Shetkari Shikshan Prasarak Mandal's

Krishna Mahavidyalaya, Rethare Bk

IQAC 2018-2019

ACTIVITY REPORT PHYSICS DEPARTMENT

IQAC ACTIVITY No:

NAME OF THE ACTIVITY: "Lead college Activity-Research Project: "Application of nanostructured PANI film for electrochromic smart window and supercapacitor application"										
DATE	ATE FACULTY DEPARTMENT/COMMITTEI									
Throughout the academic year	Science	Physics	Dr. Dhanaji S. Dalavi							
TIME	VENUE	NUMBER OF PARTICIPANTS	NATURE: Outdoor/Indoor							
10.00 am-11.00 am	Physics laboratory	04 students+01 teacher	Indoor							
SUPPORT/ASSISTANCE:		Nil								

BRIEF INFORMATION ABOUT THE ACTIVITY (CRITERION NO. -):

TOPIC/SUBJECT	"Lead college Activity-Research Project: "Application of nanostructured								
OF THE ACTIVITY	PANI film for electrochromic smart window and supercapacitor application"								
OBJECTIVES	to analyze a scientific occurrence with an investigation or to solve a problem								
	with an invention.								
METHODOLOGY	Experimental work								
OUTCOMES	students become active, engaged learners. It also helped students to develop								
	independent critical thinking skills.								

PROOFS & DOCUMENTS ATTACHED (Tick mark the proofs attached):

Detters			
6. Feedback 7. News analysis clip with	8. Certificate	9. Any other	10.

IQAC CELL ACTIVITY NUMBER:

NAME OF TEACHER &	NAME OF HEAD/ COMMITTEE INCHARGE	PRINCIPALS SIGNATURE	IQAC COORDINATOR (SEAL & SIGNATURE)
Dr. Dhanaji S. Dalavi DEP. KRIS Retha	Dr. Dhahaji S. Dalavi HEAD ARTMENT OF PHYSICS HNA MAHAVIDYALAKAshna re Bk; Shivnagar - 415108Ta	Principal a Mahavidyalaya, R al. Karad : \$15 108	IQAC, Coordinator, RISHNA MAHAVIDYALAYA, ethare Bk; Shivnagar - 415108 Tal. Karad, Dist. Satara ethare Bk, (MS)



Ref. No. : KMR/

Date: 08/09/2018

To, The Co-coordinator Lead College Activity SGM College, Karad

Subject: Submission of application for financial support to research project Reference: SU/Post graduate admission/6780 dated 5th July, 2018

Respected Sir,

With reference to the above mentioned subject, herewith I am forwarding project proposal entitled **"Fabrication of nanostructured Polyaniline thin film for electrochromic smart windows and supercapacitor application**" under research sensitization scheme for college students initiated by Shivaji University, Kolhapur from June 2017.

Herewith I kindly request you to consider the said project proposal for possible selection.

Yours' (Fosthfwl)y PRINCIPAL (I/C) KRISHNA MAHAVIDYALAYA RETHARE (BK.), TAL. KARAD

Received 11/8/2018



To

The Principal, Krishna Mahavidyalaya Rethare (Bk.) Tal.Karad, Dist. Satara.

> Sub. : Submission of Research Project under Research Promotion Activity ofr College Students.

I am pleased to inform you that the Research Project under the Research Promotion Activity of the Shivaji University, Kolhapur is received with following details.

Name of Project Advisor	Name of Students	Title of Project	Amount Estimate Rs.
Dr. D. S. Dalavi	1) Desavale Suryashree Vilasrao	Fabrication of Nanostructured	10 0004
	2) Jadhav Amol Vijay	electrochromic smart windows and	10,000/-
	3) Harale Mohini Rajendra	supercapacitor application.	
	4) Jadhav Nikita Bharat	and is subject to final	

Financial assistance under this scheme is subject to final approval and directions of the university.

Thank you,



Yours faithfully,

Principal, Sadguru Gadage Maharaj College, KARAD



REGISTERED AD

06/03/2033

मा.प्राचार्य. कृष्णा महाविद्यालय, रेठरे बु ॥ जि.सातारा

> विषय : अग्रणी महाविद्यालय योजनेअंतर्गत रिसर्च प्रोजेक्टसाठी द्यावयाच्या ॲडव्हान्सबाबत.

संदर्भ : आपलेकडील जा.क्र. केएमआर दि.०८/०९/२०१८ चे पत्र.

महोदय,

प्रति,

सहो

आपलेकडील वरील संदर्भपत्रास अनुसरून कळवू इच्छितो की, शिवाजी विद्यापीठाच्या Research Promotion Activity for students of the affiliated Colleges या योजनेअंतर्गत आपल्या विद्यार्थ्यांच्या "Fabrication of Nanostructured Polyaniline thin film for electrochromic smart windows and supercapacitor application" या रिसर्च प्रपोजलसाठी विद्यापीठाने रू. १००००/-मंजूर केले असून सदर रिसर्च प्रपोजलसाठी सोबत रू.८०००/- चा ॲडव्हान्स रकमेचा चेक नं. しろ ४२० 🕐 /०१/२०१९ ने सोबत पाठविला आहे. कृपया सदर रकमेची पोहोच पावती त्वरीत पाठवून दि. द्यावी.

वरील रिसर्च प्रोजेक्टसाठी मंजूर रक्कम रू.१०,०००/– खर्च करून त्याचा हिशोब व प्रोजेक्ट रिपोर्ट या अग्रणी महाविद्यालयाकडे त्वरीत सादर करावा म्हणजे उर्वरीत रक्कम अदा करणे सोईद होईल,

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KARAD

आपला वि

अग्रणी महाविद्यालय

सद्गुरू गाडगे महाराज कॉलेज, कराड

कळावे, ही विनंती.

अग्रणी महाविद्यालय, स.गा.म.कॉलेज, कराड

सोबत : वरीलप्रमाणे.



Ref. No. : KMR/

Date :

प्रति_. मा . समन्वयक अग्रणी महाविद्यालय सदगुरू गाडगे महाराज कॉलेज कराड जि . सातारा .

विषय :- अग्रणी महाविद्यालया अंतर्गत राबवलेल्या रिसर्च प्रोजेक्टच्या खर्चाचा अहवाल.

महोदय.

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शिवाजी विद्यापीठाच्या Research Promotion activity for students of the affiliated collages या योजनेअंतर्गत या महाविद्यालयातील विद्यार्थ्यांच्या "Fabrication of Nanostructured Polyaniline thin films for electrochromic window and supercapacitor application" या रिसर्च प्रोपोसलं साठी विद्यापीठाने रु. १००००/- मंजूर केले होते. सदर रिसर्च प्रोपोसलं साठी आपणाकडून रु. ८०००/- चा ऍडव्हान्स रकमेचा चेक नं. ७३४३० दि. १०/०१/२०१९ रोजी मिळाला असून त्यानुसार वरील रिसर्च प्रोजेक्टसाठी मंजूर रकमेच्या खर्चाचा तपशील व अहवाल आपणाकडे पाठवीत आहे.

तरी उर्वरित रु.२०३२/- या महाविद्यालयास पाठविण्यात यावेत हि नम विनंती

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२	Shri. Samarth Trading Company	Glasswares	2026.00
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۲	Agrani Workshop, SGM college, Karad	Students and	150.00
		Advisor Travelling	
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Dr. C. B. Salunkhe PRINCHAL (SIL) KRISHNA MAHAVIDYALAYA RETHARE (BK.), TAL. KARAD

Department Physics Date- 27-2-2019

The Frincipal,

KRISHNA MAHAVIDY LYA; SHIVNAGAR

Subject- Request to pass the bills for payment,

Sir.

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Please find herewith the following bills for the payment while passing the bills I have checked the price of each item and is according to the price quoted by the party.

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Ref. To, GSTIN: 27AMVPP2791E1ZG

TAX INVOICE

C Shri Samarth Trading Company

Peth Sangli Road, Opp. Ganesh Servicing Center, Shripadnagar, ISLAMPUR - 415 409 Tal. Walwa, Dist. Sangli. Tel. (02342) 225394, 225773 Mob. 9822256373 E-mail : samarth.trading@yahoo.com samarth4092@gmail.com



Original Buyer's Copy Involce No: CO/0345/2018-19 (Physics Dept.) **Transport Mode:** Involce date: 22 / 02 / 2019 Vehicle number: Reverse Charge (Y/N): PO No. Date of Supply : State: Maharashtra Date : Challan No. Code 27 Bill to Party Ship to Party Name: The Principal, Krishna Mahavidyalaya, Name: Address : Shivnagar Address: Dist: Satara GSTIN: GSTIN: State: Maharashtra Code 27 State: Code CGST SGST S. No HSN code Taxable Valu Total **Product Description** GST Qtv Rate Amount Discount Rate Rate Amount Ferric Chloride Hexa. 500 gm. 1 18% 1 270.00 270.00 108.00 162.00 14.58 14.58 191.16 2 2 Potassum Ferrcyanide 500 gm. 18% 1500.00 1500.00 600.00 900.00 81.00 9 81.00 1062.00 1 ¢ Polyvhyl Alcohol 500 gm. 30.24 396.48 18% 1 560.00 560.00 224.00 336.00 30.24 9 4 Ammonia (25-30%) 2.5 Lit. 18% 580.00 232.00 348.00 31.32 31.32 410.64 1 580.00 9 5 Hydrogen Peroxide (35%) 500 ml. 37.80 495.60 37.80 18% 2 350.00 700.00 280.00 420.00 9 6 Sodium Dodecyl sulphate 500 gm. 30.24 396.48 30.24 189 1 560.00 560.00 224.00 336.00 9 7 Absolut Ethanol 500 ml. 38.88 509.76 18% 2 360.00 720.00 288.00 432.00 9 38.88 8 Polyethylenye Glycol 500 ml. 189 1 400.00 400.00 160.00 240.00 9 21.60 21.60 283.20 9 Zinc Acetate 500 gm. 18% 1 530.00 530.00 212.00 318.00 9 28.62 28.62 375.24 10 Potassium Hydroxide 500 gm. 17.82 233.64 330.00 9 18% 330.00 132.00 198.00 17.82 g 1 11 Acetonitrile 500 ml. 18% 1 530.00 530.00 212.00 318.00 9 28.62 9 28.62 375.24 12 Hexamethylenetetramine (HMTA) 500 gm. 18% 1 300.00 300.00 120.00 180.00 9 16.20 9 16.20 212.40 13 Dietanolamine 500 ml. 1 360.00 360.00 144.00 216.00 9 19.44 9 19.44 254.88 18% 14 Potassium Persulphate 500 gm. 18% 1 470.00 470.00 188.00 282.00 9 25.38 9 25.38 332.76 Potassium Chloride 500 gm. 15 18% 1 190.00 190.00 76.00 114.00 9 10.26 10.26 134.52 16 Whatman Paper Pkt.No. (12.5cm) 72.90 955.80 18% 1 1350.00 1350.00 540.00 810.00 9 72.90 504.90 6619.80 Total 18 9350.00 3740.00 5610.00 504.90 Total Invoice amount in words 他。如何能够不同种性的利用的 **Total Amount before Tax** 5610.00 Add: CGST 504.90 Add: SGST 504.90 Six Thousand Six Hundred Twenty Rupees Only. **Total Tax Amount** 1009.80 **Total Amount after Tax:** 6619.80 Bank Details 6620.00 Round Off Total Amount ading Compa Bank A/C: 579505040000105 Bank Name : Union Bank of India Ceritified that the particulars given above are true and correct Bank IFSC: UBIN0557951 Branch : Islampur For SHRI SAMARTH TRADING COMPANY 15183 840. 69.5 J.199 Declaration : 12 mg We declare that this invoice shows the actual price of the goods (Sanwi) described and that all particulars are true and correct. Company GSTIN/UIN : 27AMVPP2791E1ZG : AMVPP2791E Common Seal **Company PAN**

Authorised signatory

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TAX INVOICE

SIC Shri Samarth Trading Company

Peth Sangli Road, Opp. Ganesh Servicing Center, Shripadnagar, ISLAMPUR - 415 409Tal. Walwa, Dist. Sangli. Tel. (02342) 225394, 225773Mob. 9822256373E-mail : samarth.trading@yahoo.comsamarth4092@gmail.com



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Shri Samarth Trading Company Peth-Sangli Road, Opp. Ganesh Servicing Center Shripadnagar, ISLAMPUR. 'in 415 409, Tal. Walwa, Dist. Sangli. Tel (02342) 225394, 225773 Mob. 9822256373 E-mail : samarth.trading@yahoo.com
GSTIN : 27AMVPP2791E1ZG
Date: 05103/2019 Receipt No.: 540
Received with thanks from M/s. <u>The prhupal</u> <u>krichna</u> Mahaviddaya, Rothane Bk
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Six puperes Ohly.
By Cash / D.D. / Cheque No. 024361 Date : $65703/20.19$
In Part / Full / Advance Payment of Our Bill No Date : / / 20
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Dr. FRINCHAMIDT KARAU KRICHMARE (EK.), TAL. KARAU RETHARE (EK.), TAL.

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Krishna Mahavidyalaya, Rethare Bk.

Tal. Karad, Dist. Satara

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Shivaji University, Kolhapur RESEARCH SENSITIZATION SCHEME FOR COLLEGE STUDENTS

UNDER LEAD COLLEGE, ACTIVITY

Submission of Project Report

Title of the Project: Fabrication of Nanostructured Polyaniline thin film for electrochromic smart windows and supercapacitor application.

By

Miss. Desavale Suryashree Vilasrao, Mr. Jadhav Amol Vijay, Miss. Mohini Harale Rajendra, Miss. Jadhav Nikita Bharat

Under the Guidance of

Dr. Dhanaji S. Dalavi

Assistant Professor,

Krishna Mahavidyalaya, Rethare (Bk)

Academic Year: 2018-2019

DECLARATION

We hereby declare that, the project report entitled **"Fabrication of Nanostructured Polyaniline thin films for electrochromic window and supercapacitor application**" submitted by us has been completed and written by us, has not previously formed and published in any other University in India or any other country or examining body to the best of our knowledge.

Place: Shivnagar

Date: 27/02/2019

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Name of project students.

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CERTIFICATE

This is to certify that thesis entitled "Fabrication of Nanostructured Polyaniline thin films for electrochromic window and supercapacitor application" which is being submitted herewith is the result of original research work completed by Miss. Desavale Suryashree Vilasrao, Mr. Jadhav Amol Vijay, Miss. Mohini Harale Rajendra, Miss. Jadhav Nikita Bharat under my supervision and guidance and to the best of my knowledge and belief, the work embodied in this project work has not formed earlier.

Place: Shivnagar

Date: 27/02/2019

Project Advisor

Balan

(Dr. Dhanaji S. Dalavi)

1 INTRODUCTION

Conducting polymers show the remarkable properties of be combining properties of organic polymers in tandem with electronic properties of semiconductors. The ability to tailor the structure of a conjugated polymer allows the rational synthesis of conducting polymers with a broad range of electronic properties [1]. The electronic character of the polymer can be easily manipulated by changing the nature of the repeating unit and the functional groups. Over the past 25 years, the conducting polymers belonging to polyenes or polyaromatics such as polyaniline, polypyrrole, polythiophene, poly(p-phenylene) have attracted most attention [2,3] New chemical and physical properties are imparted to conducting polymers by the addition of an appropriate functional group to a conventional polymer [4]. The character and position of the side chains will affect properties like solubility, band gap, ionic conductivity, morphology and miscibility with other substances [5]. The ability to dope conjugated polymers electrochemically is significant, because of the easy combination of synthesis and characterization methods. Electrochemically synthesized polymer allows the determination of molecular weight and molecular weight distribution. Many applications of conjugated polymers, such as light emitting electrochemical cells [6,7], microactuators [8,9], energy storage [10], photovoltaic[11] and electrochromic devices (ECDs) [12,13,14], and sensors [15] are based on electrochemical transition between doped and neutral states or rely on the stability of a specific doping level.

Of the many conducting polymers available, PANI is emerging as a novel material due to its techno-commercial applications and ease of synthesis [16]. Polyaniline (PANI) exists in a variety of forms that differ in chemical and physical properties [17–20]. The most common green protonated emeraldine has conductivity on a semiconductor level of the order of 10 S cm⁻¹, many orders of magnitude higher than that of common polymers ($<10^{-9}$ S cm–1) but lower than that of typical metals (>104 S cm⁻¹). The changes in physicochemical properties of PANI occurring in the response to various external stimuli are used in various applications [21–22], e.g., in organic electrodes, sensors, and actuators [23–25].Other uses are based on the combination of electrical properties typical of semiconductors with materials parameters characteristic of polymers, like the development of "plastic" microelectronics [26],electrochromic devices [27], tailor-made composite systems [28,29], and "smart" fabrics [30].

The establishment of the physical properties of PANI reflecting the conditions of preparation is thus of fundamental importance by an occasionally expressed opinion that "there

are as many polyaniline as the number of people who prepare them". The efficient polymerization of aniline is achieved only in an acidic medium, where aniline exists as an anilinium cation. PANI film is a multichromic polymer i.e. several colors appear as the polymer traverses from the oxidized state to reduced state. Fully reduced PANI is transparent and called leucoemeraldine, with a chemical structure as shown in Figure 1. The dark blue semi-oxidized state in which both the forms are in equal proportion is named emeraldine base and the violet blue fully oxidized material is termed pernigraniline base. Unlike other polyaromatics, none of these states are electronically conducting, not even the fully oxidized pernigraniline form. Instead, PANI becomes conducting when the oxidized states are protonated and a green emeraldine salt is formed. This highly conducting doped form can actually be reached through two completely different pathways. If the emeraldine base is treated with any acid, protonic acid doping occurs as protonation of the imine nitrogen atoms -N==) creates positively charged protonatedimines (-NH⁺-), balanced by negative ions from the acid. This is called as non-redox doping. Chemical or electrochemical doping of the reduced leucoemeraldine base can also be utilized to obtain the very same conducting salt [31]. Colorless leucoemeraldine which constitutes the bleached state is formed by chains of benzoid rings separated by nitrogen. This is in the insulating state with a single absorption band at 3.8 eV corresponding to Π - Π ^{*} transitions in the benzoid rings. When the Nitrogen atoms become charged, a sharp polaron band appears at~3eV.In ES, 1eV absorption is attributed to intrachain free carrier excitation [32] Anodicaly coloring PANI is reported to have high contrast and multichromic efficiency [33]. A variety of inorganic and organic acids of different concentration have been used in the syntheses of PANI; the resulting PANI, protonated with various acids, differs in solubility, conductivity, and stability Higher acidity of the reaction medium also leads to the increase in the conductivity. Variation in pH on deposition of PANI is very profound. Acid doping of PANI leads to an increase in conductivity by more than eight orders of magnitude [34]. PANI obtained at lower potentials yield higher coloration yields. Over oxidation of PANI leads to degradation of polymer, so that is another parameter which needs to be looked into.



Fig.1. Various possible oxidation states of polyaniline.

The electrochromic process occurring in a PANI ECD in an electrolyte comprising of $LiClO_4$ in a solvent like Propylene Carbonate and Acetonitrile can be written as

$PANI + xClO_4^- \leftrightarrow (PANI^{x+})(ClO_4^-)_x^{-----1}$

Many deposition methods like CBD, electrodeposition, dip coating, etc exist for the deposition of PANI films. However, the In-situ chemical polymerizaion approach has several advantages in that the conducting polyaniline blends and composites are supplied in the form of free standing films and also that the electrical properties of the composites can be modified by simplyvarying the conditions of electrolysis [31]. The chemical synthesis is clean. When PANI film is oxidized by chlorate ions, it turns bluish green due to formation of emeraldine base. PANI exists in the quininoid form in this case. When ions reduce the film, the PANI film achieves the insulating state changing from bluish green to transparent yellow due to the benzoid form. An ECD having the following configuration Glass/ITO/PANI/LICIO₄+PC+ACN/Graphite was set up and tested for its coloration efficiency, response time and optical density.

2. Experimental Procedure and Characterization Technique.

In a typical experiment 0.5 g of PVA powder with an average degree of polymerization of 1750 was dissolved in 50 ml distilled water at 80 °C and stirred for an hour. An FTO electrode of 2 cm² with resistance of about 15–20 cm² was washed with distilled water and acetone successively. After drying the electrode at room temperature the PVA solution was casted onto FTO substrate to form a PVA thin film by spin coating method. The electrode coated with the PVA film is ready after drying at room temperature for one day. The polyaniline solution was prepared at room temperature using a chemical bath (In-situ chemical polymerizaion) consisting of ammonium persulphate (APS), hydrochloric acid (HCl), aniline and distilled water. 2ml of

aniline was dissolved into 30 ml of 1M HCl in a beaker. In another beaker 1.15 g of $(NH_4)_2S_2O_8$ (APS) was dissolved in 20 ml of 1M HCl. The solution in the second beaker was poured slowly into the first beaker and PVA coated electrode was dipped into PANI solution for 10 min. After deposition, the electrodes were rinsed with distilled water for removing loosely bound PANI precipitate particles. The thickness of films increases by increasing the deposition cycles. The thin films of PVA/PANI were allowed to dry at 100°C for 5 h.

Prior to deposition, ITO glass substrates were given full cleaning treatment. First they were cleaned with distilled water, acetone, ethanol, isopropyl alcohol and ultrasonic bath. Then they were kept in the vacuum oven for 10 minutes. These cleaned ITO's were stored for further use of deposition of films. The number of cycles was varied in order to obtain smooth, well adherent films. SEM images were taken to obtain information regarding the morphology of PANI films. The films were characterized for the vibrational spectra using FT-RAMAN spectroscopy. The Fourier transform Raman (FT-Raman) spectra of the films were recorded in the spectral range of 250-1000 cm⁻¹ using FT-Raman spectrometer (Bruker MultiRAM, Germany) that employs Nd:YAG laser source with an excitation wavelength 1064 nm and resolution 4 cm⁻¹. Electrochemical characterization were carried our using electrochemical quartz crystal microbalance (EQCM) measurements (model-CHI-400A) made by CH Instruments, USA. Optical characterizations were carried out using UV-Vis spectrophotometer (UV 1800, Schimadzu, Japan). In-situ transmittance studies were carried out using a He-Ne Laser (λ =632.8 nm), a Si photodiode and a storage oscilloscope. Colorimetric studies were done using computer controlled software for a 2° observer using D-65 illuminant. Colorimetric determinations were done with the help of Shimadzu color analysis software by analyzing the transmittance spectra of color/bleach state to evaluate the L*a*b* and Yxy co-ordinate values. These obtained values were used as reference data in order to get the observed color in reduced and oxidized state for all samples from online color analysis software with 1931 2° observer and D-65 illuminant proposed by CIE *Yxy* and $L^*a^*b^*$ coordinates.

3. Results and Discussion:

3.1 Scanning electron microscopy study

The morphological features of PANI samples deposited by in-situ chemical bath deposition are shown in Fig.1. As the number of layers increases PANI thin films transfers its

morphology from smooth to granular structure which provide enough pathways for movement of ions and solvent molecules within the films, thereby improving its coloration efficiency [35].



Fig.1 SEM images of PANI thin films

3.2 Raman Spectroscopy:

Raman spectroscopy is a powerful tool to understand the vibrational properties of molecules. It provides definite structural characterizations of PANI because of characteristic dependence of Raman spectrum on the ring constituents of aromatic compounds.



Fig.2. Raman spectra of PANI films deposited for different number of cycles.

Fig.2 shows the Raman spectra of PANI films deposited for different number of cycles. In the spectra,-C-H bending of quinoid ring at 1180 cm⁻¹, –C-H bending of benzoid ring at 1247 cm⁻¹, and C-C stretching of the benzene ring was observed at 1498 cm⁻¹ and 1600 cm⁻¹ respectively revealing the presence of doped emeraldine PANI structure [36,37].

3.3 Optical studies

The UV-Vis absorbance spectra of PANI film was studied by measuring their visible absorption spectra in the range of 190-1100 nm range. The Fig.3 shows the absorbance vs wavelength studies of PANI thin film in two different states. In the as deposited state or the colored state, the absorbance spectra show a broad absorption peak at 600 nm. When insertion of ClO_4^- ions takes place, PANI turns to a transparent pale yellow color. The absorbance in this case is into the far NIR and the film appears transparent. Similar reports have been reported by other groups [38].



Fig.3. Absorption spectra of PANI (P5) sample in their colored and bleached state in the range of 190-1100 nm. Potential was swept from +1 V to -1 V vs SCE.

3.4 Cyclic voltammetry

Cyclic voltammetry of PANI films was performed in the three electrode cell in 0.5 M $LiClO_4+PC+CAN$ (Fig.4). A potential window of -1 to 1 V for cyclic voltammetry studies was chosen at different scan rates from 20mV/s to 100 mV/s. PANI film shows two cathodic peaks at +0.38 V (C1) and -0.28V (C2). Upon the reversal of the potential from -1 V to +1V two anodic peaks were observed at -0.45 V (A1) and +0.6 V (A2) respectively. The cyclic voltammetry was carried out at different scan rates to gather information about the intercalation/deintercalation kinetics.



Fig.4 Cyclic voltammograms of PANI film recorded in 0.5 $\text{LiClO}_4+\text{PC}+\text{CAN}$ electrolyte. The potential swept from -1 to +1V versus SCE at the scan rate of 20 mV/sec to 100 mV/sec.

Fig.5 shows the plot of square root of scan rate vs the peak anodic and cathodic current. The linear curves show that the reaction is not limited by the ion mobility in the film. The diffusion coefficient calculated for the anodic and cathodic peak current were found to be $6.7 \times 10^{-11} \text{ cm}^2/\text{s}$ and $4.4 \times 10^{-11} \text{ cm}^2/\text{s}$



Fig.5. Graph showing linear variation of peak current with root of scan rate.

3.5 In-situ Transmittance-Response time studies:

In-situ characterizations of PANI films were carried out to find the transmittance modulation as a function of time. A square wave potential of $\pm 1V$ was applied with a pulse width of 15s. Initially as deposited PANI is in the colored state. When a negative pulse of -1V was applied, the film switched from its conducting emeraldine state to transparent leucoemeraldine state. The bleaching time is defined as the time taken for the transmittance to change from 0 to 80% of its maximum value. This switching time referred to as bleaching time t_b as seen from the graph was found to be 0.80 s. In the reverse cycle, on the application of a positive pulse, the film started to regain its colored state. This time is referred to as coloring time t_c. The coloring time is defined as the time taken for the film transmittance to change from100% to 20% of its maximum value. This time was found to be1.10 s.Such fast response time makes the conducting polymers ideal candidates for switching applications.



Fig.6 In-Situ Transmittance-Time response of PANI thin film in colored and bleached state a) for one cycle b) for 10 cycles.

3.6 Coloration Efficiency

The coloration efficiency (η) at a particular wavelength correlates with the optical contrast, i.e. the change in optical density with charges intercalated per unit electrode area (q/A) and it can be expressed as:

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$$\frac{\Delta OD}{Q_i} = \frac{2.303 \log \frac{T_b}{T_c}}{q/A}$$
.(3)

where T_b and T_c are the transmittance in the colored and bleached state and Q_i is the number of charges into the film. The coloration efficiency was found to be 90.60 cm^{2/}/C

3.7 Colorimetric studies

Fig.7 shows the PANI films were characterized using color software for a 2° observer using D-65 illuminant. The values of Lab are listed in the table. 1. The xy value plotted for different values of the applied potential. Unlike other polymers, PANI exhibits a parabolic curve on the chromaticity diagram. The trajectory of PANI film follows a curved path is shown in the chromaticity diagram. In the initial state, when PANI is in as deposited condition, it exhibits a bluish green color. As the applied negative potential increases, the color of the film changes from blue to green.With further increase in the negative potential, the film becomes light yellow or nearly transparent in color. The Lab values in the initial and final stages are listed in the table.1. In the colored state, L value is 57.17 i.e. in this case, the transmittance is low. The negative value of 'a' at -11.44 and a high value of 'b' at 26.59 signify the bluish green tinge in the film. In the bleached state, the L value changes to 86.25 signifying an increase in transparency of the film. The value of 'a' and 'b' now fall down to -2.77 and 7.65 indicating a weak yellow color. The dominant wavelength is found by drawing a straight line from the white point through the position of the point at a specific coordinate. In the transparent state this wavelength is given by 575 nm. In the colored state, the dominant wavelength is found to be 500 nm. The changes in L values in the colored and bleached state give the transmittance attenuation. This change in transmittance is found to be 31.78.



Fig.7. CIE 1931 xy chromaticity diagrams for oxidation/reduction (colored/bleached) of PANI thin film.

4 Conclusions

PANI films were successfully deposited by in-situ chemical polymerization. The films s had a smooth surface with a good adherence to the substrate. The thickness of the films was varied with the number of cycles. SEM studies show transfer from smooth to granular structure of in-situ chemically polymerized PANI films with increase in deposition cycle which are advantageous for easy ion insertion /extraction.Raman spectra show the characteristic stretching and bending vibrations. ECD comprising of PANI films show an optical modulation of 50 %. The device shows a fast response time of 1.10 sec and 0.80 sec for coloring and bleaching respectively. The films show a large variation of 31.78 in L^* value showing a good optical modulation.

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