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Synthesis and Characterization of CSA protonated Poly(2,5-dimethoxyaniline)/TiO_2 Hybrid Thin Film

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Abstract

In this work, Poly (2,5-dimethoxyaniline) has been synthesized by oxidative polymerization using ammonium per sulfate as oxidant and protonated by camphor sulfonic acid. Protonated Poly (2,5-dimethoxyaniline) was doped with TiO_2 for different weight ratio and spin coat as thin film using m-cresol as solvent. Tio_2 doped Poly(2,5-dimethoxyaniline) thin films were characterized using X-ray diffraction, UV-Vis spectrophotometer, Photoluminescence and Fourier transform infrared spectroscopy for the analysis of structural confirmation, band gap, electronic transition and chemical composition. SEM micrograph images of the film confirmed the rod like structure. The band gap value and DC conductivity of the hybrid films found to be influenced by the ratio of TiO_2 nanoparticles.

Keywords: Camphor sulfonic acid, poly (2,5-dimethoxyaniline), Tio_2, hybrid thin film, photoluminence

1. Introduction

Tailoring organic and inorganic materials have potential applications as gas sensors [1], PV cells [2], DSSC [3], photo catalyst [4], electro chromic devices [5] etc. Organic conducting polymers are semiconductors and have conjugate molecular structure and possess delocalized π-electrons over the whole polymer chain. One of the well investigated conjugate polymer with environmental stability, low cost, controllable electrical property is Polyaniline[6]. Polyaniline (PANI) exist in three forms known as Leucoemeraldine base (fully reduced state), emeraldine base (50% oxidized state) and pernigraniline base (fully oxidized state). Emeraldine base (EB) with protic acid gets protonated by H^+ ions forming the Emeraldine salt (ES) which is the conducting form of PANI [7]. Poly (2,5-dimethoxyaniline) (PDMA) which is a derivative of PANI with methoxy group ($-OCH_3$) at ortho and meta position where it is acting as an electron donor substituents[8]. Though CdS, CuS, MnO_2, ZnO are most studied inorganic semiconductors, among the list, selected is TiO_2 due to nontoxic, high chemical and thermal stability, large band gap, and rapid recombination of photo generated electron hole pairs.

Many studies on PANI/ TiO_2 nano- composite have been reported so far but for the first time, studies on CSA protonated poly(2,5-dimethoxyaniline)/ TiO_2 nano composite hybrid thin films have been reported in this work.

2. Experimental

2.1. Chemicals

The chemicals monomer Dimethoxyaniline (DMA), (1s)-(+)-10 Camphorsulfonic acid were purchased from Sigma Aldrich. Ammonium persulfate, HCl (37%), m-cresol and diethyl ether were purchased from Merck. All chemicals were used without any further purification.

2.2. Synthesis of Poly (2, 5-dimethoxyaniline)

PDMA have been synthesized by oxidative polymerization by taking 1:1 molar ratio of DMA monomer and Ammonium peroxodisulfate (APS) as an oxidant. DMA dissolved in 1M HCl and stirred at a temperature of 0-5°C for half an hour. To this precooled solution an aqueous solution of APS in 1 M HCl is added drop by drop until brown color monomer turns into green color solution of HCl doped Emeraldine Salt (ES) indicating the formation of polymer, PDMA. The solution was stirred for another 5 hours, then filtered using Whatman paper and washed with deionized water to remove the unreacted monomers. The filtered ES - PDMA was dried in open hot air condition for 2 hours. Emeraldine Base (EB) has been prepared by suspending a part of ES-PDMA in 1M NH_4 OH solution. The solution was stirred for 3 hours., filtered and washed with diethyl ether to obtain EB form of PDMA. It was dried in open hot air condition for an hour to get deep blue color powder form of EB- PDMA.

The protonated ES-PDMA obtained by treating EB–PDMA with CSA of same weight to maintain 1:1 ratio.

2.3. Synthesis of Poly (2,5-dimethoxyaniline) / TiO_2 hybrid thin film:

ES –PDMA with different weight ratio of TiO_2 was dissolved in 2ml of m-cresol solvent with constant stirring for 30 mins. The viscous solution was spin coated under 1500 rpm for 60 sec to get thin film over precleaned fluorine doped tin oxide coated glass substrate and as well as on glass substrate. The thin films were dried under open air condition over a hot plate maintained at 60°C for 5hrs.The films were designated as CPT1, CPT2, CPT3 corresponding to weight ratio 1:0.5, 1:1, 1:2 respectively.

2.4. Material characterization

X-ray diffraction of the thin films were performed using XPERT-PRO Diffractometer with Cu Kα2 radiation. Scanning electron microscopic (SEM) of PDMA thin films were observed using ZEISS EVO 18. Fourier transform infrared (FTIR) spectra of the thin films were obtained by Perkin Elmer spectrum Rx1 spectrometer. UV-Vis spectra of the thin films were obtained using Lambda 365 Perkin Elmer spectrophotometer. Photoluminence spectra of the thin films spectro-flurometer (Jobin Yvon_Flurolog- FL3-11). DC conductivity by two probe method for thin films were carried out by Kiethley sourcemeter model 2450.The thickness of the films were measured using Gravimetric method.

3. Results and Discussion

3.1. X-ray diffraction

The X-ray diffraction pattern of EB, ES, CPT1, CPT2, CPT3 are shown in Fig1. The small peaks around 2θ = 25°, 37°, 48° are assigned to (101), (004), (200), (105) planes of anatase phase of TiO_2 [9]. Peaks observed at 2θ = 18° and 19° are due to CSA dopant in the hybrid films and it is well observed in the ES form of PDMA[10]. The peak at 2θ = 26° found to increase in intensity with increasing TiO_2 ratio. High crystallinity observed for PDMA/ TiO_2 hybrid films when compared with CSA doped PDMA which may be due to symmetric effect of polymer chain. The peak at 27° shows the characteristic distance between the ring planes of Benzene ring in adjacent chain and also the close contact interchain distance [11]. The peak at 2θ = 33° due to periodicity which is perpendicular to the polymer chain. The peaks showed minimum shift for different weight ratio of TiO_2 that shows the impact of TiO_2 in PDMA matrix [12]. Using Scherer equation the average crystallite size found to be ~29nm.

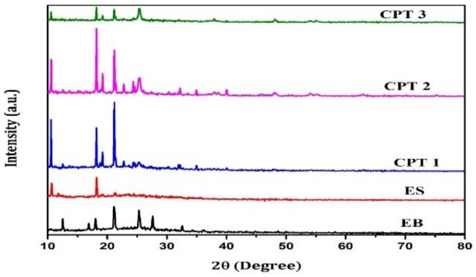

Figure 1. XRD pattern of Emeraldine base, Salt and CSA-PDMA/TiO_2 (1:0.5,1:1,1:2)

3.2. Surface morphology

The SEM images of CSA protonated PDMA/ TiO_2 for the weight ratio 1:1, 1:2 are shown in figure 2(a) and 2 (b) respectively. The SEM images illustrates the morphological changes from plate structure for ratio1:0.5 to rod with the increase of the dopant concentration. The plate like structure may be due to agglomeration of polymer particles representing the amorphous nature of the material. On doping with CSA the main chain of the polymer stretches due CSA - PDMA as well as CSA- m-cresol-PDMA bond. The CSA- PDMA bond is due to association of H^+ with Nitrogen of PDMA and the second bond is formed due to π- π stacking interaction of m-cresol with PDMA and TiO_2[13]. Owing to the linearization of main chain the rod like structure is observed representing the crystalline nature of the material figure 2(b) and (c). Beyond the limiting concentration of the dopant material become less crystalline may due to the predominant CSA-PDMA bonding disturbing the linear structure figure 2(d).

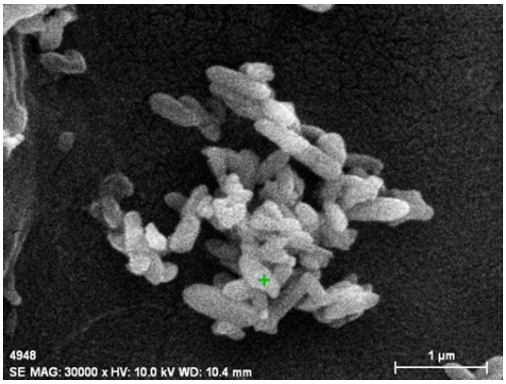

Figure 2 (a). CSA-PDMA /TiO_2 (1:1)

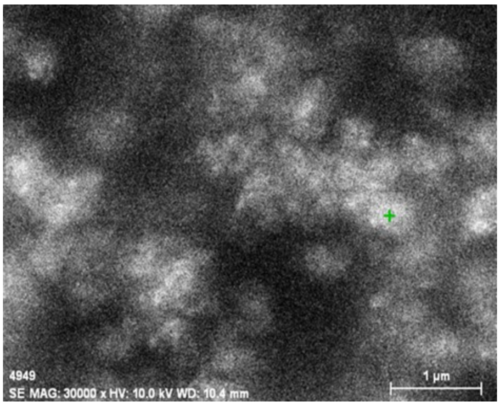

Figure 2(b). CSA-PDMA /TiO_2 (1:2)

3.3. Optical characterization

3.3.1. UV-Vis spectroscopy

UV-Vis absorption spectra shown in Fig 2. A broad hump observed around 620nm shows the formation or existences of EB of PDMA[7]. A shoulder at 480nm and 900nm represents the CSA protonated ES form of PDMA [14]. For different weight ratio of TiO_2 the absorbance of the films were found to be varied thereby indicating the influence of TiO_2in PDMA matrix. The absorption edge at 406nm shows slight blue shift for the ratio 1:2 due to redistribution of polar density in the Band gap of PDMA emeraldine due to the presence of TiO_2 [1] A broad hump around 480nm for all the hybrid film confirms the emeraldine phase of PDMA and due to π –π transition.[15]

To determine the optical band gap, the fundamental law,

$$\alpha = A\,(E_g - h\nu)^n$$

was followed, where α is the absorption coefficient, $h\nu$ is the photon energy in eV, A is a proportionality constant and n = ½ for direct transition and n = 2 for indirect transition. By plotting $(\alpha h\nu)^n$ versus $h\nu$ for different values of n to get a linear graph from which the optical band gap of the material was noted from the extrapolation of the linear portion of the graph shown in fig 4. The optical band gap of EB, ES of PDMA and for different dopant level of TiO_2 were determined as 4.03eV, 2.92eV, 2.34 eV and 3.06 eV respectively. ES and 1:0.5 ratio film found to be of same band gap which may be due to weak interaction of TiO_2 with PDMA. Band gap found to be decreased for the weight ratio 1:1 whencompared to CSA protonated PDMA thin film.

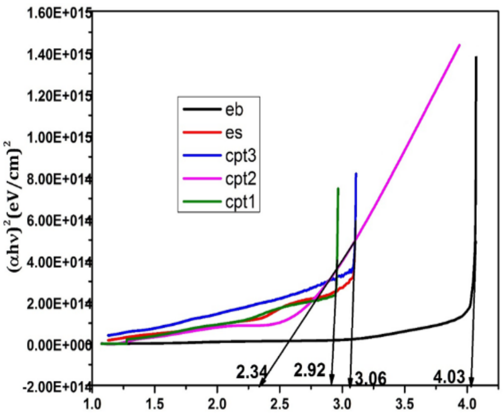

Figure 3. Band gap of Emeraldine base, Salt and CSA-PDMA/TiO_2(1:0.5,1:1,1:2)

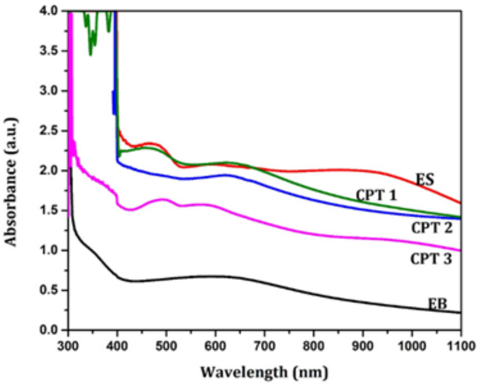

Figure 3(b). UV-Vis absorption spectra of Emeraldine base, Salt and CSA-PDMA/TiO2 (1:0.5, 1:1, 1:2)

3.3.2. Photoluminescence

The Photoluminescence spectra for the samples CPT1, CPT2, CPT3 and CPT4 are shown in the figure 5. In the present work, all the samples were excited with the excitation wavelength of 300nm. CSA PDMA/ TiO_2 films shows sharp and defined peak both in UV and visible region particularly at 360nm and 496nm which are attributed to $\pi \rightarrow \pi^*$ and polaron $\rightarrow \pi$ transition respectively [16]. A small peak observed around 410nm for all the samples with less intensity for EB and higher for higher dopant concentration may be due to protonation and TiO_2 in the polymer matrix. The occurrence of these peaks marked an impression of semiconducting nature by Shimano et al. PDMA thin films with different concentration of TiO_2 showed enhanced PL spectra which may be due to regular alignment of Benzenoid and Quinoid units which prefers the exciton generation and the extension of delocalization length of an exciton [17].

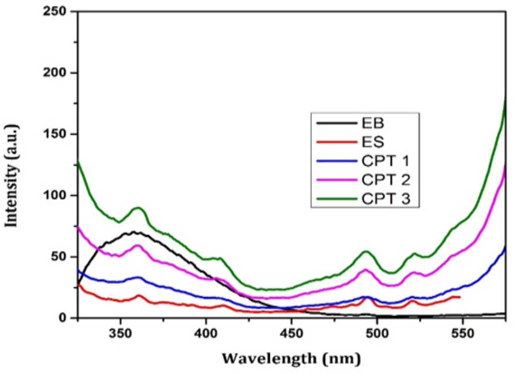

Figure 4. Photoluminescence spectra of Emeraldine base, Salt and CSA-PDMA /TiO_2 (1:0.5, 1:1, 1:2)

3.4. Functional group confirmation

Figure 6 shows the FTIR spectrum of EB, ES and CSA–PDMA/TiO_2 thin films for the wavelength range of 4000cm^{-1} to 400 cm^{-1}. The absorption peaks at 1586 cm^{-1}, 1590 $cm^{-1,}$ 1555 cm^{-1} and 1531 cm^{-1}, 1553 cm^{-1}, 1494 cm^{-1} are attributed to stretching modes of C=N, C=C for Quinoid and Benzoid rings [18]. The bands at 1230 cm^{-1}, 1202 cm^{-1}, 1243 cm^{-1} and 951 cm^{-1}, 974 cm^{-1}, 979 cm^{-1} are due to presence of –OCH_3 group of DMA[19]. The peaks observed at 1293 cm^{-1}, 1285 cm^{-1} are due to C-N stretching [20]. All hybrid films showed peaks at 1079 cm^{-1} and 1769 cm^{-1} due to stretching vibration of sulfonic and carbonyl groups of CSA [21]. Presence of band around 600 cm^{-1} and strong vibration around lower wavenumber region confirms TiO_2 anatase phase [16].

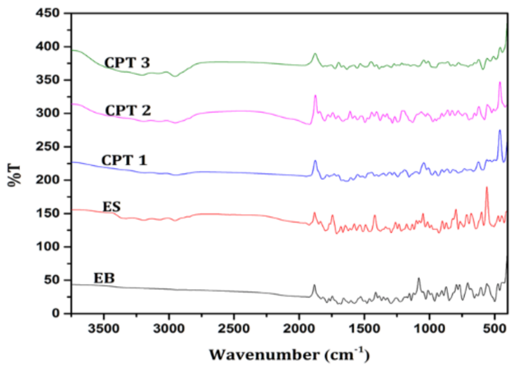

Figure 5. FTIR spectra of Emeraldine base, Salt and CSA-PDMA /TiO2 (1:0.5, 1:1, 1:2)

3.5. DC conductivity

Electrical conductivity of the pristine and doped PDMA thin film coated on a FTO substrate was measured at room temperature. The voltage, current and resistance of the thin films have been measured. The specific resistivity of the samples were calculated using the following equation,

$$\rho = RA/L$$

where R is the resistance of the thin film measured, A is the cross sectional area of the film and L is the thickness of the film. For all the films the thickness was maintained around 1μm. the DC electrical conductivity of the EB and CSA- PDMA/TiO_2 are shown in the table 1. DC conductivity of CSA-PDMA/TiO_2 hybrid thin film for the ratio 1:1 is found to be low when compared to other ratio.

Table 1

PDMA thin film	DC conductivity S/cm
EB	4.5×10^{-7}
1:0.5(TiO_2)	1.4×10^{-7}
1:1(TiO_2)	7.7×10^{-5}
1:2(TiO_2)	3×10^{-7}

Conclusion

For the first time, Camphor sulfonic acid protonated Poly (2,5-dimethoxyaniline)/TiO_2 thin films were fabricated by spin coating technique. Poly (2, 5-dimethoxyaniline) has been synthesized by oxidative polymerization and doped with different weight ratio of TiO_2 and principle investigation were carried out. From UV-Vis absorption spectra the optical band gap was calculated as 2.92eV, 2.34 eV and 3.06 eV for hybrid thin films. The crystalline nature of the CSA-PDMA / TiO_2 thin films were identified from their XRD pattern. The functional groups have been identified by FTIR spectrum. Semiconducting nature of the thin films were confirmed by the PL spectrum. The optimization of dopant level has been done by DC electrical conductivity. This material can be used as solar absorber in organic solar cells, thin film capacitor, electrodes in DSSC, gas sensors and exploring the right application may be the future work.

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