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Doping Induced Modifications in Physicochemical and Optoelectronic Properties of Polyaniline Thin Films

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Abstract

The present article deals with study of transition element doping effect on physicochemical and optoelectronic properties of Polyaniline thin films synthesized by using solution polymerization method at room temperature over the glass substrates. These as deposited and doped thin films have been comparatively analysed for structural, compositional, morphological, optical absorbance properties with the intension to study its effect over the NH_3 gas sensing behaviour. From the Fourier transform infra-red spectrum of as deposited and doped thin films shows shift in peaks corresponding to 1632 cm^{-1} and 1354 cm^{-1} attributed to C=C stretching vibrations of benzenoid and quinoid rings, while peaks 1193cm^{-1} and 833cm^{-1} are associated with the protonation and doping. Raman spectrum for as deposited and doped thin films exhibits sharpening of the characteristic peaks 1599 cm^{-1} for C-C stretching in benzenoid, 1509 cm^{-1} for C=C stretching in quinonoid while 1374 cm^{-1} for C~N+ vibrations of delocalized polaronic structures and C=N stretching vibrations in quinonoid units. Morphological images observed from the scanning electron microscopy (SEM) shows granular distribution of particles over the substrate surface for as deposited thin films which gets improved and or reduction in size for doping some elements. Optical absorbance spectra revealed improvement in absorbance coefficient upon doping, peak at 625nm corresponds for exciton induced charge transitions. The NH_3 gas sensing characteristics when studied revealed almost similar response and recovery time for doped and as deposited thin films while increment in gas sensitivity is observed upon doping, for Au doped thin films have represented higher sensitivity.

Keywords: Thin Film, Polyaniline, Benzenoid and Quinoid, Sensor, Polaron, Doping.

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1. Introduction

Human beings are always in search of instruments and devices which could make his/her life more luxurious and comfortable as such industrial developments [1, 2]. On the contrary innovating and developing instruments and goods, could be associated with adverse effects, one such aspects is emission of hazardous gases and chemicals by industries, vehicles etc. The gases emitted out of these industries and vehicles comprised of H_2S, CO_2, CO and NH_3 etc. as pollutants. One such common pollutant in and around is NH_3 gas, when emission of this polluting NH_3 gas exceeds the human acceptable level it could lead different disorders like etching of skin, difficulty in breathing, irritation in eyes etc. [3-5]. Hence to monitor the emission of this gas there needs to have gas sensor. Till date many more researchers have worked for development of gas sensors based on metal oxide thin films, nanomaterials etc. but very few reports are available showing use of polymer as sensor materials [4-6]. These gas sensors developed and studied so far possesses issues like response, recovery, sensitivity and materials stability etc. In overcoming all these, Polyaniline being one of polymer materials which could be used as gas sensor owing to its higher optical absorbance coefficient, C-H bonding induced polaronic charge transportations etc. which can facilitate it for fast response and quicker recovery time along with higher sensitivity [5-8]. Literature have revealed that the sensitivity can be improved either by providing post deposition treatment like annealing the thin films or by doping with transition elements. While issue pertaining to stability could be solved by synthesis using soft chemical route such as solution polymerization method at room temperature. Hence the present article deals with synthesis of polyaniline thin films using soft chemical solution method and doping of transition elements Zn, Cu, Al, Ag and Au in it. These as deposited and doped thin films have been characterized for physicochemical and optoelectronic properties using Fourier transform infra-red (FTIR), Raman spectrum, surface morphology using scanning electron microscopy (SEM), Optical absorbance spectra and NH_3 gas sensitivity.

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2. Experimental Details

Thin film of Polyaniline was prepared by solution polymerization method using HCl as dopent, while ammonium peroxidisulphate (APS) as an oxidant and aniline as a monomer. Commercial glass slides supplied by Bluestar Company, Mumbai (India) were used as substrates for the deposition. Aniline was distilled under high pressure prior to use, other chemicals were used as they received. Solution polymerization process proceeded as follow, 0.2ml aniline was added in 1ml concentrated HCl solution with constant stirring at room temperature then 0.25ml APS was prepared in an aqueous media, before mixing, these reactants were pre cooled in an ice bath container. Thereafter 20ml APS was added slowly to the aniline solution with constant stirring at room temperature. While doping of Zn, Cu, Al, Ag, Au carried using source $ZnCl_2$, $CuCl_2$, $AlNO_3$, $AgCl_3$ and $AuCl_3$ respectively. Cleaned glass substrates were immersed in the reaction bath using substrate holder. After 120 minutes substrates were removed from the reaction bath which then washed with distilled water to remove the granules attached over the surface of the substrate, dried and preserved in dark desiccators, the reaction kinematics can be seen as in Fig 1 for induction and final synthesis (completion of reaction) [5-9]. The reaction was carried for 2h resulting in green color precipitate which confirms formation of polyaniline emeraldine salt as can be seen in Fig 2.

These as deposited and doped thin films have been characterised for understanding compositional chemical bonding using Fourier transform infra-red (FTIR) recorded over Perkin Elmer MS 632 Spotlight 200i while Raman spectrum obtained on Renishaw in Via spectrophotometer. The surface morphology on Field Emission Scanning Electron Microscope (FESEM), Carl Zeiss Supra 55 and Atomic Force Microscope over instrument NT MDT while the optical absorbance measured on Perkin Elmer Lambda 25. These obtained results have been comparatively analysed for understanding the doping effect on physicochemical and optoelectronic properties with the intension to study its net effect on gas sensing behaviour.

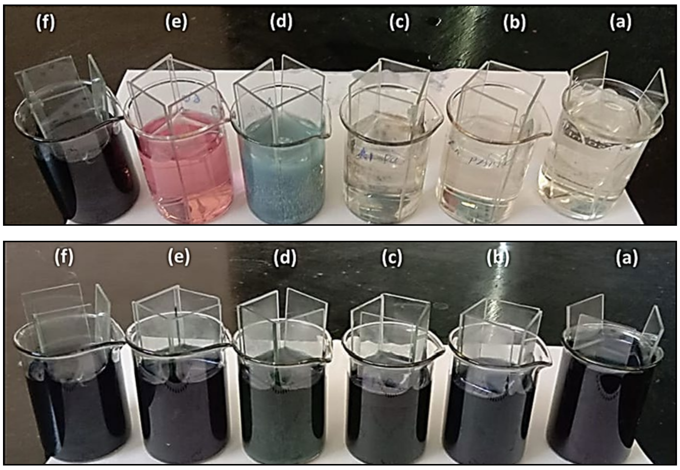

Fig 1: Images of Polyaniline thin film synthesis reaction (a), (b), (c), (d), (e), (f) representing as deposited, Zn, Al, Cu, Ag and Au doping respectively. The upper images represent induction mechanism while below images corresponds for reaction saturation (completion) stage.

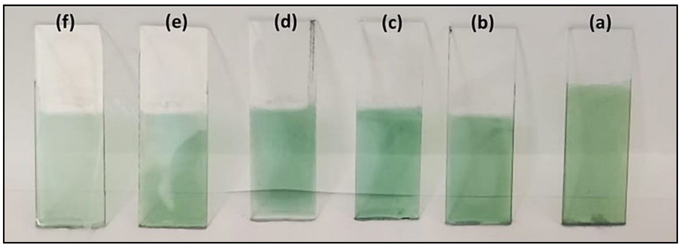

Fig 2: Actual images of Polyaniline thin films synthesized by solution polymerization method at room temperature (a), (b), (c), (d), (e), (f) representing as deposited, Zn, Al, Cu, Ag and Au doping respectively.

3. Results and Discussion

3.1. Chemical Analysis using FTIR Spectrum

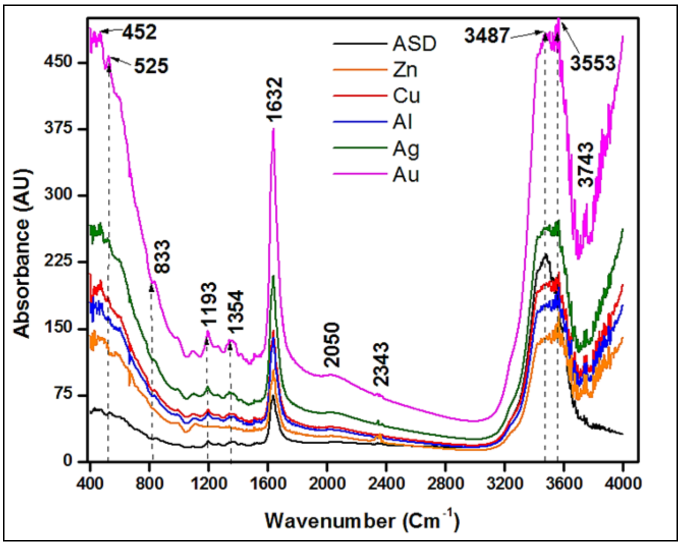

Fig 3: FTIR spectrum of as deposited and doped polyaniline thin films synthesized by solution polymerization method over glass substrate at room temperature.

Fig. 3 represents the Fourier transform infra-red spectrum (FTIR) obtained from the as deposited and doped polyaniline thin films synthesized by soft chemical route over the glass substrate. From the figure it can be seen that the chemical binding shifted upon doping with transition elements. From FTIR peak corresponding to 1632 cm^{-1} and 1354 cm^{-1} attributed to C=C stretching vibrations of benzenoid and quinoid rings, while peaks 1193cm^{-1} and 833cm^{-1} are associated with the protonation, doping which is crucial for its conductivity. While other notable bands include those around 2050Cm^{-1}, 2343 cm^{-1}, 3487 Cm^{-1}, 3553 Cm^{-1}, 3743Cm-1, 452 and 525 cm^{-1} [10-11]. The peak at 3487 cm^{-1} corresponding to -NH2 stretching, peak observed at 2343 cm-1 may be due to C-H stretching while C-N stretching can be seen at 2050 cm-1 [11]. The peaks observed between 525 Cm^{-1} and 452Cm^{-1} may be due to protonation of polyaniline which are the characteristic bands [12-13]. The observed peeks have been observed to be slightly shifted and intensity is increased which may be due to elemental doping which changes the orientations and impacts over the film protonation and compositions there by the elemental variations occurs across the polyaniline.

3.2. Raman Analysis

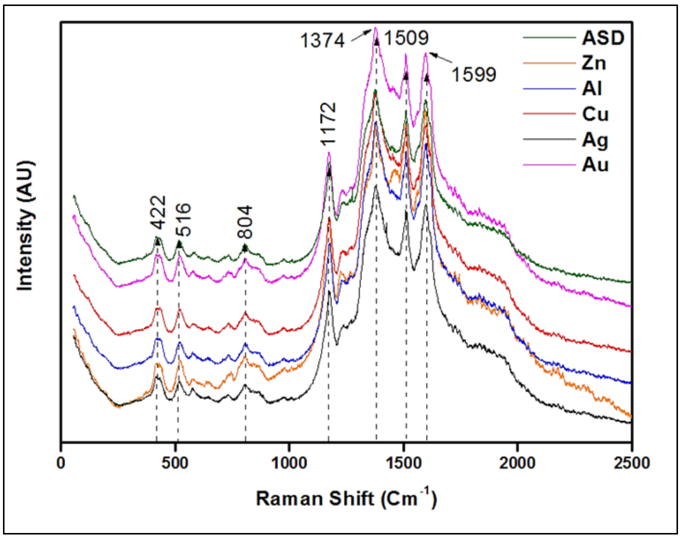

Fig 4: Raman spectrum of as deposited and doped Polyaniline thin films prepared by solution polymerization method at room temperature over glass substrate.

Raman spectrum obtained from the Polyaniline thin films doped and as deposited, the spectrum contains characteristic peak marked for polyaniline, located at 1599 and 1509 cm^{-1} corresponding to carbon-carbon single and double band stretching vibrations in benzene and quinine rings, respectively. Peaks are also observed for specific bands of C=N stretching modes of imine located at 1374 cm^{-1} and C-N stretches of amine sites at 1172 cm^{-1} [14, 15]. The stretching vibrations of an intermediate bond C~N+ are seen in Raman spectra with characteristic frequency around 1330 cm^{-1} [15]. Furthermore, other bands in the Spectrum are located around 516 and 804 cm^{-1}, which correspond probably to imine site deformation vibrations and amine deformations, while upon doping with the elements no significant peak corresponding to formation of any secondary compounds are observed but there seems to be change in the peak broadening and shoulder kink formations around the peaks particularly between 1172 to 1599 cm^{-1} which signifies that the doping may have been intercalated hence, instead of separate peak the position gets broader.

3.3. Surface Morphology

Fig 5 represented the scanning electron microscopy images of the as deposited and doped polyaniline thin films; from the images it can be seen that the surface morphology varies as the doping elements are varied. The morphology for the as deposited thin films is observed to be homogenous distribution of grains over the substrate surface while on doping with Zn the net like porous structure is observed which on doping with Cu shows granular surface with rod like distribution over the substrate surface, that becomes like dry land after doping with Al, which in turns observed to be converted into compact rods or sticks buried under mud structure on doping with Ag while the Au doped thin films have shown very excellent morphology i.e. nano rod like structure with viewing in each other with porous nature having large surface area. Such large area porous structure may be very beneficial for applications based on surface morphology i.e. gas sensing etc. [16, 17].

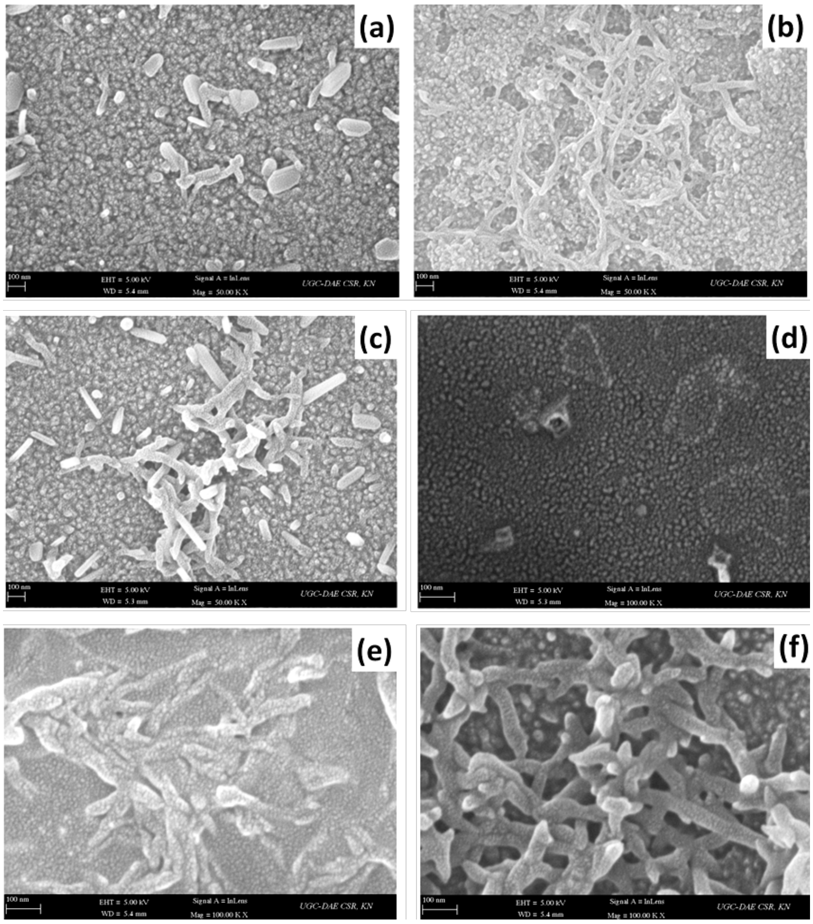

Fig 5 (a), (b), (c), (d), (e) and (f): Representing the SEM images of as deposited and Zn, Cu, Al, Ag and Au doped polyaniline thin films respectively prepared by solution polymerization method at room temperature over glass substrate.

3.4. Optical Absorbance Spectrum

Fig. 6 shows the optical absorbance spectra for polyaniline as deposited and doped polyaniline thin films, which shows two peaks observed in figure at ~ 650nm and at ~ 830 nm (~ 1.5 eV) respectively. These peaks may be due to charge excitation to the polaron band. Peak at 830 nm indicates the transition from the valence band to the hole polaron called as polaron band which is a strong transition [18, 19]. The other peak at 650 nm indicates the transition from polaron band to the conduction band. Polaron can be considered as a type of electronic defect that occurs with π orbital of the polymer backbone which produces molecular asymmetry responsible for high conductivity of the doped polyaniline. From graph, the flat breadth observed in every sample may be related to variation in the order of quinoid and benzenoid ring and the molecular conformation [20-22]. The intraband absorption is due to excitation of polarons as the doping of the elements there is increase in corresponding absorbance this may cause by molecular symmetry operations by virtue of bore size matching of the atoms, there by the restructuring of the electronic orientation occurs which may vary the absorbance peaks positions. The absorbance is observed to be increased from the elements Zn, Cu, Al, Ag and Au doping, the Au doping have shown maximum absorbance in comparing to the others this could cause the additional charge exciton induced electron hole pair formations.

This optical absorbance data obtained have been used for plotting energy band gap spectrum, it is observed that the energy band gap 2.7eV to 2.5eV on doping [21]. The minimum Eg is observed for the Au doped polyaniline thin films, it may be related to the aniline in monomer chain get restricted for delocalization which can results in decrease in presence of alternating electron for transitions and thereby the conductivity may be lower while on doping restructuring may provide an opportunity for increasing concentrations of charge delocalization and charge transfer from benzenoid to quinoid and vice versa rings this effects predominate over the electronic charge localizations effects and lead to increase in conductivity [21-23]. This seems understandable since conductivity is dependent on the orientation of the phenyl rings as well as on the electron density of the ring.

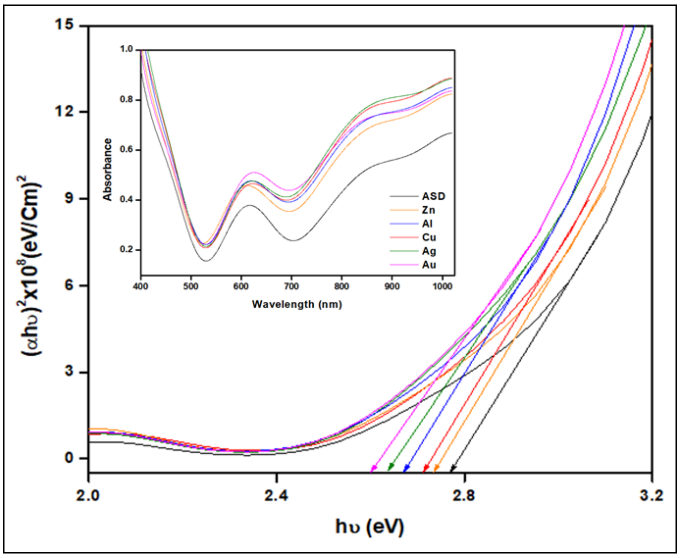

Fig 6: Graph of $(\alpha h\nu)^2$ verses hν used for calculations of energy band gap while inset image corresponds for optical absorbance spectrum drawn as absorbance against wavelength for as deposited and doped polyaniline thin films deposited by solution polymerization method at room temperature over glass substrate.

3.5. Gas Sensing Characteristics

Ammonia gas sensing property checked with the help of resistivity based four probe ammonia gas sensing using silver paste for making ohmic contacts. Fig. 7 shows the sensing characteristics graph obtained for all samples. From the results obtained response of each sample was calculated which was further used for calculating sensitivity of the polyaniline thin films. Response and sensitivity found to be increasing with varying the doping compositions. For ASD the sensitivity is observed to be almost 72% which is increased in linear way 74%, 76%, 77%, 79% and 83% for Zn, Cu, Al, Ag and Au doped polyaniline thin films respectively. In emeraldine salt, polarons were found to be charge carrier which occurs by electron-phonon interaction. The density of charge carrier (polarons) may be increased by varying the doping level which also enhances the conductivity of polyaniline emeraldine salt [24-26].

The doping is achieved by protonation of backbone nitrogen site of polyaniline. The charge transfer is introduced through oxidation of aniline in which the total number of electrons in the film remains same but the vacancies are created in film. The chemical structure of polyaniline has three benzene rings separated by amine (-NH-) group and one quinoid ring separated by imine (-N=) group.

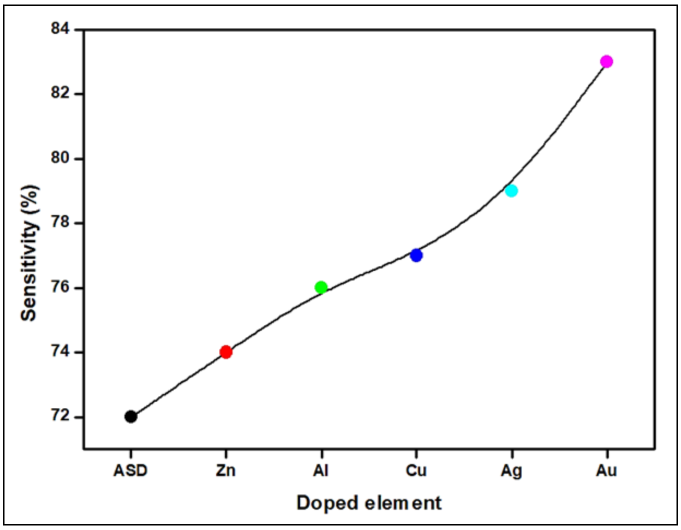

Fig 7: Ammonia gas sensing response obtained for as deposited and doped polyaniline thin films while inset image shows the response and recovery time graph for as deposited polyaniline thin films.

The quinoid ring has two pair of carbon atom and a double band with nitrogen atom with four π electrons. Upon protonation the imine group gets transformed to semiquinone radical cation state [26-27]. This cation is more localized with degradation generating polarons. The protonation leads to increase H^+ ion concentration so numbers of holes are increased in the imine group which surround quinoid ring. This addition of holes creates charge localization in the valence band of polyaniline. Increase in doping level increases number of valence band charges resulting significant change in significant change in molecular orbital and band structure. The double bond in imine reorganizes changing the quinoid configuration as three carbon atoms with six π electrons. So, this change in geometry weakening the double bond between nitrogen and quinoid ring [27-30]. This would increase the charge carrier density and strength of interaction between carrier states. The large carrier mobility of charges is permitted by the doping in the film.

Conclusion

From the above study it is observed that the doping of Zn, Cu, Al, Ag and Au elements in polyaniline thin films can be achieved using the solution polymerization method at room temperature. These as deposited and doped thin films have been comparatively analysed for structural, compositional, morphological, optical absorbance properties with the intension to study its effect over the NH_3 gas sensing behaviour. From the Fourier transform infra-red spectrum of as deposited and doped thin films shows shift in peaks corresponding to 1632 cm^{-1} and 1354 cm^{-1} attributed to C=C stretching vibrations of benzenoid and quinoid rings, while peaks 1193cm^{-1} and 833cm^{-1} are associated with the protonation and doping. Raman spectrum for as deposited and doped thin films exhibits sharpening of the characteristic peaks 1599 cm^{-1} for C-C stretching in benzenoid, 1509 cm^{-1} for C=C stretching in quinonoid while 1374 cm^{-1} for C~N+ vibrations of delocalized polaronic structures and C=N stretching vibrations in quinonoid units. Morphological images observed from the scanning electron microscopy (SEM) shows granular distribution of particles over the substrate surface for as deposited thin films which gets improved and or reduction in size for doping some elements. Optical absorbance spectra revealed improvement in absorbance coefficient upon doping, peak at 650nm corresponds for exciton induced charge transitions. The NH_3 gas sensing characteristics when studied revealed increment in gas sensitivity upon doping from 72% increase in linear way 74%, 76%, 77%, 79% and 83% for Zn, Cu, Al, Ag and Au doped polyaniline thin films respectively.

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References

1. Mude KM, Mude BM, Raulkar KB, Yawale SS,Yawale SP. Conducting Polymer Polyaniline as CO_2 gas sensor, *International Journal of Chem Tech Research*. 2017; 10:494-500.
2. Abdulazeez O. Mousa, Shaymaa Hussein Nawfal, Study of Some Optical Properties of Polyaniline Polymer, *International Journal of Chem Tech Research*. 2017; 10:581-588.
3. Priyanka Kolhar, Basavaraja Sannakki, Meenakshi Verma, Siddaramappa Suresha, Mansoor Alshehri, Nehad Ali Shah, Investigation of Structural, Dielectric and Optical Properties of Polyaniline Magnesium Ferrite Composites, Nanomaterials. 2023; 13:2234.
4. Mahdi Aleahmad, Hamidreza Ghafouri Taleghani, Hossein Eisazadeh, Effect of Synthesis Conditions on the Morphology of Polyaniline, Asian Journal of Chemistry. 2010; 22:7353-7360.
5. Dixya AS, Vijayalaxmi Reddy, Anilkumar Bidve, Praveen BC, Structural, electrical, optical and gas sensing properties of $MgTiO_3$-B doped polyaniline thin films, *International Journal of Advanced Biochemistry Research*. 2024; 8:40-43.
6. Jonas Tokarsky, Michal Maixner, Pavlina Peikertova, Lenka Kulhankova, Jaroslav V. Burda, The IR and Raman spectra of polyaniline adsorbed on the glass surface; comparison of experimental, empirical force field, and quantum chemical results, *European Polymer Journal*. 2014; 57:47–57.
7. Muhamad Rasyidi Husin, Agus Arsad, Siti Samahani Suradi, Othman Alothman, Norzita Ngadi, Mohd Johari Kamaruddin, Fourier Transforms Infrared Spectroscopy and X-ray Diffraction Investigation of Recycled Polypropylene/Polyaniline Blends, Chemical Engineering Transactions. 2017; 56:530.
8. Partha Pratim Sengupta, Pradip Kar, Basudam Adhikari, Influence of dielectric constant of polymerization medium on processability and ammonia gas sensing properties of polyaniline, Bull. Mater. Sci. 2011; 34:261–270.
9. Anil Kumar Harish Mudil, Structural Characterization of Polyaniline, Plant Archives. 2020; 20:2670-2672.
10. Said Ali Akbar, Achmad Rochliadi, Veinardi Suendo, Nurdin Saidi, Lelifajri Ainun Mardhiah, A Raman Spectroscopy Study of the Polyaniline Electrode On Zn-Polyaniline Rechargeable Batteries Rasayan J. Chem. 2018; 11:1525-1531.
11. Hasoon Salah Abdullah, Electrochemical polymerization and Raman study of polypyrrole and polyaniline thin films, *International Journal of Physical Sciences*. 2012; 7:5468-5476.
12. I Baltog, M Baibarac, L Mihut, N Preda, T Velula, C Bucur, M Husanu. Vibrational Properties of Polyaniline Functionalized PbI_2, *Rom. Journ. Phys*. 2024; 54:677–688
13. HA Salih, GG Ali, MM Uonis. Structure and optical properties of polyaniline-based hybrid nanocomposites by chemical oxidative method, *Digest Journal of Nanomaterials and Biostructures*. 2023; 18:1261-1267.
14. WS Huang, AG MacDiarmid. Optical properties of polyaniline, Polymer. 1993; 34:1833.
15. K Vikas, G Rajesh, AS Md. Yusuf, K Vishwanath, H Jakeer and B Shridhar. Synthesis, Characterization, and Investigation of Electrical, Magnetic, Sensor, and Mechanical Properties of Polyaniline/Zinc Dioxide Nanocomposites, *Rasayan J. Chem*. 2023; 16:1390-1395.
16. Bogdan Butoi, Andreea Groza, Paul Dinca, Adriana Balan and Valentin Barna, Morphological and Structural Analysis of Polyaniline and Poly(o-anisidine) Layers Generated in a DC Glow Discharge Plasma by Using an Oblique Angle Electrode Deposition Configuration, Polymers. 2017; 9:732.
17. Arunima Verma and Tanuj Kumar, Ag/Cu doped polyaniline hybrid nanocomposite based novel gas sensor for enhanced ammonia gas sensing performance at room temperature, RSC Adv. 2024; 14:25093.
18. Hasoon Salah Abdulla and Abdullah Ibrahim Abbo, Optical and Electrical Properties of Thin Films of Polyaniline and Polypyrrole, *Int. J. Electrochem. Sci*. 2012; 7:10666-10678
19. Maria Grzeszczuk, Anna Grańska, Roman Szostak, Raman Spectroelectro chemistry of Polyaniline Synthesized Using Different Electrolytic Regimes – *Multivariate Analysis Int. J. Electrochem. Sci*. 2013; 8:8951–8965
20. Fatiha Saouti, Said Belaaouad, Abdelouahed Cherqaoui, Youssef Naimi, Polyaniline Thin Film Prepared by

Electrochemical Polymerization Method, Biointerface Research in Chemistry. 2022; 12:5523-5533

21. Xinpeng Chen, Xiangdong Chen, Xing Ding and Xiang Yu, Gas Sensitive Characteristics of Polyaniline Decorated with Molybdenum Ditelluride Nanosheets, Chemosensors. 2022; 10:264.
22. Vadiraj KT, SL Belagal. Characterization of Polyaniline for Optical and Electrical Properties, IOSR Journal of Applied Chemistry. 2015; 8:53-56
23. José E. Pereira da Silva, Márcia L.A. Temperini and Susana I. Córdoba de Torresi, Characterization of Conducting Polyaniline Blends by Resonance Raman Spectroscopy, *J. Braz. Chem*. Soc. 2005; 16:322-327.
24. Hasoon Salah Abdullah, Electrochemical polymerization and Raman study of polypyrrole and polyaniline thin films, I*nternational Journal of Physical Sciences*. 2012; 7:5468-5476.
25. SG Pawar, SL Patil, AT Mane, BT Raut, VB Patil. Growth, characterization and gas sensing properties of polyaniline thin films, Archives of Applied Science Research. 2009; 1(2):109-114.
26. Priyanka D, KS Venkatesh. Synthesis, Characterization and Electrical Properties of Polyaniline Doped with Different Acids, Priyanka D. *Int. Journal of Engineering Research and Applications*. 2015; 5:53-61.
27. Anil G. Sonkusare, Sachin Tyagi, Ranjan Kumar, Sunita Mishra, Room Temperature Ammonia Gas Sensing Using Polyaniline Nanoparticles Based Sensor, *International Journal of Materials Science*. 2017; 12:283-291.
28. Oxana L. Gribkova and Alexander A. Nekrasov, Spectroelectrochemistry of Electroactive Polymer Composite Materials, Polymers. 2022; 14:3201.
29. GA Rimbu, I Stamatin, CL Jackson, K Scott. The morphology control of polyaniline as conducting polymer in fuel cell technology, *Journal of Optoelectronics and Advanced Materials*. 2006; 8:670-674.
30. Naseem Deshpande, Sanjay Chakane and Ranjit R. Borude, Synthesis and Characterization of Polyaniline, using Different Dopant, for Sensing Application of Pollutant Gases. *Journal of Atomic, Molecular, Condensate & Nano Physics*. 2016; 3:27-33.