https://doi.org/10.30799/jtfr.030.25080101
J. Thin Films Res. - Volume 8 Issue 1 (2025) 63–66

ISSN: 2581-3811

Share Your Innovations through JACS Directory

Journal of Thin Films Research

Visit Journal at http://www.jacsdirectory.com/jtfr

Physicochemical and Optoelectronic Properties of Polyaniline Thin Films

Karan K. Rathod, Nikhilesh S. Bajaj, Rajesh A. Joshi*

Thin films and Nanotechnology Lab., Dept. of Physics, Toshniwal Arts, Commerce and Science College, Sengaon, Hingoli – 431 542, Maharashtra, India.

ARTICLE DETAILS

Article history:
Received 25 September 2025
Accepted 10 October 2025
Available online 17 October 2025

Keywords:
Thin Films
Polymer
Polaron
Compositional Modifications
Sensor

ABSTRACT

The present article mentions about the physicochemical and optoelectronic properties of polyaniline (PANI) thin films synthesized by using solution polymerization techniques over the glass substrate at room temperature with the intension to study its physicochemical and optoelectronic properties specially as gas sensing materials. These as deposited thin films have been synthesized by varying the deposition time (substrate dipping) intervals of 40 min. The Fourier transform infra-red spectroscopy (FTIR) revealed the characteristics peaks at 1582 cm^{-1} related to C = C stretching deformation of quinoid (Q) ring, 1492 cm^{-1} corresponds for C = C stretching of benzenoid (B) ring, while 1109 cm^{-1} shows B–NH^+ = Q stretching. The surface morphology represented the porous nature granular distribution of grains over the substrate surface. The optical band gap energy calculated from the absorbance spectrum shows decreases in energy band gap from 2.57 eV to 2.51 eV with the increase in deposition time which can be attributed to variation in the structural morphology with increase in thickness of the materials. The ammonia gas sensing when studies revealed that the films deposited for 240 min reponed to ammonia gas of 90% which can be inferred to increase in charge carrier's concentrations upon increasing the films deposition time and thickness.

1. Introduction

Polyaniline thin films are the conducting polymers sensing materials, which can be prepared by chemical route solution polymerization method at the room temperature. These polymer thin films show reversible pH dependent spectroscopic and gas dependent electrical conductivity modifications. Such polymer provides structure to immobilize ligands, enzymes and antibodies hence used in the development of novel chemical and biological sensors [1-3].

Semiconducting gas sensors commonly depends on change in conductivity upon exposure to sensing gases like conductivity of a PANI decreases with increasing ammonia gas concentration [4]. At room temperature, gas sensing response time of these polymers were few minutes; by varying the temperature from 20 to 100 °C, the response time may be reduced by few minutes. Even upon treatment with NO_2, the response time and gas sensitivity of sensor may deteriorate. There are some issues with PANI thin films as gas sensor like response and recovery time which may be due to composition of the materials [5-8].

Hence the present article deals with synthesis of PANI thin films with varying deposition time, so that the parameter of materials synthesis time can be optimized. The synthesis of thin films through the solution polymerization method follows ion by ion induction over the substrate surface hence the saturation may be achieved at particular deposition time and thereafter the growth of PANI thin film may stop [9-11]. Therefore, considering the theory of ionic polymerization chain growth, the present article deals with synthesis of varying time deposition PANI thin films and testing its physicochemical and optoelectronic properties along with ammonia gas sensing properties. These as deposited 40 minutes time interval difference deposition (dipping time) thin films have been characterized for Fourier transform infrared spectroscopy (FTIR), atomic force microscopy (AFM) for surface morphology and optical energy band gap along with ammonia gas sensing properties [12-14].

2. Experimental Methods

2.1 Substrate Cleaning

In solution growth technique, extreme cleanliness of the substrate is required, since the contaminated surface provides nucleation sites facilitating the growth, and resulting into non-uniform, porous and non-adherent film. The glass slides of the dimension 7.3 x 2.5 x 0.1 cm^3 have been used as the substrates. The following procedure has been used for cleaning of the substrates. The slides were washed with water, then boiled in concentrated chromic acid (0.5 M) for 1 h and kept in it for 24 h. The boiled substrates were washed with double distilled water and finally, the substrates were dried, degreased in AR grade acetone and were kept in dust free airtight container.

2.2 Preparation of Solution

All chemicals used for preparing PANI thin films were of A.R. grade as follows: Ammonium peroxidisulphate (APS) [$(NH_4)_2S_2O_8$], hydrochloric acid [HCl], and aniline [$C_6H_5NH_2$] as the reactants. For the deposition of PANI thin films, solutions of APS and aniline were prepared separately using double distilled water.

2.3 Polyaniline Thin Film Synthesis

Thin film of PANI was prepared by solution polymerization method using HCl as dopent, 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; the other chemicals were used as they received. Solution polymerization process proceeded as follow, 0.2 mL aniline was added in 1 mL concentrated HCl solution with constant stirring at room temperature then 0.25 mL APS was prepared in an aqueous media, before mixing, these reactants were pre cooled in an ice bath container. Thereafter 20 mL APS was added slowly to the aniline solution with constant stirring at room temperature. Cleaned glass substrates numbered from R_1 to R_7 were immersed in the reaction bath using substrate holder. After every 40 minutes one substrate was removed from the reaction bath which then washed with distilled water to remove the granules attached with the surface of the substrate, dried and preserved in dark desiccators. The reaction was carried for 5 h resulting in green color precipitate which confirms formation of PANI emeraldine salt [15,16]. Thickness of R1 sample was found to be 21.3 nm while for

*Corresponding Author:urajoshi@gmail.com(Rajesh A. Joshi)

https://doi.org/10.30799/jtfr.030.25080101

Cite this Article as: Karan K. Rathod, Nikhilesh S. Bajaj, Rajesh A. Joshi, Physicochemical and optoelectronic properties of polyaniline thin films, J. Thin Films Res. 8(1) (2025) 63–66.

sample of critical thickness (R_6) it was 191.1 nm and for the R_7 sample it became 174.6 nm.

2.4 Characterizations

The as-deposited PANI films were characterized for their physical and chemical properties by using following characterization techniques.

2.4.1 Film Thickness

Film thickness measurement of PANI was carried out by measuring the optical absorbance spectra. By using the formula, the absorbance at 400 nm wavelength gives the value of film thickness. It can be calculated as below.

$$Thickness(t) = \frac{A_{400}}{(5.4 \pm 0.2)x10^{-4}} \text{nm}$$

2.4.2 Atomic Force Microscopy (AFM)

The surface morphology was studied by using Veeco-III for Digital Instruments. Scanning Probe Microscope (SPM) is used in dynamic atomic force microscope mode for surface morphology and roughness analysis of the film in two and three-dimensions. Si tip of 10 nm diameter was used.

2.4.3 Optical Energy Band Gap

The variation of absorbance with wavelength for all films has been carried out with Perkin Elmer Lambd-25 UV-VIS spectrophotometer which is used for extrapolating the energy band gap of the polyaniline thin films.

2.5 Ammonia Gas Detection Testing

Ammonia gas (NH_3) detection experiments were carried out on Lambda-25 Perkin Elmer spectrophotometer. The spectrophotometer was used in absorbance mode. In this instrument special arrangement was made for the insertion of ammonia gas and to protect the instrument from possible destruction due to corrosion. The ammonia gas was introduced into the chamber by using small diameter pipe line from gas cylinder. Gas detection was carried out by performing cycles of purging ammonia gas and dry air in the chamber.

3. Results and Discussion

3.1 Growth of Polyaniline Thin Films

The oxidative polymerization of aniline with APS in the presence of HCl shows an exothermic nature of the reaction which can be observed by monitoring the reaction temperature. Fig. 1 shows the initial induction period characteristic for aniline polymerization in acidic media, which was followed by rapid exothermic reaction. Initial temperature of the reaction was ~27 °C and the final temperature became ~34 °C. Increase in the temperature confirms the exothermic nature of the reaction.

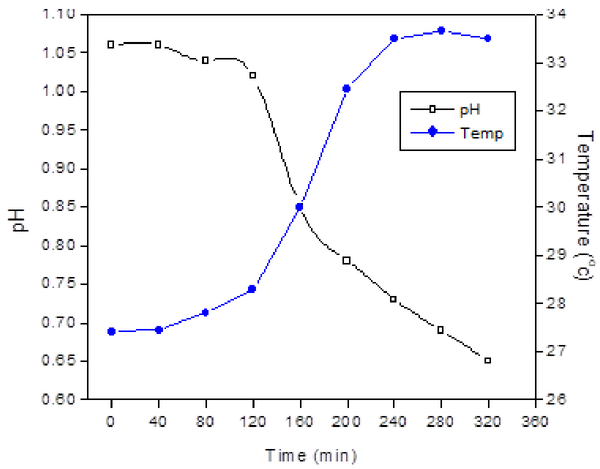

Fig. 1 Variation of pH and temperature with polyaniline thin film deposition time

The acidity of the reaction bath increases continuously this may be attributed to increase in H^+ ion concentration in the reaction bath. Upon protonation the imine group of quinoid ring gets transformed into semiquinone radical cation [17]. This leads to add H^+ ion to the reaction. This increase in H^+ ion concentration corresponds to decrease in pH of the reaction bath. Initial pH of the reaction bath was ~1.06 and at the completion of the reaction it became ~0.6. The stepwise decrease in pH indicates increase in doping level. The steps involved in the oxidative polymerization of aniline are as follows: When the reactants were mixed, within few minutes the induction of film in the form of layer starts on substrate. The time required for such induction is called as induction period [18]. Induction of layer starts with nucleation at a point on the substrate around which then further growth of film occurs [19].

This structural enhancement proceeds with increase in protonation of acid which causes increase in chain length and number of oxidized state sites. The process continues till it reaches a maximum thickness called as critical thickness (T_c). Film at this stage is dense, rigid forming highly open structure containing large fraction of pores leading to inhomogeneous or multilayered structure [20]. Upon attaining T_c, partial decrease in thickness is observed this may be attributed to depletion of either oxidant or monomer or both. The time at which depletion occurs is called as depletion period. Here we found the critical thickness as 191.1 nm for R_6 sample. Further increase in deposition time shows slight decrease in thickness, which may be attributed to increase in rate of dissolution than the rate of deposition after attaining the critical thickness (T_c) as represented in Table 1.

Table 1 Deposition time and thickness of the polyaniline thin films

Sr. No.	Sample ID	Deposition time (min)	Thickness (nm)
01	R1	40	21.3
02	R2	80	68.5
03	R3	120	111.2
04	R4	160	162.6
05	R5	200	184.9
06	R6	240	191.4
07	R7	280	174.2
08	R8	320	169.0

3.2 Fourier-Transform Infra-Red (FTIR) Study

Fourier-transform infra-red (FTIR) spectrum of the green PANI powder was conducted, which was collected and filtered after the polymerization process was over. Fig. 2 shows the FTIR spectra of PANI powder. The peak at 1582 cm^{-1} is related to C = C stretching deformation of quinoid (Q) ring, 1492 cm^{-1} corresponds for C = C stretching of benzenoid (B) ring, 1303 cm^{-1} due to the carbon nitrogen (C–N) stretching of secondary aromatic amine, 1109 cm^{-1} shows B–NH^+ = Q stretching, 821 cm^{-1} is attributed to aromatic C–H out of plane deformation vibration of 1,4-disubstituted benzene ring [21], 611 cm^{-1} indicate C–S stretching vibration [22], 513 cm^{-1} is assigned for – SO_3H group absorption spectra. Existence of all these bonds confirms the presence of functional group which are basic contain of the reactants used in the reaction.

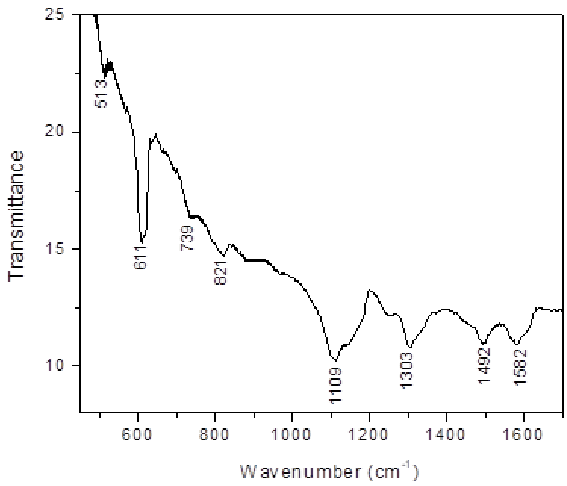

Fig. 2 FTIR spectra of polyaniline thin film

3.3 AFM Study

The atomic force microscope (AFM) images investigating surface topography of PANI samples are shown in Fig. 3(a), (b) and (c) which shows the AFM images of R_2, R_4 and R_6 samples, respectively. Surface of R_2 is featureless and smooth. As time passes up to sample R_4 the hillock formation starts. Variation in structural morphology may be attributed to multilayer deposition on substrates. Such a multilayer deposition causes increase in thickness of samples [23]. The route means square (rms) surface roughness calculated with the help of software is found to be 33.65 nm, 74.24 nm and 111.03 nm for R_2, R_4 and R_6 respectively.

https://doi.org/10.30799/jtfr.030.25080101

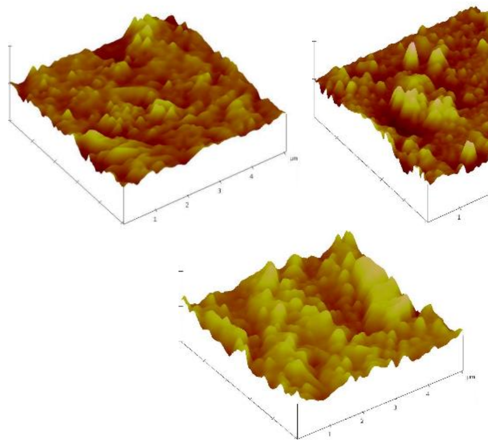

Fig. 3 AFM images of R_2, R_4 and R_6 samples

3.4 Optical Analysis

As the thickness of the sample is increased, there is increase in corresponding absorbance. This may cause by molecular symmetry variation. The increase in thickness gives rise to asymmetric molecularity, dense surface and inhomogeneous morphology. From Fig. 4 it is seen that the optical band gap energy decreases from 2.57 eV to 2.51 eV with the increase in thickness from 21.3 nm to 191.1 nm. Decrease in the energy band gap may be attributed to variation in the structural morphology with increase in thickness [24-26]. Increase in thickness shows blue shift in band gap energy (E_g) which may be related to structural morphology dependant energy band gap.

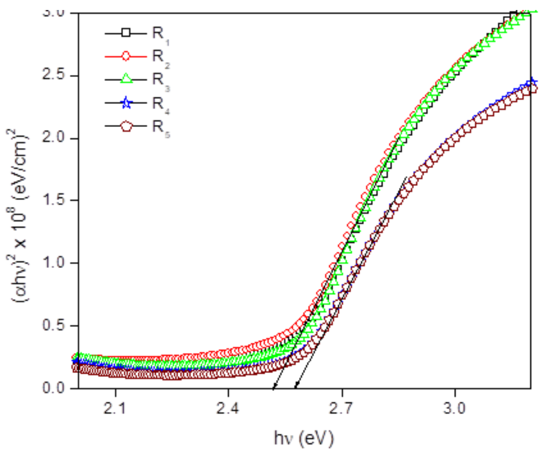

Fig. 4 Optical energy band gap of polyaniline thin films

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 PANI emeraldine salt [27]. The doping is achieved by protonation of backbone nitrogen site of PANI. 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 PANI has three benzene rings separated by amine (- NH -) group and one quinoid ring separated by imine (- N =) group. The quinoid ring has two pair of carbon atom and a double band with nitrogen atom with four π electrons [28]. Upon protonation the imine group gets transformed to semiquinone radical cation state. 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 PANI. 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. This would increase the charge carrier density and strength of interaction between carrier states.

On extending the deposition time the film thickness increases which results in interchain interaction of polymer backbone forming regularity of PANI chain giving rise to number of charge carriers [29]. The large carrier mobility of charges is permitted by the increase in thickness of the film. So, this increase in thickness of the film provides a large space for the motion of these charges through the film. On applying the external potential, the conductivity of the film gets increased.

3.5 Ammonia Gas Sensing

Ammonia gas detection testing was carried out only on R6 sample. PANI film is inserted vertically in the gas chamber and change in optical absorbance of the film was detected [30]. It is observed that absorbance of the film increases when ammonia is purged in the chamber, indicating the adsorption and surface reaction occurred between ammonia and PANI. The sensitivity of the sensor is defined by using (standard) relation, $S = (A_g - A_a)/A_a$ where A_g and A_a are the absorptions of films in gas and in air, respectively. These absorbance values are measured at 800 nm wavelength only. Fig. 5 shows the change in sensitivity of optical gas sensor with ppm gas concentration of ammonia. The sensitivity of the sensor increases with increase in gas concentration. A transient change in absorbance of sensor with time at different concentrations of ammonia is shown in Fig. 6. The response time and recovery time of the sensor are 55 sec and 115 sec, respectively.

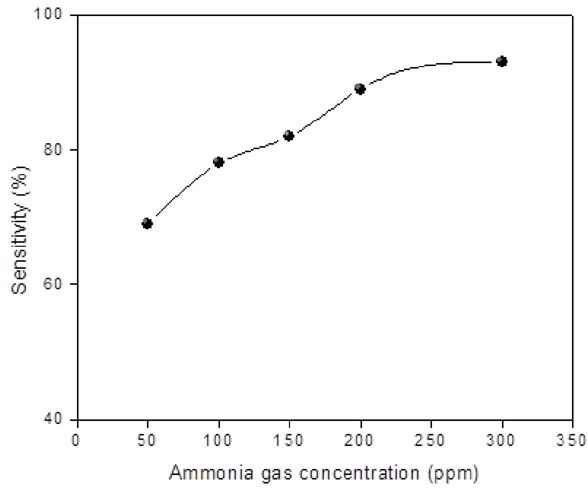

Fig. 5 Variation of sensitivity with ammonia gas concentration

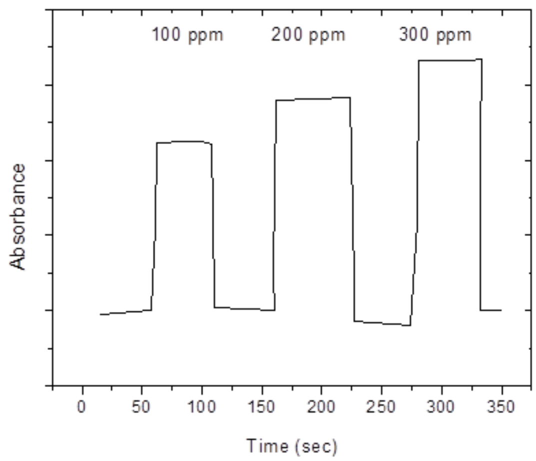

Fig. 6 Transient curve of a PANI ammonia gas sensor

4. Conclusion

From the result obtained it can be understood that the PANI thin films can be deposited using solution polymerization method on glass substrate. Films deposited for 240 min results into obtaining of stoichiometric thin films with thickness of 191 nm. The FTIR shows characteristics peaks at 1582 cm^{-1} related to C=C stretching deformation of quinoid (Q) ring, 1492 cm^{-1} corresponds for C=C stretching of benzenoid (B) ring, while 1109 cm^{-1} shows $B–NH^+ = Q$ stretching. While the surface morphology shows granular thin films which may be useful for gas sensing applications. The energy gas is observed to be increased with respect to induction and increase in thickness which may be related to polaron induced charge localizations. The ammonia gas sensing tested shown response time and recovery time of the sensor are 55 sec and 115 sec with sensitivity of 85%.

https://doi.org/10.30799/jtfr.030.25080101

Cite this Article as: Karan K. Rathod, Nikhilesh S. Bajaj, Rajesh A. Joshi, Physicochemical and optoelectronic properties of polyaniline thin films, J. Thin Films Res. 8(1) (2025) 63–66.

Acknowledgement

One of the author Rajesh A. Joshi is thankful to Swami Ramanand Teerth Marathwada University, Nanded Maharashtra for financial grants through University Minor Research Project APDS/Uni. MRP-VIII/Sci. & Tech.-Physics/2023-24/1472 dated 25-08-2023. Authors are also thankful to scientific consortium UGC DAE CSR Indore, UGC DAE CSR Kolkata and UGC DAE CSR Kalpakkam for providing thin films characterization facility.

References

[1] A. Kobayashi, H. Ishikawa, K. Amano, M. Satoh, E. Hasegawa, Electrical conductivity of annealed polyaniline, J. Appl. Phys. 74 (1993) 296-299.

[2] R.E. Delahoz, D.P. Schueter, W.N. Rom, Chronic lung disease secondary to ammonia inhalation injury: A report on three cases, Am. J. Ind. Med. 29 (1996) 209-214.

[3] N.E. Agbor, M.C. Petty, A.P. Monkman, Polyaniline thin films for gas sensing, Sens. Actuators B 28 (1995) 173-179.

[4] S. Budarvari, The Merck index, An encyclopedia of chemicals, drugs and biologicals, 12th Edn, Merck, Unites States, 1996.

[5] M.E. Nicho, M. Trejo, A.G. Valenzuela, J.M. Saniger, J. Palacios, H. Hub, Polyaniline composite coatings interrogated by a nulling optical-transmittance bridge for sensing low concentrations of ammonia gas, Sens. Actuators B chem. 76 (2001) 18-24.

[6] Timmer, W. Olthuis, A. Berg, Ammonia sensors and their applications a review Sens. Actuators B 107 (2005) 666-677.

[7] S. de. Marcos, O.S. Wolfbeis, Optical sensing of pH based on polypyrrole films, Anal. Chim. Acta 334 (1–2) (1996) 149-153.

[8] O.A. Sadik, G.G. Wallace, Pulse damperometric detection of proteins using antibody containing conducting polymers, Anal. Chim. Acta 279 (1993) 209-212.

[9] M. Brie, R. Turcu, C. Neamtu, S. Pruneanu, The effect of initial conductivity and doping anions on gas sensitivity of conducting polypyrrole films to NH_3, Sens. Actuators B Chem. 37 (1996) 119-122.

[10] L.G. Close, F.I. Catlin, A.M. Cohn, Acute and chronic effects of ammonia burn of the respiratory tract arch. Otolaryngol. 106 (1980) 151-158.

[11] S.A. Krutovertsev, S.I. Sorokin, A.V. Zorin, Y.A. Letuchy, O.Y. Antonova, Polymer film-based sensors for ammonia detection, Sens. Actuators B 7 (1992) 492-494.

[12] A.L. Kukla, Y.M. Shirshov, S.A. Piletsky, Ammonia sensors based on sensitive polyaniline films, Sens. Actuators B 37 (1996) 135-140.

[13] N.E. Agbor, J.P. Cresswell, M.C. Petty, A.P. Monkman, An optical gas sensor based on polyaniline Langmuir-Blodgett films, Sens. Actuators B 41 (1997) 137-141.

[14] B.K. Kim, Y.H. Kim, K. Won, H. Chang, Y. Choi, K. Kong, et al., Electrical properties of polyaniline nanofibre synthesized with biocatalyst, Nanotechnol. 16 (2005) 1177-1181.

[15] X.F. Yu, Y.X. Li, N.F. Zhu, Q.B. Yang, K.K. Zadeh, A polyaniline nanofibre electrode and its application in a self-powered photoelectrochromic cell, Nanotechnol. 18 (2007) 15201-15205.

[16] M.M. Ayad, E. Azaki, Quartz crystal microbalance and spectroscopy measurements for acid doping in polyaniline films, Sci. Technol. Adv. Mater. 9 (2008) 15007-15017.

[17] H.A. AlAttar, Q.H. Alalawina, A.P. Monakam, Spectroscopic ellipsometry of electrochemically prepared thin film polyaniline, Thin Solid Film. 429 (2003) 286-294.

[18] S.M. Conwell, C.B. Duke, A. Paton, S. Jaydev, Molecular conformation of polyaniline oligomers: Optical absorption and photoemission of three phenyl molecules, J. Chem. Phys. 88 (1988) 3331-3337.

[19] Z. Jin, Y. Su, Y. Duan, Development of a polyaniline-based optical ammonia sensor, Sens. Actuators B: Chem. 72 (2001) 75-79.

[20] M. Leung, C.L. Foo, Mass ammonia inhalational burns experience in the management of 12 patients, Ann. Acad. Med. Singapore 21 (1992) 624-629.

[21] N.C. Foulds, C.R. Lowe, Immobilization of glucose oxidase in ferrocene-modified pyrrole polymers, Anal. Chem. 60 (1988) 2473-2478.

[22] S. Stafstrom, J.L. Bredas, A.J. Epstein, H.S. Woo, D.B. Tanner, W.S. Haung, A.G. MacDiarmid, Polaron lattice in highly conducting polyaniline: Theoretical and optical studies, Phys. Rev. Lett. 59 (1987) 1464-1467.

[23] M. Magnuson, J.H. Guo, S.M. Butorin, A. Aguli, C. Sathe, J. Nordgren, A.P. Monkam, The electronic structure of polyaniline and doped phases studied by soft x-ray absorption and emission spectroscopies, J. Chem. Phys. 111 (1999) 4756-4761.

[24] J. Yuan, Z. Wang, Q. Zhang, D.Han, Y. Zhang, Y. Shen, L. Niu, Controlled synthesis of 2D Au nanostructure assembly with the assistance of sulfonated polyaniline nanotubes, Nanotechnol. 17 (2006) 2641-2647.

[25] J.B. Yadav, R.B. Patil, R.K. Puri, Vijaya Puri, Optical properties of the chopped and non-chopped vacuum evaporated polyaniline thin film, J. Non-Cryst. Solid. 353 (2007) 4691-4696.

[26] H. Qiu, H. Li, K. Fang, J. Li, W. Mao, S. Luo, Micromorphology and conductivity of the vacuum-deposited polyaniline films, Synth. Met. 148 (2005) 71-74.

[27] M.M. Ayad, M.A. Shenashin, Film thickness studies for the chemically synthesized conducting polyaniline, J. Euro. Poly. 39 (2003) 1319-1324.

[28] C.L. Zhu, S.W. Chou, S.F. He, W.N. Liao, C.C. Chen, Synthesis of core/shell metal oxide/polyaniline nanocomposites and hollow polyaniline capsules, Nanotechnology 8 (2007) 275604-275610.

[29] N.C. DeSouza, M. Ferreira, K. Wohnrath, J.R. Silva, O.N. Oliveira Jr. Jose, A. Giacometti, Morphological characterization of Langmuir–Blodgett films from polyaniline and a ruthenium complex (Rupy): Influence of the relative concentration of Rupy, Nanotechnol. 18 (2007) 75713-75720.

[30] Janosevic, G.C. Marjanovic, B. Marjanovic, P. Hollar, M. Trachova, J. Stejkal, Synthesis and characterization of conducting polyaniline 5-sulfosalicylate nanotubes, Nanotechnol. 19 (2008) 135606-135612.

https://doi.org/10.30799/jtfr.030.25080101

Cite this Article as: Karan K. Rathod, Nikhilesh S. Bajaj, Rajesh A. Joshi, Physicochemical and optoelectronic properties of polyaniline thin films, J. Thin Films Res. 8(1) (2025) 63–66.