

## Effect of oxidizing agent on the properties of polyaniline thin films

Sagar Gore, Ashwini B. Rohom, Priyanka U. Londhe, and Nandu B. Chaure

Citation: [AIP Conference Proceedings](#) **1832**, 080018 (2017); doi: 10.1063/1.4980478

View online: <http://dx.doi.org/10.1063/1.4980478>

View Table of Contents: <http://aip.scitation.org/toc/apc/1832/1>

Published by the [American Institute of Physics](#)

---

---



**SUMMER SALE!**

**30% OFF**  
**ALL PRINT**  
**PROCEEDINGS!**

**AIP** | Conference Proceedings

ENTER COUPON CODE  
SUMMER2017

# Effect of Oxidizing Agent on the Properties of Polyaniline Thin Films

Sagar Gore, Ashwini B Rohom, Priyanka U. Londhe, Nandu B Chaure\*

Electrochemical Laboratory, Department of Physics, Savitribai Phule Pune University, Pune-41100, India

\*Email ID: [n.chaure@physics.unipune.ac.in](mailto:n.chaure@physics.unipune.ac.in)

**Abstract.** Conducting polymers have been widely investigated because of their fascinating electrical and optical properties. In the present work, the oxidation of aniline was carried out in acidic aqueous media using chemical bath deposition method. Aniline, hydrochloric acid and ammonium dichromate (ADC) are used as aniline oligomers, dopant acid and oxidizing agent, respectively. Effect of oxidizing agent concentration on various properties of polyaniline thin films were studied extensively with the aid of Raman spectroscopy, UV-Vis spectroscopy, PL spectroscopy, scanning electron microscopy and current-voltage measurements. UV, PL and Raman studies reveals that the higher concentration of ADC leads to the formation of emeraldine base form of PANI and at lower concentration supports the growth of conducting emeraldine salt. SEM micrographs confirm the compact and uniform growth of PANI. PANI films grown at lower concentration of ADC shows higher conductivity.

**Keywords:** Polyaniline, Chemical bath deposition, Emeraldine salt, Raman spectra, etc.

**PACS:** 32.30.JC, 33.20.FB, 61.05.CC, 68.37.HK, 68.55.AM

## INTRODUCTION

Polyaniline (PANI) is nowadays the most studied conducting polymer exhibiting unique electrical and optical properties, good redox reversibility and high environmental stability. Research on the synthesis and characterization of PANI has attracted great attention for last two decades due to their wide range of promising applications [1, 2]. PANI has three different allowed oxidation states characterized by the ratio of imine to amine nitrogens. The emeraldine form is associated with partially oxidized or reduced state. They are distinguished by four different colors Leucoemeraldine- white/clear and colorless, Emeraldine salt- green, Emeraldine base- blue, Pernigraniline- blue/violet. Polyaniline is generally synthesized by chemical or electrochemical method [3]. However, the electrochemical method generates a low soluble polyaniline which is difficult to process and has restricted applications. Chemical bath deposition yields stable, adherent, uniform and compact films with good reproducibility. The major advantage of CBD is that it requires only solution containers and substrate mounting devices [3]. In this work, synthesis of PANI layer is carried out by simple chemical bath deposition and the effect of oxidizing on structural, optical, morphological and electrical properties are studied.

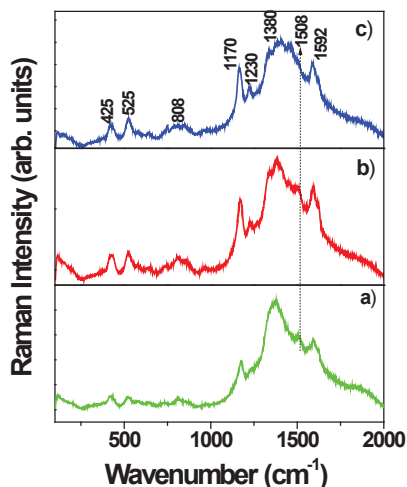
## EXPERIMENTAL DETAILS

Aniline ( $C_6H_5NH_2$ ), hydrochloric acid (HCl) and ammonium dichromate (ADC,  $(NH_4)_2Cr_2O_7$ ) are used as aniline oligomers, dopant acid and oxidizing agent, respectively. Double distilled water (DDW) is used as solvent. Initially, 0.05 M aniline and 0.5 M HCl was dissolved in 30 ml double distilled water at room temperature and stirred continuously until it turns to clear solution. The concentration of ADC was varied from 10 mM to 30 mM. Color of the solution changes from pale yellow to green/blue depending upon the concentration of ADC. After 30 minutes, uniform and adherent PANI films were obtained and rinsed in DDW water to remove loosely bound particles.

The samples were characterized by means of Raman spectra, with Invia Renishaw Raman Microscope coupled with Philips CCD camera with 785 nm excitation laser to study the structural properties. Optical absorption measurements were carried by JASCO UV-Vis-NIR spectrophotometer. Photoluminescence were recorded using Perkin Elmer LS-55 spectrophotometer. Scanning electron microscopy (SEM) images were recorded using a JEOL JSM-6360A microscope with operating voltage 20 kV. The electrical conductivity of PANI was measured by a standard two probe method at room temperature using Biologic potentiostat SP-300 model.

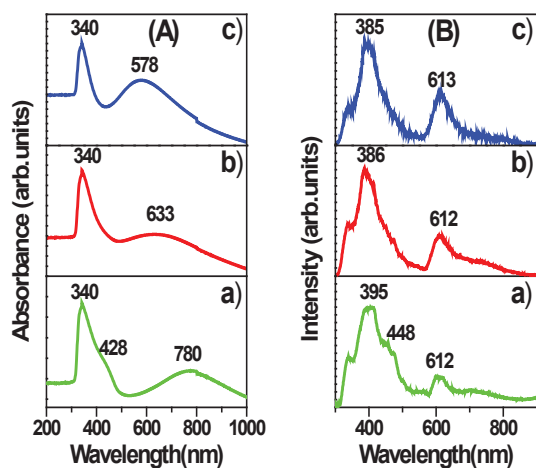
## RESULTS AND DISCUSSION

The structural analyses of the PANI thin films are carried out using Raman spectroscopy. The resonance Raman spectra of samples is shown in figure 1.



**FIGURE 1.** Raman spectra of PANI films with various concentrations of ADC a) 10 mM, b) 20 mM M and c) 30 mM prepared by CBD.

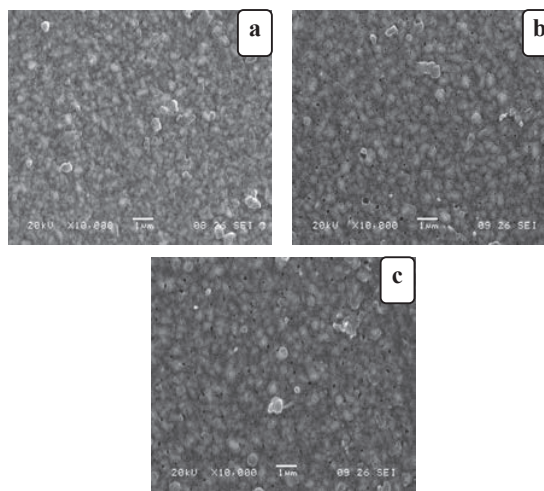
The bands appeared between the wavenumber range of 400-1700  $\text{cm}^{-1}$  corresponds to the Emeraldine form of PANI [5]. The Raman band observed at 1594  $\text{cm}^{-1}$  is assigned to the C-C stretching vibrations of benzene ring. The band attributed at 1508  $\text{cm}^{-1}$  is assigned to N-H deformation vibrations in the film prepared with less concentration of ADC. Whereas upon increasing the concentration of ADC the intensity of this peak is reduced due to the growth of base form of PANI.



**FIGURE 2.** Absorption (A) and PL (B) spectra of PANI thin films prepared with various concentrations of ADC a) 10 mM, b) 20 mM M and c) 30 mM

Figure 2A depicts the absorption spectra of PANI thin film grown in various concentrations of ADC. Strong absorption peaks attributed at 340 nm, 428 nm, 578-633 nm and 780 nm are associated to  $\pi$ - $\pi^*$  electronic transition, polaron, exciton and bipolaron band transition [6-7]. Presence of three peaks confirms the formation emeraldine salt form of PANI. Two peaks appeared in the absorption spectra with 20 and 30 mM ADC confirms the formation of emeraldine base. The peak related to exciton observed in figure b) and c) shifted towards lower wavelength with increasing ADC are related to changes from salt to base. The change in the form of PANI can be associated to the conversion of benzoid units of PANI into quinoid units upon increasing the contents of ADC [8].

Figure 2B depicts the photoluminescence spectra of PANI thin films prepared with various concentrations of ADC a) 10 mM, b) 20 mM and c) 30 mM. The samples were excited at wavelength 270 nm. Three peaks related to PANI in Emeraldine salt form are attributed for the layer prepared with 10 mM ADC. The presence of only two peaks  $\sim$  385 nm and 613 nm, revealed the salt form of PANI for higher concentration of ADC.

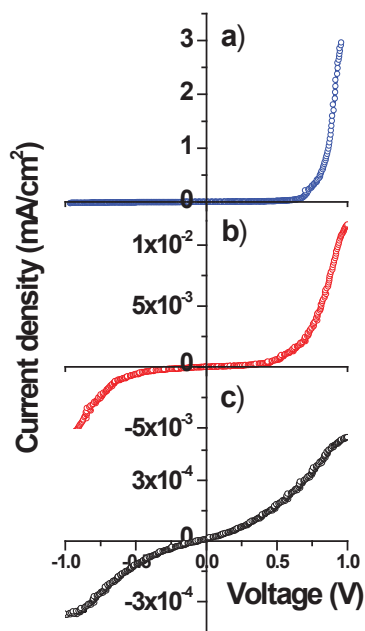


**FIGURE 3.** SEM images of PANI thin film deposited with various concentrations of ADC, a) 10 mM, b) 20 mM and c) 30 mM.

The morphology of PANI layer obtained at various concentrations of ADC is shown in figure 3. All samples were compact, uniform and smooth. A very similar morphology was observed for all samples.

The effect of concentration of ADC on the conductivity of sample is studied and the measured current-density versus voltage curves is shown in figure 4. It can be clearly observed that upon increasing the concentration of ADC the conductivity of the film decreases due to formation of base form of

PANI [9]. It has been previously demonstrated that the polyaniline chain can be formed by various combinations of the two repeating units known as the X and Y components of polyaniline. Owing to this, PANI has many unique properties and electronic conduction mechanisms that distinguish it from the rest of the conducting polymers. For example the conductivity of PANI varies with the extent of degree of oxidizing agent. For lower concentration of ADC, the form of PANI remains in emeraldine salt therefore the conductivity was found to be decreased.



**FIGURE 4.** J-V characteristics of PANI thin films deposited with various concentrations of ADC, a) 10 mM, b) 20 mM and c) 30 mM.

## CONCLUSIONS

PANI thin films exhibiting both emeraldine salt and base form were successfully prepared using a simple chemical bath deposition technique. The effect of concentration of oxidizing agent was studied on the properties of PANI layer. Lower contents of ADC, exhibits the bands all the intense bands 340 nm, 428 nm and 780 nm associated to emeraldine salt state of PANI. The bands exhibited at 340 nm and 578 nm for higher contents of ADC are associated to base form of PANI. Optical absorption spectra agree very well with the Raman analyses. SEM images reveal the growth of compact, uniform and smooth morphology for PANI films. High conductivity layers are grown for lower contents of ADC and a vice versa. The optical, structural and electrical results are very well agreeing

to each other. The reported optical and electrical properties of PANI are useful for solar cell application.

## ACKNOWLEDGMENT

The financial support received from Department of Science and Technology (DST), New Delhi under the major project grant DST/TM/SERI/FR/124/G is gratefully acknowledged. One of the author ABR is thankful to CSIR for financial support under the senior research fellowship program (CSIR fellowship No. 09/137/(558)/2015-EMR-I).

## REFERENCES

1. F. Tan, S. Qun, Wu, J. Jin, Z. Wang, *Sol. Energy Mater. Sol. Cells* **95**, 440-445 (2011).
2. F. W. Zeng, X. X. Liu, D. Diamond, K. T. Lau. *Sensors Actuators B: Chemical* **143**, 530-534 (2010).
3. H hallin, J Saniger, J Banuelos, *Thin Solid Films*, **347**, 241-247 (1999).
4. A B Rohom, P U Londhe, S K Mahapatra, S K Kulkurni, N B Chaure, *High Performance Polymers*, **26**, 641-646 (2014).
5. M. Cochet, G. Louran, S. Quillard, M.I. Boyer, J.P Buisson, S. Lefrant, *J. Raman Spectrosc.* **31**, 1029-1031 (2001).
6. H Adulla, A Abbo, *Int J Electrochem Sci.*, **7**, 10666- 10678 (2012).
7. S Banerjee, S Sarmah, A Kumar, *J. Optics*, **38**, 124-130 (2009).
8. W Focke, G Wnek, Y Wei, *J Phys. Chem*, **91**, 5813-5818 (1987).
9. A Baba, R Avincula, W Knoll, *J Phys. Chem B*, **106**, 1581-1587 (2002).