



Characterization Studies on Structural, Optical, Thermal and Non-Linear Properties of Carbocyanine Dye Film Using Low Temperature Plasma

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Abstract : Cellulose Triacetate films incorporating cyanine dyes have been inclined by dip coating method and the optical, structural, Non-Linear and thermal properties have been researched. Depiction by FTIR spectroscopy revealed a small difference between the untreated and plasma treated film. SEM analysis confess the change in surface morphology when treated with plasma. DTA/TGA measurements manifest thermal stability of the plasma treated film. SHG assessment showed the efficiency of the plasma treated film correlated to untreated one.

Keywords : Carbocyanine dye, Glow discharge plasma, Cellulose Tri Acetate (CTA).

1. Introduction

Organic molecules with π -conjugated electrons have been studied due to their strong light absorption and emission in the visible range [4,9]. The advantages of organic materials over inorganic materials are its flexibility in molecular design and ease of fabrication. In this paper we investigated the interaction between a

CTA film and cyanine dye, and plasma induced spectral behavior for the CTA film and the cyanine dye. We demonstrated that the plasma induced CTA film and cyanine dye shows spectral changes. This study is expected to give new information on the methodology to introduce plasma treatment for industrial applications.

2. Experimental

2.1 Materials

Cyanine dye of CY 522C (C₂₄H₃₁N₄) was used without further purification. Figure 1 represents the chemical structure of carbocyanine dye. Methylenechloride and Methanol was used as solvent for the Cellulose Tri Acetate (CTA) film preparation [6].

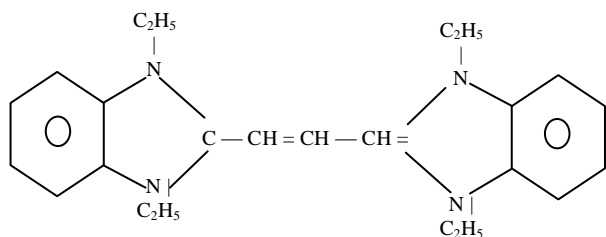


Figure 1 Structure of Carbocyanine dye

2.2 Sample Preparation

100 grams of cellulose triacetate is weighed in a one liter wide mouth glass stopper bottle added to an 500 ml of solvent mixture (Methylene chloride and methanol by 9:1 ratio). The mouth of the bottle is closed with stopper. When the mass becomes fairly thick, mount the bottle onto a tumbling type shaker till the solution is complete. Obtained viscous solution was then casted on Au-coated glass plate and dried at room temperature and transparent CTA films were prepared. CTA films were dip coated from carbocyanine dye solution. The obtained films is hereafter referred to as the carbocyanine dye film.

2.3 DC glow discharge setup

The setup consists of cylindrical stainless chamber of 50cm length and internal diameter of 30cm. Through an inlet, air or other desired gases could be introduced in to the chamber. A pair of 15cm length aluminium plates were used as anode and cathode inside the chamber. Inside the chamber vacuum was created. A pressure of 0.03mbar measured by a pirani gauge was maintained inside the chamber. At this low air pressure, dc voltage of 450v was applied between the electrodes to ignite the glow discharge. In this investigation the surface of the carbocyanine dye film was modified by DC glow discharge through air across aluminium electrode having a fixed spacing of 6cm, for different times of exposure at 10w power level.

2.4 Measurement

X-ray diffraction (XRD) patterns were measured with a XPERT PRO diffractometer using $\text{CuK}\alpha$ radiation source operating at 40kv and 30mA as the source applied voltage and current respectively. Scanning Electron Microscope (SEM) was used for the morphological characterization of carbocyanine dye film. FT-IR reflection spectra of films were taken using a variable angle reflection accessory at an incident angle of 45degrees. The characteristics of samples were examined through a UV –Vis spectro photometer type UV-2250 produced by Japanese shimadzu company where the scan speed was medium, the slit width was 2nm, wavelength was 200nm-800nm. The DTA/TGA analysis was carried out with the help of instrument DTA /TGA 6200 simultaneous thermal analyzer between 30°C to 800°C at a heating rate of 20°C/min in a nitrogen atmosphere with alumina crucible as the reference and the graph was plotted using pyris software. The second harmonic generation efficiency of the dye film was determined by employing Kurtz-Perry powder technique using Q-switched ND-YAG laser as a source.

3. Results and Discussion

3.1 XRD analysis

XRD analysis of carbocyanine dye film has been carried out for the untreated and those exposed to DC glow discharge for 5 min and 10 min and at 10 w power levels under aluminium electrodes. The x-ray diffractogram of the deposited and plasma treated carbocyanine dye film surfaces for different time was illustrated in Figure 2. It is noted there is no significant change in shape and position of the diffraction peaks, except that the peaks are more intense in the case of treated samples. The full width at half maximum increases with increasing time due to the crystallinity increase of the carbocyanine dye film surface induced by the plasma treatment.

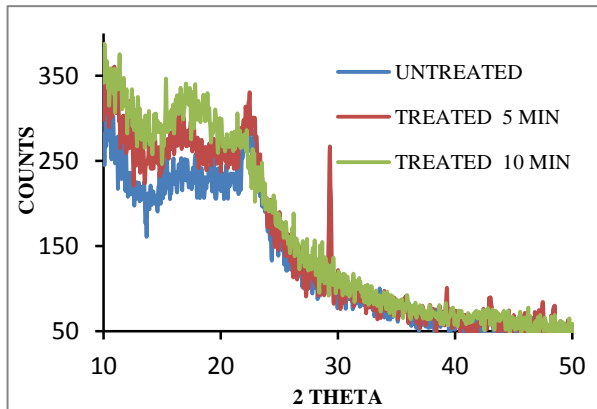


Figure 2 X-ray diffraction patterns of untreated and plasma treated carbocyanine dye film

These results confirm that the plasma treatment considerably improves the crystallinity of the carbocyanine dye film surface.

3.2 SEM analysis

Carbocyanine dye film surfaces of both unexposed and exposed to DC glow discharge across aluminium electrodes have been examined under scanning electron microscopy. Figure 3a shows the SEM images of the unexposed carbocyanine dye film surface. It is observed that a few filler particles appearing white and bubble type particles were present on the unexposed surface [10].

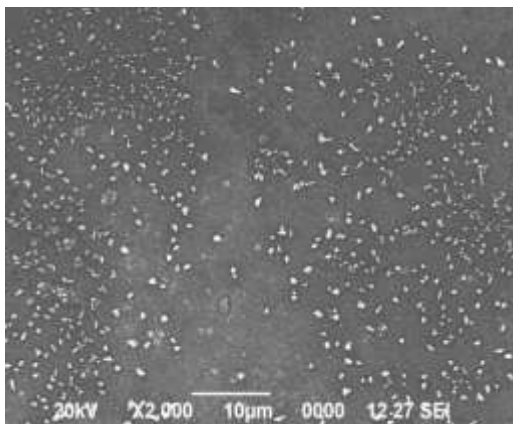


Figure 3(a)

The SEM image of carbocyanine dye film surface exposed to DC glow discharge at 10w for 300s across aluminium electrode is shown in Figure 3b. The figure reveals that the image of the carbocyanine film surface exposed to DC glow discharge is significantly different from that of the unexposed surface. (See Figure 3a). When the surface is exposed to DC glow discharge there is numerous amounts of spherical shaped apatite nucleation and deposition on the surface.

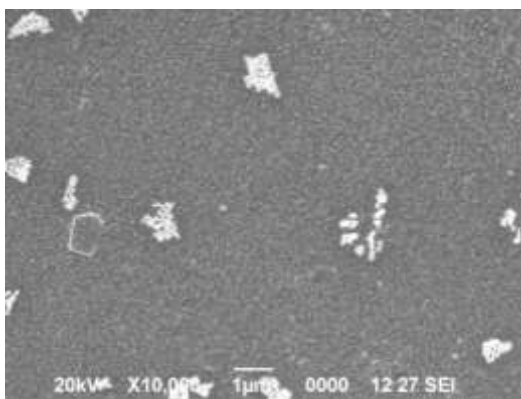


Figure 3(b)

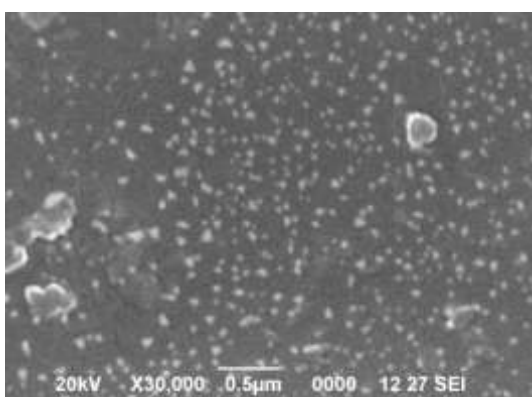


Figure 3(c)

Figure 3 (a), 3 (b) and 3 (c) SEM representation of untreated and plasma treated carbocyanine dye film surface

Figure 3c shows the SEM picture of carbocyanine dye film exposed to DC glow discharge across aluminium electrode at 10w for 600s. The figure reveals that when the carbocyanine dye film surface is exposed under this electrode the extent of formation of crystals are significantly higher in comparison to those observed under exposure to DC glow discharge for 300s.

3.3 FTIR analysis

Fourier transform infrared spectra was recorded with an IR spectrophotometer employing KBr pellet technique with a resolution of 4cm^{-1} . The spectral analysis of the film deposited by means of dip coating is based on comparison of the spectral bands of the plasma treated thin films in a region where most of the uncharacteristic fundamental vibrations appear. For this study $1700\text{-}600\text{ cm}^{-1}$ spectral interval is selected. The spectral analysis will be illustrated with the detailed comparison of three spectra of carbocyanine dye film.

The $1700\text{-}600\text{ cm}^{-1}$ region of the IR spectrum of untreated and plasma treated film for 300s and 600s is shown in Figure 4 [3]. It can be seen that the three spectral analysis look pretty similar and the bands of the film at $1651.07, 1442.75$ and 1226.76 cm^{-1} are preserved in the spectrum of the thin film. On the other side some of the bands are shifted to up to 10 cm^{-1} which is expected as the compound is embedded in to the Carbocyanine dye film. The strong bands of this type are 1751 cm^{-1} shifted to 1743 cm^{-1} and 1049 cm^{-1} shifted to 1165 cm^{-1} [2,12]. The interaction of the deposited dye with the substrate and the plasma treatment is also a reason for widening of most of the bands.

In the spectrum two or three bands close in the compound spectrum can appear as one band in the thin film spectrum. In the figure these are at 1442.75 cm^{-1} triad, 964.41 cm^{-1} triad and 902.69 cm^{-1} triad. There are three to four bands in the spectrum of the deposited dye that cannot be explained as a result of deposition of these are strong 3988.7 cm^{-1} , 3873.06 cm^{-1} , 2924.09 cm^{-1} and 2306.86 cm^{-1} band. The explanation is that only the partial degradation of the deposited dye happens. It appeared that the substrate did not influence the quality of the

deposited dye material and the only factors which determine the dye’s chemical degradation by the deposition process are the plasma treatment and the chemical structure of dye

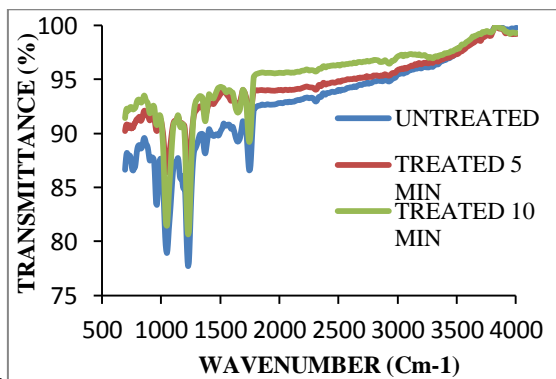


Figure 4 FTIR spectra of untreated and plasma treated Carbocyanine dye film

3.4 UV-VIS SPECTROSCOPY

Figure 5 shows the UV-Vis spectra of CTA film for untreated and plasma treated films in the 400-600 nm. It can be seen from that, the spectra in the wavelength range 522 nm light absorption was relatively small.

Absorb light beginning between 400-500 nm, and the wavelength was shifted to shorter wavelength as the absorption was obvious. The spectral curve changed when compared with untreated carbocyanine dye film. The absorption peak was shifted. Summarized in Table (1) are the values of absorption spectra and Peak intensity for untreated and plasma treated dye Thin film.

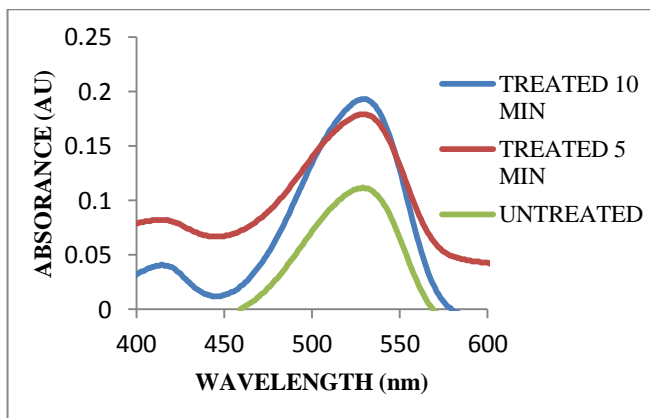


Figure 5 Absorption Spectra of untreated and plasma treated Carbocyanine dye film for 450V 5min and 10min

Table (1) Absorption Spectra and Peak Intensity for Untreated and Plasma Treated Dye Thin

Absorption peak position in			Intensity		
Untreated film(nm)	Treated film 300s (nm)	Treated film 600s (nm)	Untreated film(nm)	Treated film 300s (nm)	Treated film 600s (nm)
522	526	534	0.108	0.178	0.194

3.5 DTA/TGA analysis

Temperature is another factor that has a significant role in destabilizing the cyanine dye molecular structure. In DTA analysis of untreated carbocyanine dye film, Figure 6a, degradation proceeds through two stage process which occurs at 300°C and 390°C. From Figure 6b, it is revealed that TGA trace for the treated film of 300s degradation occurs at 310°C and 385°C through two stage process. The Figure 6c reveal that when carbocyanine dye film is exposed to 600s, degradation occurs through three stages at 300°C, 395°C and 490°C. This suggests that carbocyanine dye film treated with plasma for 600s are thermally labile than untreated and treated one of 300s.

Decomposition temperature of carbocyanine dye films was measured by TGA, and these were at 600 °C for both untreated and plasma treated film. From the figure it is revealed that there is no significant change in the decomposition temperature. The DTA response curve shows a sharp exothermic peak at 289.6 °C and 393.2 °C which can be attributed to the melting point of the material of the dye for the untreated film [1, 5].

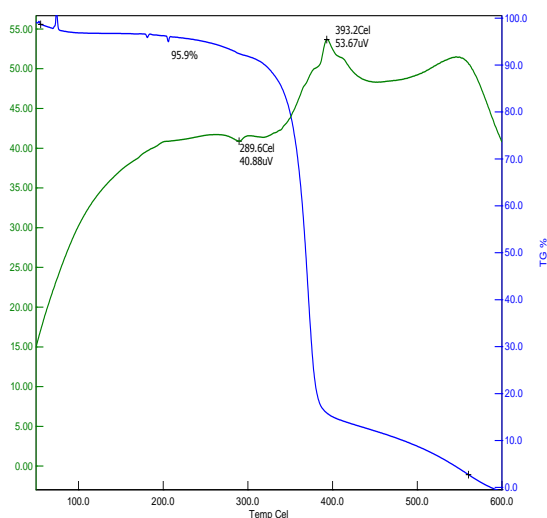


Figure 6 (a) DTA and TGA trace of untreated Carbocyanine dye film

For the treated film 300s the material is stable up to 310 °C, which is the melting point of the substance.

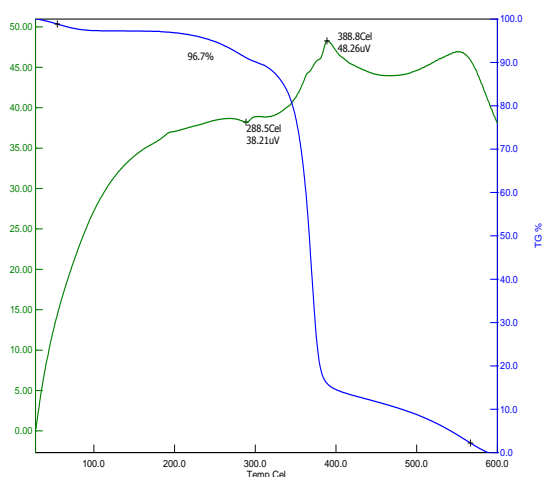


Figure 6(b)

Above this point the material begins to attain an exothermic transition and begins to decompose. The sharpness of this peak shows the degree of crystallinity of the sample.

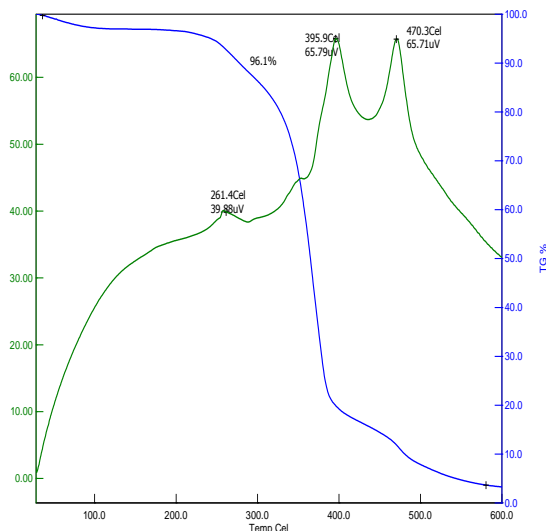


Figure 6(c)

Figure 6 (b) 5min & 6(c) 10 min DTA and TGA trace of treated Carbocyanine dye film

For the treated film 600s the decomposition of the Sample is taking place in three different stages. There is a sharp exothermic peak at 261.4 °c. It coincides with the first stage of weight loss in TGA trace. There is one more sharp exothermic peak at 359.9 °c. This corresponds to the second stage of weight loss in the TGA trace and the third stage of weight loss in TGA trace coincides with the sharp exothermic peak at 470.3 °c in DTA trace. The maximum temperature for NLO applications of carbocyanine dye film is limited to 261.4 °c.

3.6 NLO studies

The most widely used technique for confirming the SHG efficiency of NLO materials, to identify the materials with non centro symmetric crystal structures, is the Kurtz powder technique[8]. Q-switched ND-YAG laser beam of $\lambda=1064$ nm width a pulse energy of 8.8mJ and 10ns pulse width was used. The output from the sample was collected using a monochromator to collect the intensity of 532nm [7,11] component and to eliminate the fundamental. The generation of second harmonic was focused by a lens and detected by photomultiplier tube. A sample of KDP (Potassium Dihydrogen Phosphate) was used as reference materials in SHG measurement.

The measured pulse energy for 300s treated carbocyanine dye film was 1.1mJ as against 8.8mJ for KDP crystal. The SHG conversion efficiency was found to be 0.125 times that of standard KDP crystal. For untreated and 600s treated carbocyanine dye film there was no pulse energy measured. Thus the carbocyanine dye film treated with plasma for 300s has the NLO property as compared to untreated and plasma treated film for 600s.

4. Conclusion

Carbocyanine dye film surface was treated on plasma at atmospheric air and at different treatment time. SEM and XRD characterization studies showed roughness and crystallinity of the cyanine dye film surface. Results of UV and FTIR shows increase in absorbance spectrum and shifts in the wave numbers. DTA/TGA analysis shows thermal stability for the plasma treated film compared to untreated one. Second harmonic generation has more efficiency compared to untreated carbocyanine dye film. The above changes in carbocyanine dye film surface confirm that it is suitable for industrial applications.

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