

# Synthesis and Characterization of Nano Zinc Oxide Emeraldine Salt Composite

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**Abstract**—with the rapid development in semiconductor industries and increasing demand of superior performance for devices, the ability to precisely modulate material interfaces is playing an increasingly dominant part in development of new technologies relevant to our lives. The composite materials showed improved performance of solar cells, and sensors which require high sensitivity are demanded by the surface characteristics of the materials. Therefore, controlling the structures of material surface and fabricating surfaces with composite materials are extremely important. In the present work, Nano Zinc Oxide (ZnO) thin film was prepared using chemical bath deposition on glass substrate. Polyaniline (PAni) thin film was prepared using chemical oxidative method at room temperature. Using the same technique Nano ZnO-PAni thin film composite was prepared. The prepared sample was characterized using FTIR, XRD, UV-visible spectrometer and SEM. Formation of ZnO thin film was confirmed by XRD and FTIR analysis, also crystalline form of polyaniline was confirmed by UV analysis. Increased in the absorbance of Pani-ZnO composite indicate the interaction between them.

**Keywords**— Nano Oxide; Polyaniline; Composite Material

## I. INTRODUCTION

Conducting polymers or their composites have been successfully applied in batteries, sensors, electrochromic devices, capacitors, solar cells, corrosion inhibitor's, light emitting diodes, metallization, coating for metal surfaces etc [1]. Conducting polymer can be deposited on conducting surface by electrochemical methods, spray pyrolysis, chemically in acidic media using an oxidizing agent. The extensive use of Polyaniline(PAni) and their composites is due to its ease of synthesis, light weight, less processing cost, chemical stability and conductivity which can be as high as  $10$  to  $10^3$   $\text{Scm}^{-1}$ . Polyaniline exists in three different forms such as leuco-emeraldinebase (fully reduced), emeraldine base, (partially oxidized) and pernigraniline base (fully oxidised). Among the different oxidation states of polyaniline, the emeraldine salt (ES) is only one to show electrical conductivity. The emeraldine base can be converted to emeraldine salt (ES) and viceversa, by protonation/deprotonation with acid /base. Zinc Oxide is a compound semiconductor, having a band gap around 3.37eV exhibit a large exciton binding energy of 60meV. Today different morphology of Zinc Oxide has been prepared like flower, nanorods, tetrapods, nanowires etc. depending upon the preparation method employed. From applications point of view, zinc oxide has high refractive index, high thermal conductivity, antibacterial and UV-protection properties. Consequently, it is added into materials and products

including plastics, ceramics, glass, cement, rubber, lubricants, paints, ointments, adhesive, sealants, concrete manufacturing, pigments, foods, batteries, ferrites, fire retardants, etc.[3]. Nanocomposite formed by combining the potential of conducting polymer and zinc oxide will possibly have new application in different field with enhanced in their properties.

## II. EXPERIMENTAL

### Synthesis of ZnO thin film

Thin film of ZnO was prepared by Chemical Bath Deposition (CBD) method. The chemicals used for the preparation was Zinc nitrate hexa-hydrate  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , Sodium hydroxide (NaOH) [4]. Preparation procedure is as follows. Make a solution of 0.04M of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in distilled water in a beaker by continuous stirring with the help of magnetic stirrer. Heat the mixture upto the temperature of  $(50 \pm 3)^\circ\text{C}$ . Now place the substrate into the mixture with the help of stand and clamp on which the film has to be made, in our present work we have used quartz glass substrate. At a temperature of  $50^\circ\text{C}$  put NaOH (0.08M) in the reacting mixture, wait for 20 minute. Remove the quartz plate from the solution, keep for some time at room temperature. The films are annealed at  $(425 \pm 10)^\circ\text{C}$  and  $(500 \pm 10)^\circ\text{C}$  for 15 minutes by placing it in the furnace. The process was repeated on the same quartz plate to get 3 times deposited film[4].

### Synthesis of Polyaniline (PAni) film

Polyaniline thin film was prepared using chemical oxidative

method. In most of the research paper PANi was synthesized at 0°C to get high molecular weight and uniform thin film. In the present work an attempt was made to prepare PANi film at Room temperature. For the synthesis of Polyaniline the chemical used were Hydrochloric Acid (HCl), O-Anisidine and Ammonium Persulphate (APS). HCl is used to get acidic medium, O-Anisidine is used as a starting monomer and Ammonium persulphate as oxidising agent. The chemical O-Anisidine which is as starting monomer gets easily oxidised when exposed to air, hence it is needed to purify the chemical before use since it will change the amount of oxidising agent used each time. During synthesis distillation of O-Anisidine was done each time it was utilized for the reaction, so that same condition can be maintained at each time of reaction. To get the uniform film of PANi at room temperature is a big task, so many trial was made. It's comes out that when a clean quartz substrate was used to form film for the first time, no film formation takes place. But it was observed that when the same substrate was cleaned with acetone and used for film formation, green color film of polyaniline forms on the substrate. Carefully when the substrate was observed after cleaning with the acetone at the edge of the substrate a very small amount of impurity in the form of polyaniline was remaining of the previous deposition. Hence it can be said that these impurities acts as a reaction centre and accelerate the process of nucleation on the substrate so that film formation takes place.

For the preparation, 1M of HCL and 0.1M of O-Anisidine in double distilled water was taken in petri dish, solution was stirred at Room temperature. After 5 minutes of stirring place the quartz glass substrate in the reacting mixture. Now add 1.2 gm of Ammonium persulphate directly into the reacting mixture, wait for 8-10 minutes, green color thin film of PANi gets deposited on the substrate. Remove the substrate and keep it at room temperature to get dry.

#### *Polyaniline(PAni)-ZnO composite*

PAni-ZnO thin film composite was prepared as follows: Initially ZnO thin film was synthesized using the method describe above and then on this pre-synthesized ZnO thin film Polyaniline film was deposited. Again for the deposition of polyaniline same procedure is followed.

### III. RESULTS AND DISCUSSION

#### *Characterization of ZnO thin film*

X-Ray Diffraction was used to examine the structure and phase of the ZnO. Fig(1) shows the X-RD pattern of ZnO thin film annealed at 425°C and 500°C. The diffraction peaks of ZnO(425°C) exhibit a hexagonal plane with preferred grain orientations along (100), (002), (101), (102), (110), (103) and (112). All of the peaks are well matched with the bulk ZnO, which could be indexed as the hexagonal wurtzite structure of ZnO. The average crystallite size was calculated using

Debye-scherrer formula and was found to be 10.259nm, also its lattice parameters were calculated and was found to be  $a=3.25 \text{ \AA}$  and  $c= 5.201 \text{ \AA}$ , which are in good agreement with the literature data [5]. It can be seen that ZnO annealed at 500°C also exhibit the same peaks exhibited by the ZnO thin film *X-ray diffraction(X-RD)*

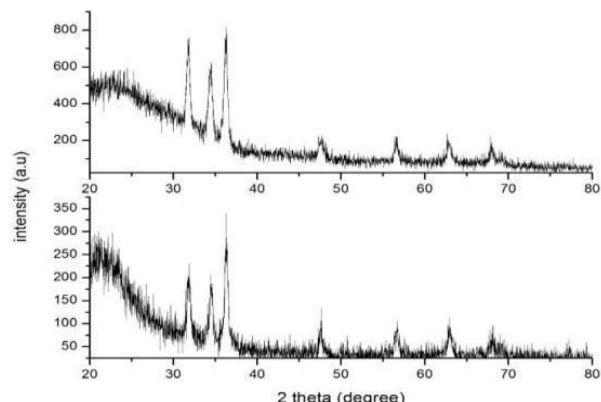


Fig.1. Xrd pattern of ZnO thin film annealed at 425 °C (up) and 500 °C (bottom)

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#### *Infrared(IR) spectroscopy*

IR spectroscopy is very useful tools for investigating vibrational properties of synthesized materials. The band positions and absorption peak not only depend on the chemical composition and structure of the thin films but on the morphology of thin films also.

For ZnO annealed at 425°C, peak at 3786.62cm correspond to the O-H stretching mode which reveals the presence of water molecule on the thin film. The absorption peak observed at 419  $\text{cm}^{-1}$  is attributed to the ZnO stretching

vibrations. Peaks at 1600.98 cm<sup>-1</sup> corresponds to the C=O bonds. Peaks at 662.07 cm<sup>-1</sup> and 832.42 cm<sup>-1</sup> corresponds to C-H deformation and C-H bending mode of vibration [9].

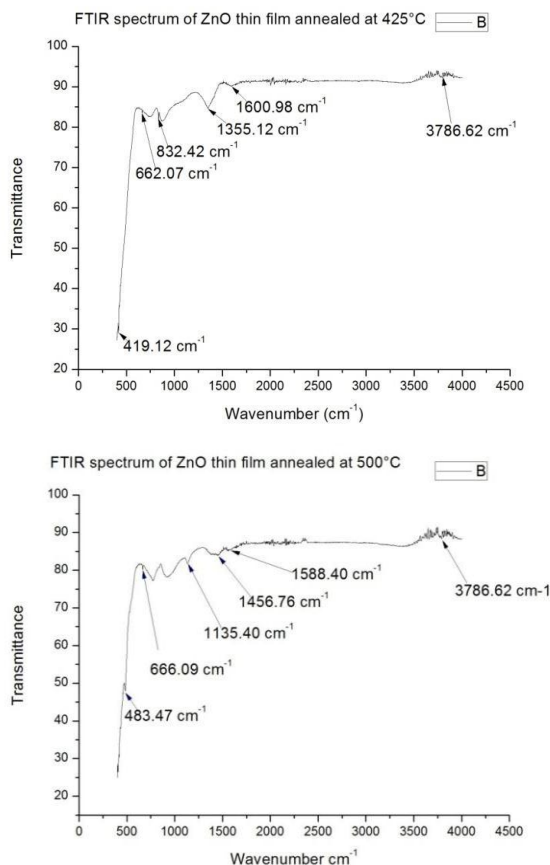


Fig.2. IR spectrum of ZnO thin films annealed at 425 °C and 500 °C

From IR spectrum of ZnO thin film annealed at 500°C it is observed there is a shift in the peak when compared to ZnO thin film annealed at 425°C. Also some of the peaks in the range 900-1500 cm<sup>-1</sup> shows a decrease in the intensity which is due to removal of organic components [11].

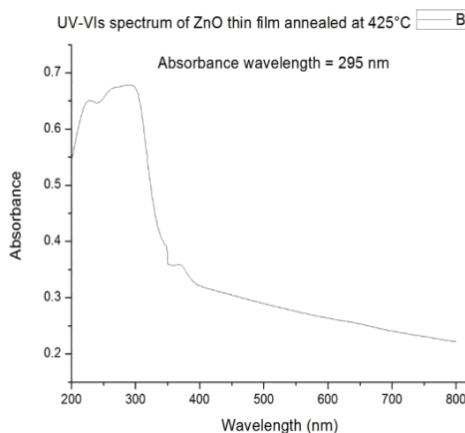
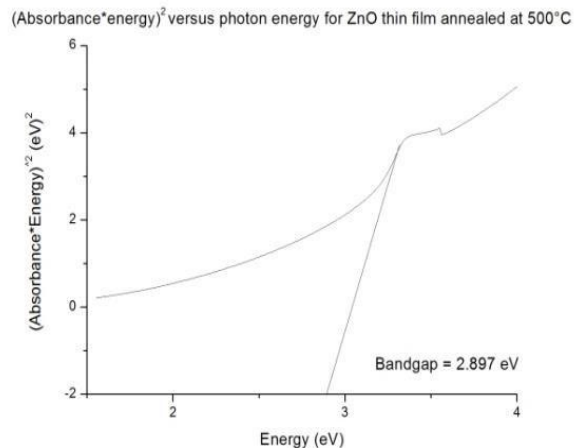
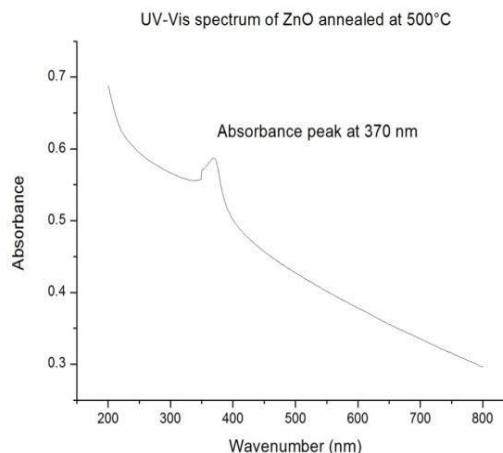
*UV-visible analysis*

In order to study the optical properties of the ZnO thin films deposited by the chemical bath deposition technique, optical absorption spectra were recorded in the 200–800 nm range.

Fig(3) shows the absorption spectra and its corresponding tauc plot in order to determine the band gap. ZnO(425) shows broad excitonic absorption band at 295 nm which is the characteristic band indicating the formation of ZnO. The band gap estimated to be 3.57eV which is found to be greater than its bulk value of about 3.36 eV.

For ZnO(500) the absorption peak around 370 nm which reveals the effect of annealing temperature on the ZnO thin film. Due to increase in temperature it is found there is a red

shift in the spectrum i.e absorption energy decrease. Same method was employed to find the bandgap and the value was found to be 2.89eV. The decrease in bandgap indicates a increase in the crystallite size which is well consistent with the X-RD results that crystallite size increases for ZnO annealed at 500°C.



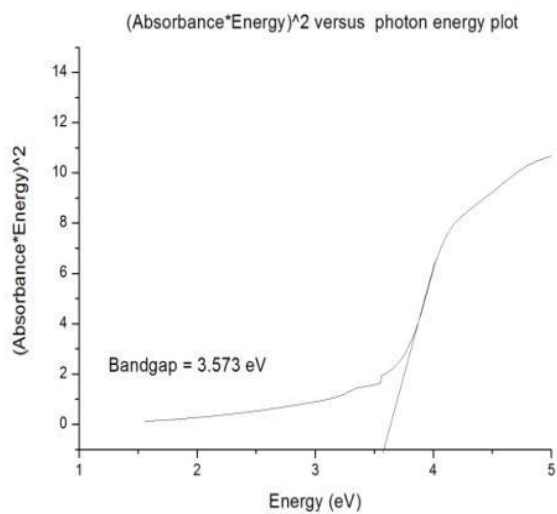


Fig.3. UV-visible plots of ZnO thin film annealed at 425, 500 (left) and corresponding its tauc plots

SEM analysis

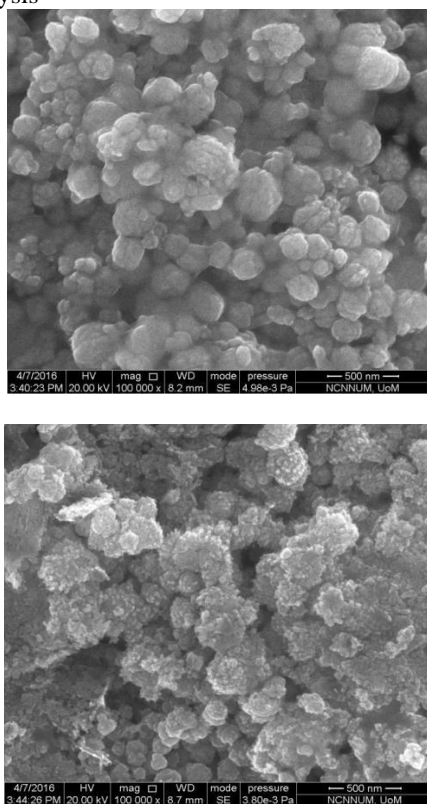


Fig.4. SEM images of ZnO film annealed at 425°C (left) and 500°C (right)

Field Emission Scanning Electron Microscope (FESEM) imaging was done at National Centre for Nanoscience and Nanotechnology University of Mumbai. The images does not reveals any fine detailed structure, since the film is non-conducting and it was not coated with any conducting

material usually gold or silver at the time of imaging. [10] Although it can be seen in fig() that for ZnO film annealed at 425°C some kind of spherical shape formation takes place, also the film form is not uniform. Same appearances for ZnO film annealed at 500°C can be seen in fig(), also it is observed that there is an increase in the particle size which confirms the X-Ray Diffraction results. Characterization of polyaniline(pani)

X-ray diffraction

X-RD of Polyaniline thin film exhibit peak at  $2\theta=20.37^\circ$  which corresponds to emeraldine salts form of Polyaniline[8]

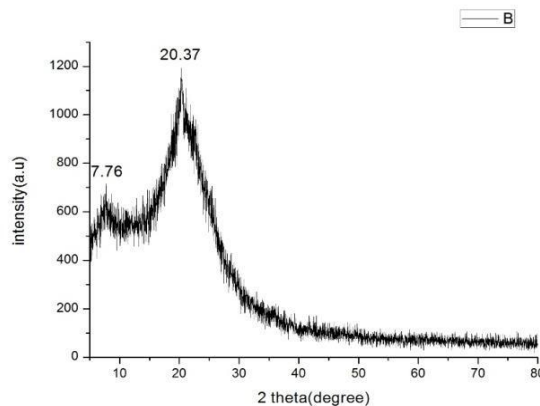


Fig.5. X-ray pattern of polyaniline

UV-visible spectrum

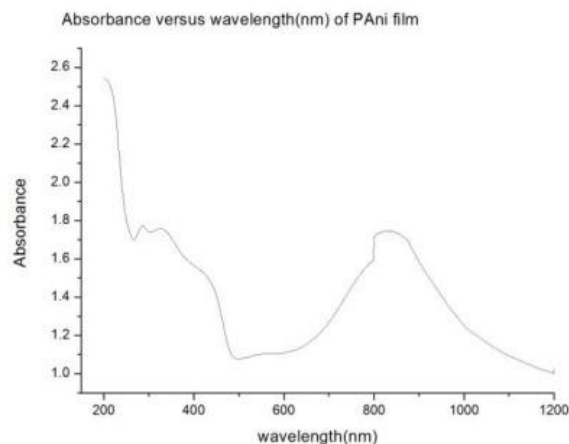


Fig.6. UV-visible spectrum of polyaniline thin film

UV-Visible absorbance spectrum of Polyaniline thin film shows there peaks, one around 850nm which confirms the formation of Poly O-Methoxy aniline in its emeraldinesalt[7].

Infrared spectrum

The characteristic absorption bands of PANI are  $476.23\text{ cm}^{-1}$  corresponds to (C–N–C bonding mode of aromatic ring),  $574.96\text{ cm}^{-1}$  and  $665.65\text{ cm}^{-1}$  corresponds to (C–C, C–H bonding mode of aromatic ring),  $831.98\text{ cm}^{-1}$ (C–H out of

plane bonding in benzenoid ring), 1016.34  $\text{cm}^{-1}$  and 1113.14  $\text{cm}^{-1}$  (S=O bonding for Ammonium per sulphate), 1477.09  $\text{cm}^{-1}$  (C-N stretching of benzenoid ring), 1566.14  $\text{cm}^{-1}$  (C=N stretching of quinoid ring), 3785.65  $\text{cm}^{-1}$  reveals the presence of water on the PANifilm[9,11].

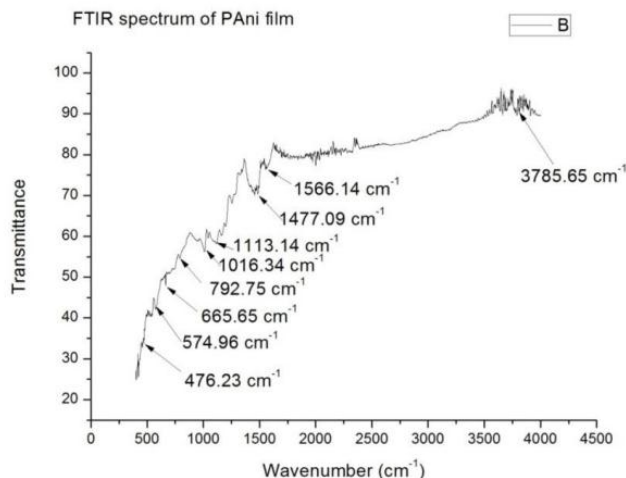


Fig.7. IR spectrum of polyaniline film

The characteristic absorption bands of PANI are 476.23  $\text{cm}^{-1}$  corresponds to (C–N–C bonding mode of aromatic ring), 574.96  $\text{cm}^{-1}$  and 665.65  $\text{cm}^{-1}$  corresponds to (C–C, C–H bonding mode of aromatic ring), 831.98  $\text{cm}^{-1}$  (C–H out of plane bonding in benzenoid ring), 1016.34  $\text{cm}^{-1}$  and 1113.14  $\text{cm}^{-1}$  (S=O bonding for Ammonium per sulphate), 1477.09  $\text{cm}^{-1}$  (C–N stretching of benzenoid ring), 1566.14  $\text{cm}^{-1}$  (C=N stretching of quinoid ring), 3785.65  $\text{cm}^{-1}$  reveals the presence of water on the PANifilm[9,11].

*Pani-ZnO composite*

**X-ray diffraction**

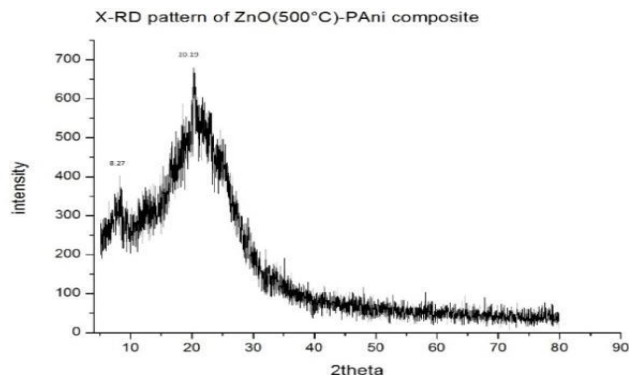
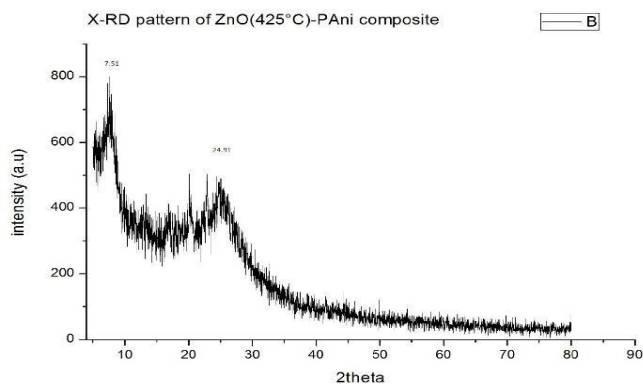


Fig.8. XRD pattern of polyaniline-ZnO composite annealed at 425(left) and 500(right)

X-RD of Polyaniline thin film exhibit peak at  $2\theta=20.19^\circ$  which corresponds to emeraldine salts form of Polyaniline[8,12].

*UV-visible spectrum*

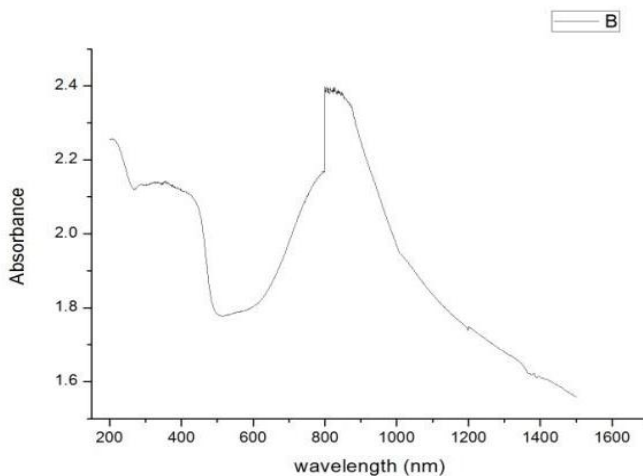


Fig.9. UV-visible spectrum of pani-ZnO composite film annealed at 500°C

UV-Visible spectrum of PANi-ZnO(500°C) composite is similar to PANi film, shows there is an increase in the intensity of peak around 823 nm due presence of ZnO, which indicates interaction between ZnO and Polyaniline. Also the peak in UV range gets diffuse into a broad peak around 352 nm.

**IV. CONCLUSION**

X-Ray diffraction of ZnO thin film annealed at 425°C and 500°C shows that crystallites size increases when annealed at high temperature, which is also confirmed from the SEM images and decrease in the bandgap is observed, estimated from the UV-Visible spectrum,. IR spectrum taken of both ZnO thin film and polyaniline shows all the characteristic peaks, hence confirm the synthesis of respective material. UV-Visible spectrum of polyaniline thin film confirms the

formation of emeraldine salt form of polyaniline.

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