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Effect Of Dopant Acid Concentration On The Properties Of Polyaniline Thin Films

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Abstract

We have described a very simple and low cost deposition method to grow polyaniline thin films. A conventional chemical bath deposition (CBD) method is used. Aniline monomer, oxidizing agent and dopant acid is used for the deposition of polyaniline thin films. The impact of dopant acid concentration on various properties of PANI thin films viz, structural, optical, morphological and electrical are investigated. Structural properties reveal the growth of PANI in emeraldine salt form at lower concentration of dopant acid while concentration of dopant acid leads to the growth of PANI in emeraldine base form. Optical studies confirm the formation of PANI in emeraldine salt form at lower concentration of dopant acid. Growth of fibrous morphology of PANI is observed using scanning electron microscopy image. Higher conductivity PANI thin films are grown at lower concentration is confirmed using the electrical studies. Higher concentration leads to the formation of emeraldine base form of PANI which leads to lower conductivity. PANI films grown at lower concentration of dopant acid leads to the formation of PANI in emeraldine salt form with fibrous morphology which will be useful for photovoltaic applications.

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

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1. Introduction

Conducting polymers has gained great interest and emerged very important class of materials due to their distinctive optical, electrical, morphological and chemical properties. Conducting polymers are organic polymers that conduct electricity. Engineering conducting polymers having fibrous morphology showing good conductivity is fascinating to achieve various applications. Various polymers viz, poly (p-phenylene vinylene) (PPV), poly (3,4-ethylenedioxythiophene) (PEDOT), polypyrrole (PPY), polythiophene (PT), Polyaniline (PANI) are attached attention due to their wide range of promising applications [1-3].

Polyaniline showed a wide range of applications in the promising areas such as sensors, light emitting diodes, corrosion inhibitors, batteries, supercapacitors and solar cells [4-5]. Polyaniline is one of the most studied conducting polymers among the above listed polymers due to its high conductivity. PANI can be formed in two forms viz, emeraldine salt and emeraldine base form. The prepared PANI in emeraldine salt form has various applications due to its highest conductivity while PANI in emeraldine base form shows the low conductivity. The conductivity of PANI can be characterized using the imine to amine nitrogen ratio. PANI has band gap 2.8 eV of Emeraldine base (EB) form and after doping we get band gap within 2 eV to 3 eV of Emeraldine salt (ES) form. Conductivity of PANI is from 10^{-8} to 10^{+1} Siemens/cm [6].

PANI nanostructure materials such as nanofibres, granular, nanotubes have been prepared by different strategies. Till date various methods are employed for the preparation of PANI viz, template based or by simple chemical synthesis route method and by electrodeposition method [7-8]. This work describes the simple chemical bath deposition method for the deposition of polyaniline thin films. The dopant acid concentration helps to grow both the emeraldine salt and emeraldine base form of PANI.

2. Experimental Details

Experimental details to grow PANI thin films using chemical bath deposition method is reported elsewhere [9]. Aniline is used as a aniline oligomers, ammonium dichromate is used as a oxidizing agent. Hydrochloric acid is used as a dopant acid for the protonation of aniline. The deposition is carried out at room temperature. A solution consisting of 0.05 M aniline and dopant acid is dissolved in double distilled and stirred well to get clear solution. The concentration of dopant acid is varied from 0.5 M to 1.5 M. Three different set of solution is prepared using 0.5 M, 1.0 M and 1.5 M dopant acid concentration namely A1, A2 and A3, respectively. The resultant solution is stirred until clear transparent solution gets formed. 0.025 M ammonium dichromate is then added into the solution. The deposition time for the PANI films is 30 min on glass substrate. A uniform well adherent and smooth deposition of PANI is obtained which was further rinsed in water.

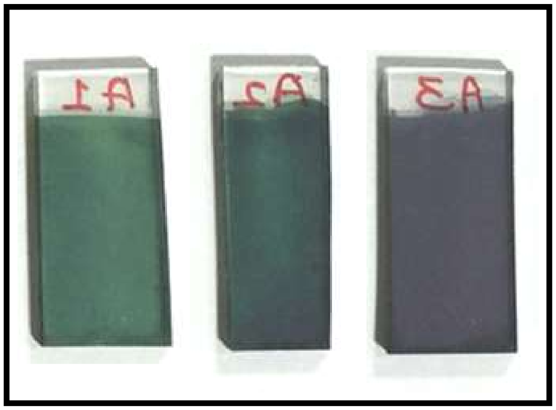

Fig. 2.1: Actual photograph of the films deposited in presence at A1) 0.5 M, A2) 1.0 M and A3) 1.5 M concentration of dopant acid.

The prepared PANI thin films are characterized with the aid of Raman spectroscopy to get the structural information via Invia Renishaw Raman Microscope coupled with Philips CCD camera having 785 nm excitation laser, JASCO UV-Vis-NIR spectrophotometer is used to study the optical absorption spectra, Perkin Elmer LS-55 spectrophotometer is employed to study the photoluminescence spectra of PANI thin films. Morphological properties of PANI are studied with the help of Scanning electron microscopy (SEM) JEOL JSM-6360A microscope with operating voltage 20 kV. A standard two probe method using Biologic potentiostat SP-300 model at room temperature is used to study electrical properties of PANI thin films. Depending upon the form of PANI is green or blue is depends on the concentration of dopant acid. In this work, the effect of dopant acid concentration on optical, structural, morphological and electrical properties of PANI have been extensively studied. The actual photograph of the films deposited in presence at A1) 0.5 M, A2) 1.0 M and A3) 1.5 M concentration of dopant acid is shown in figure 2.1.

3. Results and Discussion

It is a nondestructive characterization method of choice for many recent studies of polyaniline. The resonance Raman Spectra of PANI thin films prepared using CBD at different concentrations of dopant acid are recorded using 785 nm excitation laser is as shown in figure 3.1. The bands appeared between 1100-1700 cm^{-1} gives the information about various stretching modes of different bands. The Raman band observed at 1594 cm^{-1} is assigned to the C-C stretching vibrations of benzene ring. The band at 1508 cm^{-1} is assigned to N-H deformation vibrations.

As the concentration of dopant acid increase, the intensity of this peak increase which shows the formation of emeraldine salt form of PANI. The band attributed at 1360 cm^{-1} yields information about carriers' vibrations in PANI in C-N^{+} polaronic structure. The intense band observed at 1172 cm^{-1} is related to C-H vibrations of aromatic rings. The band present in between 1000-400 cm^{-1} provides the information regarding the benzene rings deformation vibrations. The band appeared at 812 cm^{-1}, 740 cm^{-1}, 519 cm^{-1}, 428 cm^{-1} are in plane and out of plane vibrations of rings of protonated emeraldine form of PANI [10].

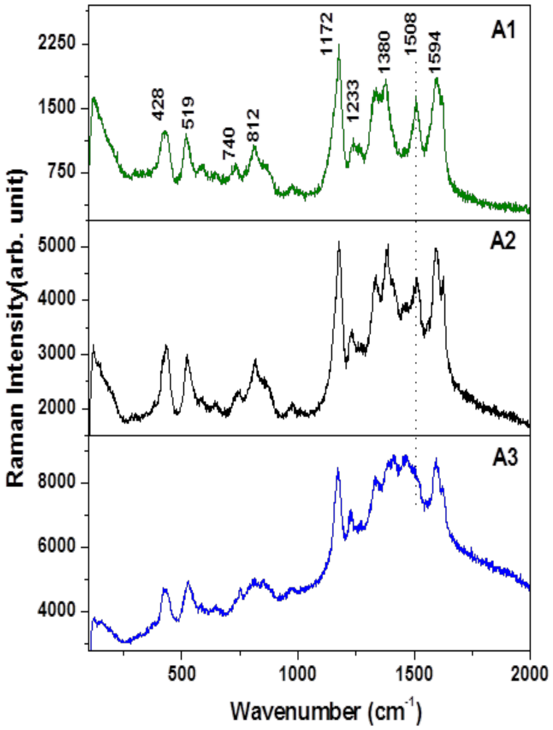

Figure 3.1: Raman spectra of polyaniline thin films prepared by CBD using various concentrations of dopant acid A1) 0.5 M, A2) 1.0 M and A3) 1.5 M

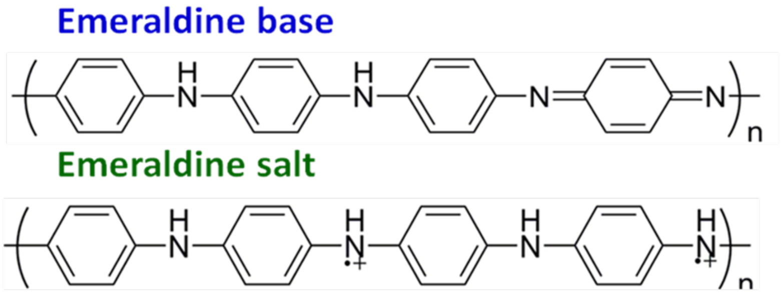

Figure. 3.2: Structure of EB & ES forms of PANI

Figure 3.2 shows the structure of emereldine base and salt form of PANI. From Raman spectra it is observed that the intensity of the peak observed at 1508 cm^{-1} of PANI deposited at 1.5 M dopant acid is higher than that of 0.5 M dopant acid because the number of benzoid units are higher in emeraldine salt form as compared to emeraldine base form since N-H deformation vibration are present only in benzoid unit.

Figure 3.3 shows the optical absorption spectra of polyaniline thin films deposited by CBD at A1) 0.5 M, A2) 1.0 M and A3) 1.5 M concentrations of dopant acid. The band diagram for PANI in ES and EB form is shown in figure 3.4. Three strong absorption peaks attributed at 333-348 nm, 412 nm, 602-680 nm and 808-828 nm are associated to π-π^* electronic transition, polaron, exciton and bipolaron band transition, respectively.

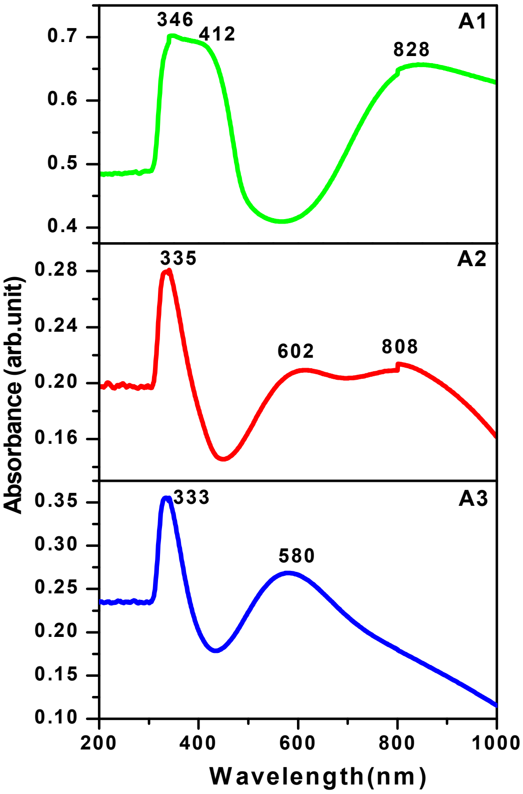

Figure 3.3: Absorption spectra of polyaniline thin films deposited by CBD at dopant acid A1) 0.5 M, A2) 1.0 M and A3) 1.5 M concentration

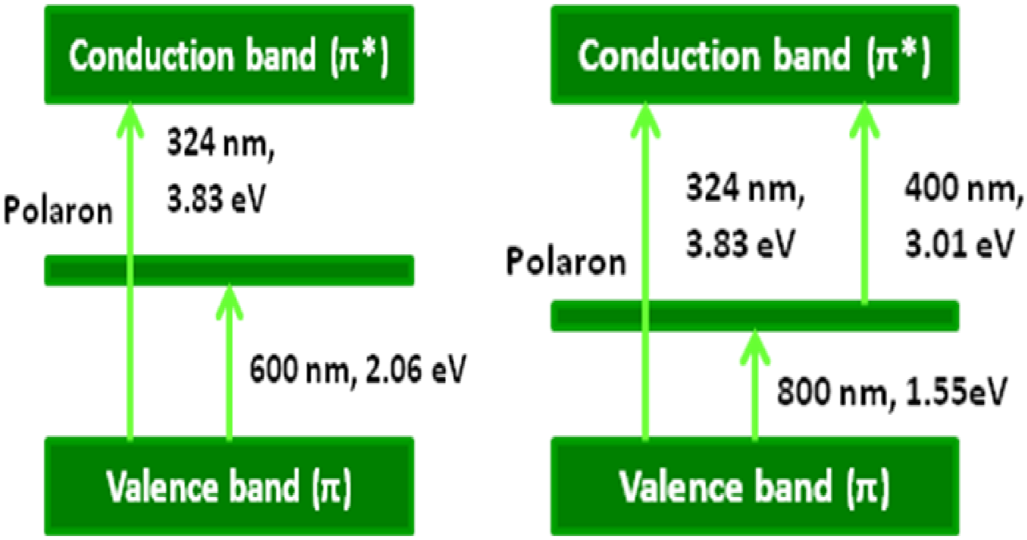

Figure 3.4 : Transition of PANI in a) ES form and b) EB form

Presence of three peaks in A1 confirms the formation PANI in emeraldine salt form. The peak observed at 348 nm is attributed to the transition of electron from highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) which is related to the π-π* electronic transition. The weak absorption peak observed at about 412 nm is associated to the polaron band transition of PANI. The broad absorption peak observed at about 808-828 nm is associated to the bipolaron band transition of PANI as shown in figure 3.4. Basically Polaron and bipolaron are the charge carriers in conducting PANI. A radical cation which is partially delocalized in some segment of polymer is called a polaron. When the electrons from top of the valence band of polymers are removed, a vacancy is created which does not delocalized completely, but only partially delocalization occurs extending over several monomeric units. From already oxidized polymers containing the polaron, if another electron is removed then this electron can come from either a different segment of the polymer chain and creating another independent polaron known as bipolaron. The presence of two peaks at 0.5 M concentration of dopant acid confirms the formation of Emeraldine base form of PANI, whereas the peak appeared at 580 nm attributed to a local charge transfer between a quinoid ring and the adjacent benzoid units [11]. At 1 M concentration of dopant acid, the film shows features of both salt and base form of PANI.

Figure 3.5 depicts the photoluminescence spectra of PANI thin films deposited by CBD at various concentrations of dopant acid A1) 0.5 M, A2) 1.0 M and A3) 1.5 M. The samples were excited at wavelength 270 nm. In PL spectra three peaks related to PANI in ES form are attributed for PANI deposited in presence of 1.5 M HCL. As the concentration of dopant acid decreases, the form of PANI converts from ES to EB and revealed the presence of two peaks.

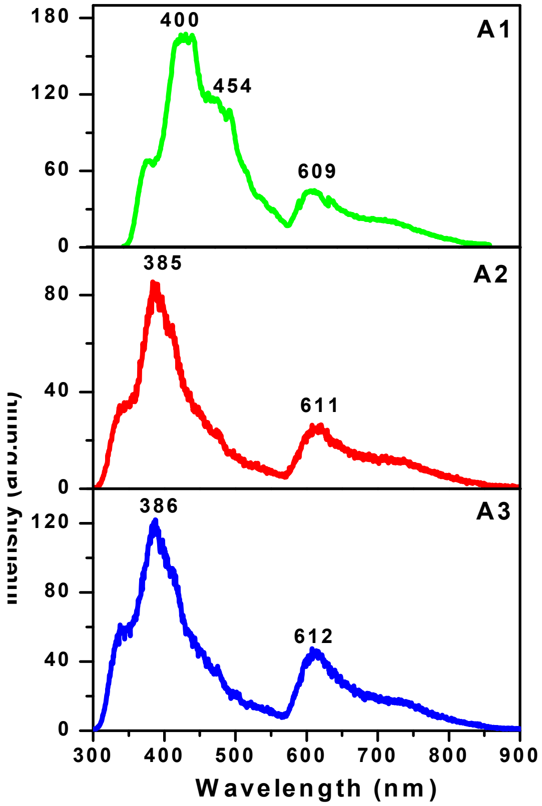

Figure 3.5: Photoluminescence spectra of PANI thin films prepared by CBD using various concentrations of dopant acid A1) 0.5 M, A2) 1.0 M and A3) 1.5 M

The morphology of PANI thin film in emeraldine salt form i.e. at higher concentration of dopant acid (1.5 M) is shown in figure 3.5. Long fibres of length few micron and diameter around ~100 to 200 nm are observed in SEM image for pure emeraldine salt form of PANI deposited in presence of 1.5 M dopant acid. For the PANI films deposited in presence of 0.5 M and 1 M dopant acid show smooth and granular morphology.

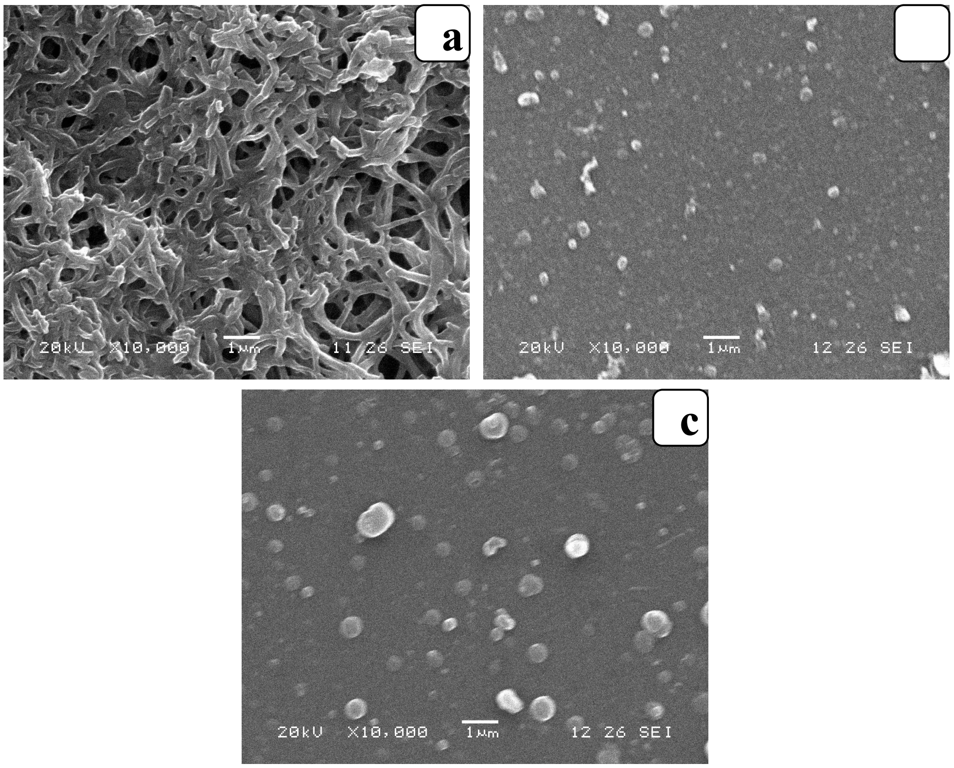

Figure 3.6: SEM image of PANI thin film deposited chemically using various concentrations of dopant acid a) 0.5 M, b) 1.0 M and c) 1.5 M

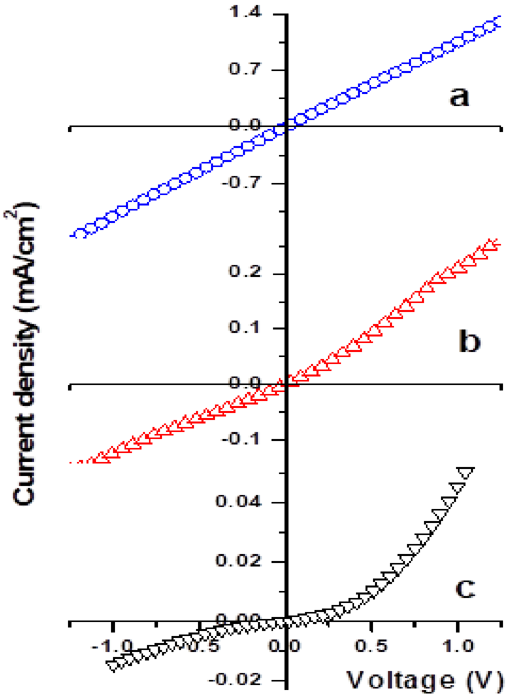

Fig.3.7: Current density characteristics of polyaniline thin film deposited chemically at a) 0.5 M, b) 1.0 M and c) 1.5 M dopant acid concentration

The electrical properties of PANI are measured with the help of two probe method. The effect of dopant acid concentration on the yield and conductivity of PANI is shown in figure 3.6.
From figure it is observed that with increase in dopant acid concentration conductivity of the film increases due to formation of ES form of PANI at 1.5 M dopant acid concentration. The results obtained from electrical conductivity measurements are in agree well with the results obtained from Raman spectra, optical absorption spectra as well as from the morphological studies also. The higher electrical conductivity could be also compare with the fibrous morphology of polyaniline grown at lower dopant acid concentration. The conductivity of polyaniline varies with the extent of degree of protonation (variation in the dopant acid) [12].

4. Conclusions

In this work, the effect of dopant acid concentration on structural, optical, morphological and electrical properties of polyaniline thin films has been extensively studied. Raman results show the formation of PANI in the emeraldine oxidation state. Higher concentration of dopant acid leads to the formation of PANI in the emeraldine salt oxidation state. Optical absorption spectra confirms the presence of absorption peaks related to п-п*, polaron and bipolaron transition for PANI films deposited at higher concentration of dopant acid, while the PANI films deposited at lower concentration of dopant acid show only two absorption peak related to EB form of PANI. PL spectra show that as the concentration of dopant acid decreases, the form of PANI converts from ES to EB, moreover, it also revealed the presence of two peaks. SEM images depicts the growth of long fibers of PANI with diameter ~100-200 nm prepared using 1.5 M dopant acid concentration, while smooth morphology is seen for PANI films in presence of lower dopant acid concentration. PANI films grown in presence of higher concentration of dopant acid shows higher conductivity which confirms the formation of conductive emeraldine salt form of PANI. The above properties of the PANI will be useful to have a wide application in solar cell.

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