Rev.* 127 (1962) 750-761.
- [25] G.S. Ofelt, Intensities of crystal spectra of rare-earth ions, *J. Chem. Phys.* 37 (1962) 511-520.
- [26] Wang, C., Zheng, W., Yue, Z., Too, C. O., & Wallace, G. G. (2011).Buckled, stretchable 295 PS-PVDF electrodes for battery applications. *Advanced Materials*, 23(31), 3580-3584.
- [27] ShaziaFarheen, FirdousJahan, Hajeebaba K. Inamdar and R.D. Mathad, Effect of polymer blending on mechanical and thermal Properties, *Indian J.Sci.Res.* 12(2015)520-522
- [28] Sharanabasamma M Ambalgi, Hajeebaba K Inamdar, Manjula V T, SannakkiNagaraja, Shrishail G Hogade and, BasavarajaSannakki, Synthesis, Characterization and Electrical Properties of Polyaniline/Cobalt oxideNanocomposites, *International Journal of Engineering Research* 5 (2016) 119- 122
- [29] Chandra, V., &Kim, K. S. (2011).Highly selective adsorption of Hg₂⁺ 237 by a PS-PVDF- 238 reduced graphene oxide composite. *Chemical Communications*, 47(13), 3942-3944.
- [30] Liu, Z., Liu, Y., Poyraz, S., & Zhang, X. (2011). Green-nano approach to nanostructured 261 PS-PVDF. *Chem. Commun.* 47(15), 4421-4423.
- [31] B.C. Kim, J.M. Ko, G.G. Wallace, A novel capacitor material based on Naf ion doped PS-PVDF, *J. Power Sources* 177 (2008) 665–668.
- [32] Hajeebaba K. Inamdar, Arjun N. Shetty,S. Kaveri, Basavaraj Sannakki, M. V. N. Ambikaprasad, Aloe vera (L.) Burm. F Assisted Green Synthesis and Biological Applications of Y₂O₃:Mg²⁺ Nanocomposites, *Journal of Cluster Science* 29 (2018) 805–813
- [33] P.Naresh, B. Kavitha; H. K Inamdar, D. Sreenivasu, N. Narsimlu, C. Srinivas, V. Sathe,and K. Siva Kumar, *Journal of Non-Crystalline Solids*,**514**, 35–45(2019).
- [34] Diao K, Zhou M, Zhang J, Tang Y, Wang S, Cui X. High response to H₂S gas with facile synthesized hierarchical ZnO microstructures. *Sens Actuators B* 2015;219:30–7.
- [35] Rout CS, Hegde M, Govindaraj A, Rao CNR. Ammonia sensors based on metal oxide nanostructures. *Nanotechnology* 2007;18:205504–13
- [36] Chen YJ, Zhu CL, Xiao G. Reduced-temperature ethanol sensing characteristics of flower-like ZnO nanorods synthesized by a sonochemical method. *Nanotechnology* 2006;17:4537–41.
- [37] Calestani D, Zha M, Mosca R, Zappettini A, Carotta MC, Natale VD, et al. Growth of ZnO tetrapods for nanostructure-based gas sensors. *Sens Actuators B* 2010;144:472–8.