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# Novel microstructure in spin coated polyaniline thin films

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## Abstract

Polyaniline (Pani) thin films doped with camphor sulfonic acid (CSA) have been deposited on glass substrates using the spin coating technique. Pani is chemically synthesized by an oxidation method at  $\sim 0^\circ\text{C}$ . Pani-CSA films show a hexagonal structure in scanning electron micrographs, which occurs due to the crystalline growth of CSA. A dense hexagonal structure is visible for film deposited at 800 rpm, but it becomes sparser as the revolutions per minute are increased (1200, 1500 and 2000 rpm). Electronic transition of quinoid units cause an absorption shoulder at  $\sim 900$  nm for films deposited at 1200, 1500 and 2000 rpm, which is not observed for film deposited at 800 rpm.

## 1. Introduction

Pani exhibits high electrical conductivity on doping using organic dopants. It has potential as a highly tailorable organic semiconducting material for use in electronics and optoelectronics devices. Several device applications, including electrodes for rechargeable batteries [1], sensors [2], electrochromic displays [3], electronic switches [4] and photovoltaic devices [5, 6], have been developed using Pani.

Pani exists in a variety of protonation and oxidation forms [7]. Doping and oxidation levels are the most important factors affecting the electrical and optical properties. Among all its forms, the protonate emeraldine form is produced by the oxidative polymerization of aniline in aqueous acids [7]. Pani offers extensive chemical versatility, allowing its properties to be tuned to appropriately meet the needs of a given application. Compared to other conducting polymers, Pani can easily be switched from an insulating form to a conducting form via either protonic acid doping or base de-doping processes. The main problem is the insolubility of the Pani in any common solvents. Therefore, the Pani is doped with organic acids like camphor sulfonic acid (CSA) [8], dodecylbenzenesulfonic acid (DBSA) [9], hydrabenzosulfonic acid (HBSA) [10],

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p-toluenesulfonic acid (PTSA) [11] and poly (2-acrylamido-2-methyl-1-propane-sulfonic acid) (PAAMPSA) [12] etc. Pani doped with CSA is particularly interesting because of its solubility in the conducting state, a metallic type of conductivity in a certain temperature range, and the high degree of crystallinity.

In this paper, we report on our observation of hexagonal microstructure in the solution-processed Pani-CSA thin films using the spin coating technique. Though hexagonal structure in surface morphology has been suggested theoretically [13], there are no experimental results showing the same.

## 2. Experimental details

Pani was synthesized chemically by the oxidation method at  $\sim 0^\circ\text{C}$  [7]. 0.22 M aniline was dissolved in 240 ml of 1 M HCl solution and then cooled to  $\sim 0^\circ\text{C}$  in an ice bath. 80 ml of 0.8 M  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  and 1 M HCl solution was added to the aniline solution drop-wise over 2 h with continuous stirring at  $\sim 0^\circ\text{C}$ . Stirring was continued for a further 4 h. The precipitate produced in the reaction was removed by filtration, washed repeatedly with 1 M HCl and dried under vacuum for 48 h. The Pani powder thus obtained was in the HCl doped state (Pani-HCl). For emeraldine-base Pani, the Pani-HCl powder was put in 0.1 M ammonia solution and stirred for 3 h at room temperature. The precipitate was filtered, washed with deionized water until the water became neutral, and then dried in vacuum for 48 h to obtain emeraldine Pani.

Pani (0.4 g) and CSA (2.0 g) were dissolved in 30 ml m-cresol to prepare the solution. The solution preparation requires 4–5 days of stirring to make the solution homogenous. Thin films of Pani-CSA were deposited on glass substrates using the spin coating technique (Milman-6000) at a speed of 800 rpm called film (A), 1200 rpm called film (B), 1500 rpm called film (C), and 2000 rpm called film (D). Film E is deposited using Pani-CSA in chloroform. These films were dried at  $\sim 60^\circ\text{C}$  in air. Thickness measurements were carried out using a Tencor alphastep (100). Fourier-transform infrared (FTIR) spectroscopy was performed in reflectance mode using a Perkin Elmer Spectrum BX2. An optical absorption study was carried out using a Perkin Elmer Lambda 900 ultraviolet–visible–near-infrared (UV/vis/NIR) spectrometer. Surface morphological studies were carried out using a LEO 435 VP scanning electron microscope.

## 3. Results and discussion

Figure 1 shows the FTIR spectra for the films (A, B, C and D). The band characteristics of the conducting protonation form are obtained at  $\sim 1275\text{ cm}^{-1}$  and interpreted as C–N<sup>+</sup> stretching vibration in the polaron structure. The band at  $\sim 1146\text{ cm}^{-1}$  is assigned to a vibration mode of the –NH<sup>+</sup> = structure, which occurs due to the protonation of Pani. The  $1028\text{ cm}^{-1}$  band is assigned to C–H in plane bending vibration. Peak broadening occur with a decrease in film thickness (from film A to D), which is due to the change from a ordered to a disordered film.

Figure 2 shows the absorption spectra for the films A, B, C and D. These films show the absorption edge at  $\sim 470\text{ nm}$  (benzene  $\pi$ – $\pi^*$  transition). A steadily increasing free-carrier tail starting from  $\sim 750\text{ nm}$  to the near-IR region is observed for all films, with a shoulder at  $\sim 900\text{ nm}$  for films B, C and D. The band at  $\sim 770$  is assigned to the polaronic band. This behaviour is consistent with a delocalized polaron band structure [14, 15]. The absorption increases from film D to A due to an increase in thickness from  $1.2\ \mu\text{m}$  for film D,  $2.0\ \mu\text{m}$  for film C,  $2.9\ \mu\text{m}$  for film B and  $3.4\ \mu\text{m}$  for film A. The decrease in thickness is expected, since the same amount of material was used for spin coating. It has been reported [16] that thicker samples are more conductive, which should lead to an increase in the free-carrier

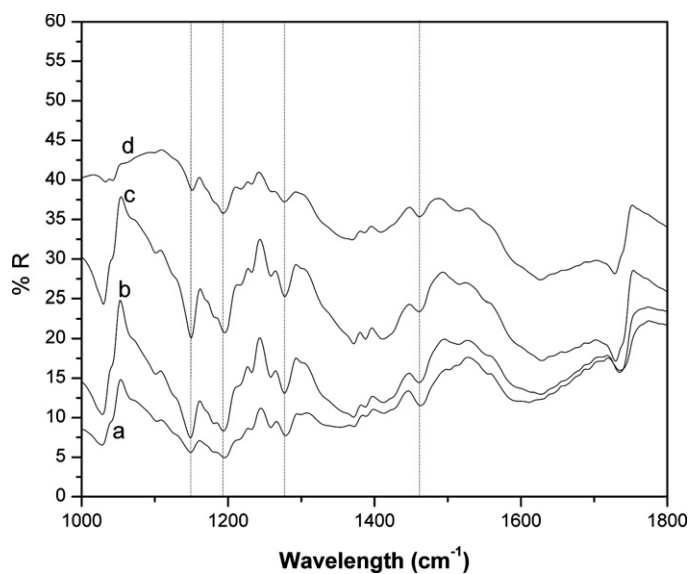


Figure 1. FTIR reflectance spectra of (a) film A, (b) film B, (C) film C and (d) film D.

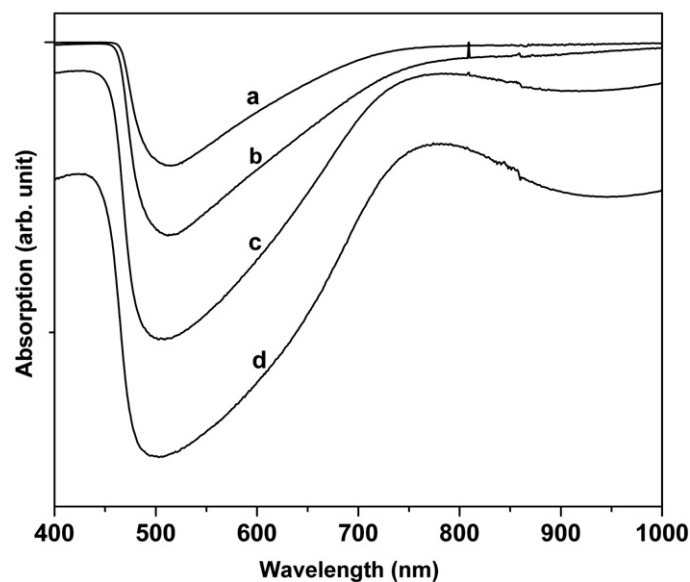
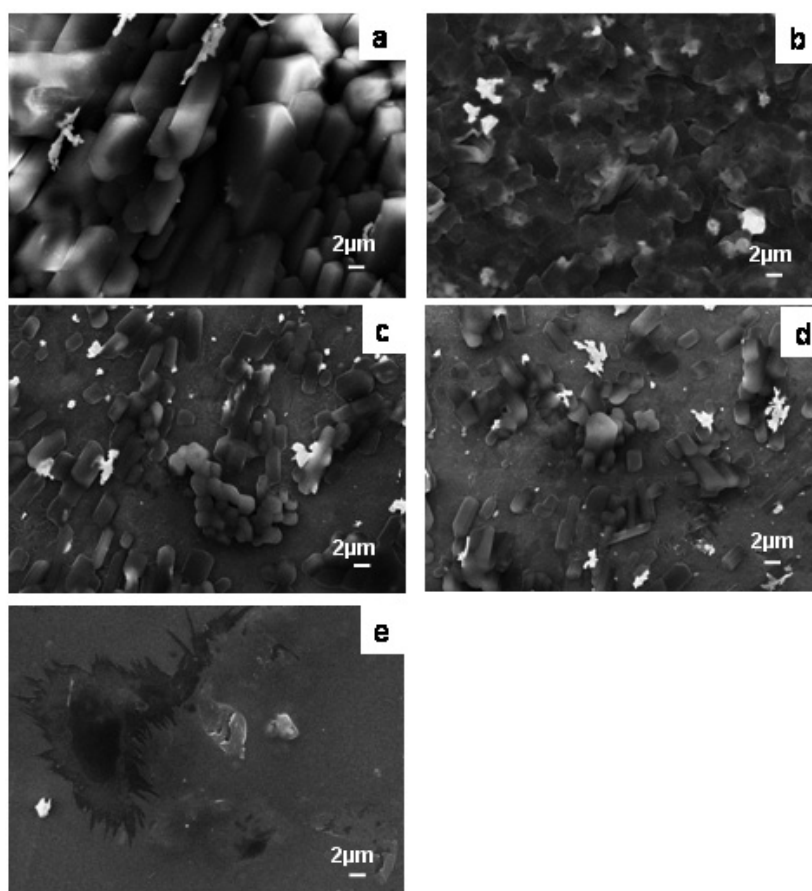


Figure 2. Absorption spectra of (a) film A, (b) film B, (c) film C and (d) film D.

absorption. This can be the reason for the appearance of the absorption shoulder at  $\sim 900$  nm in the absorption curve at lower thicknesses. The electronic transition of quinoid units gives rise to such a shoulder in transmission [17]. A similar thickness dependence of transmission is also observed in the case of electrochemically grown polyaniline films [18].

Figure 3 shows the surface morphology of films A, B, C, D and E. The micrographs of films A, B, C, and D show a well-defined hexagonal surface morphology, which is more prominent in film A. The hexagonal structure appears to be more aligned in the same direction.



**Figure 3.** Scanning electron micrographs of (a) film A, (b) film B, (c) film C, (d) film D and (e) film E.

Since FTIR analyses show that film A is more protonated, there can be electrostatic interaction between Pani and CSA in the presence of *m*-cresol solution and also hydrogen bonding between the carbonyl group of CSA and hydroxyl group of *m*-cresol [19]. There also exist phenyl–phenyl interactions between the phenyl ring of *m*-cresol and the neighbouring Pani ring. The van der Waals interaction between these phenyl rings of CSA and *m*-cresol is described by the Lennard potential. These molecular interactions are known to cause crystalline growth of CSA; this results in the growth of hexagonal structure. In the case of films C and D, hexagonal structures with small distortion lie randomly on the surface; this is due to the increase in repulsive interaction between two co-axial phenyl rings. The van der Waals forces also play an important role in maintaining the structure, which is responsible for the bending of CSA molecules relative to the Pani chain, and the atoms in the C–N bond are also rotated. Earlier, Huo *et al* also proposed the same kind of possible ideal structure for Pani-CSA LB films (Langmuir–Blodgett) [13].

This suggests that, in the absence of hydrogen bonding and phenyl–phenyl interactions between Pani, CSA and *m*-cresol, no hexagonal structure should be present. This has been proved using chloroform instead of *m*-cresol; no hexagonal structure appeared, which means that the role of hydrogen bonding and phenyl–phenyl interactions are important in the formation

of hexagonal structure, and this can be seen clearly from figure 3 for film E. Earlier, Ikkala *et al* [19] also explained the importance of hydrogen bondings and phenyl–phenyl interactions in this system.

#### 4. Conclusions

Our studies show that it is possible to deposit Pani-CSA films with well-defined surface morphology with hexagonal structure using the spin coating technique. It is found that the surface morphology of the films is influenced by the degree of protonation of Pani. These polyaniline thin films with novel micro-structure may enhance NH<sub>3</sub> sensing at room temperature.

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