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Synthesis and Effect of TIO_2 on Electrical Conductivity of Poly (2, 5-Dimethoxyaniline)/ TIO_2 Thin Film

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Abstract: ***TiO_2 has been synthesized using Titanium isopropoxide as precursor solution. Different amount of Titanium isopropoxide of 0.2, 0.4, 0.6, 0.8 and 1 mol concentration used to synthesis TiO_2. Different mol concentration solution has been blend with Camphor sulfonic acid protonated Poly (2, 5-dimethoxyaniline) and cast as thin film by dip coating. The optical and XRD analyses were carried out for the dip coated TiO_2 thin films. The DC electrical conductivity was measured for the dip coated Camphor sulfonic acid protonated Poly (2, 5-dimethoxyaniline) /TiO_2 blend thin films. The Titanium isopropoxide of 0.6 mol concentration shows better UV-Vis absorption and crystalline nature. Camphor sulfonic acid protonated Poly (2, 5-dimethoxyaniline) /TiO_2 blend thin film of 0.6 mol concentration shows higher DC electrical conductivity when compared to other mol concentration.***

Keywords: Dip coating Poly (2, 5-dimethoxyaniline) , thin film, TiO_2, Titanium isopropoxide

I. INTRODUCTION

As simple transition metal oxide, titanium dioxide TiO_2 is a n type semiconductor employed as photo catalysis, optoelectronic devices, memory elements and in cosmetic products[1][2] . TiO_2 possess appreciable transparency, high optical constant and chemical stability [3]. Anatase and Rutile are two phases of TiO_2. The rutile phase is in stabilized state than the anatase phase for range of temperatures [4]. Though many techniques have been preferred for the TiO_2 thin films, like thermal oxidation method [5],sputtering [6], pyrolysis method [7], chemical vapor deposition (CVD) [8] sol-gel[9] is the most accepted method for its own advantageous like uncomplicated, inexpensive and time saving.

In this work TiO_2 nano particles are synthesized at different mol concentration of precursor solution using sol-gel dip coating technique to study the electrical property of proton enriched p type Poly(2,5-dimethoxyaniline) /TiO_2 blend thin film. Hybrid material holds the binary properties of organic and inorganic elements[10]. The hybrid material forms a new functional material with the advantages of both the organic and inorganic structures. The organic polymer Poly (2,5-dimethoxyaniline) (PDMA) is a derivative of Polyaniline (Pani) with methoxy group at meta and para position of Pani[11].

The prepared thin films are characterized using UV-Visible spectroscopy, FTIR to find the optimum condition for thin film coating.

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II. EXPERIMENTAL PROCEDURE

A. *Synthesis of TiO_2 nano particles*

Titanium isopropoxide (TTIP-$C_{12}H_{28}O_4Ti$) was used as precursor solution. Different amount of TTIP (0.2, 0.4, 0.6, 0.8, 1mol) was mixed with 50 ml of anhydrous ethanol (C_2H_5OH) at room temperature under vigorous stirring. After through mixing of solution, 2 ml of distilled water + HCL solution (3:1 ratio) was added. The solutions was kept under stirring for 2 hours to get clear yellow solution. After 12 hours of aging time the solution was obtain proper viscos for coating. Thin films are coated on glass substrate by dip coating for known time. Thin films were allowed for air drying and heated at 150 C for 30 min. Finally films were annealed at 450 C for 1hour.

B. Synthesis of CSA protonated PDMA/ TiO_2 blend thin film

Poly (2, 5-dimethoxyaniline) was synthesized by oxidative polymerization with DMA monomer and Ammonium peroxodisulfate (APS) in 1:1 molar ratio. DMA dissolved in aqueous solution of CSA and keeping the temperature range 0 to 5°C stirred for 30 minutes. For this pre-cooled solution an aqueous solution of APS was added drop by drop until brown color monomer turned into green color solution of CSA protonated Emeraldine Salt (ES) indicating the formation of polymer, PDMA. The solution was stirred for another 5 hours, then filtered using Whattman paper and washed with deionized water to remove the unreacted monomers. The filtered ES - PDMA was dried under open hot air condition for 2 hours. The obtained ES – PDMA was blended with as prepared TiO_2 solutions. Thin films are coated on glass substrate by dip coating method for known time and the thin films are dried under open air condition for 5 hrs.

C. Characterization Techniques

UV–Visible spectrophotometer Perkin Elmer Lambda 35 and FT-IR spectroscopy Perkin Elmer Spectrum RX-1 were used for optical analysis of the thin films. Structural analysis by XRG 3000 X-ray diffractometer (XRD).

III. RESULT AND DISCUSSION

A. UV – Visible absorbance spectroscopy

Figure. 1 shows UV – Visible absorbance spectra of TiO_2 thin films coated on glass substrates. All the films are exhibited absorption peak at 380 nm corresponding to the absorption of electrons from VB to CB of titania [12]. With increasing concentration the light absorption is changed and reaches a maximum for 0.6mol concentration. This is due to the formation of titania nanoparticles with good crystalline nature[13]. Thin film coated with 0.8 and 1mol concentration showed decreased light absorption due to the formation of larger sized Titania particles which scattered the light. Thus the increase in concentration not only increase the light absorption but also changes absorption edge towards higher wavelength which is attributed to decrease in band gap energy. Due to the influence of change in morphology of TiO_2 thin film, crystallite size of titania and structural change of TiO_2 phase showed a shift in the wavelength. The band gap value is calculated from the absorption edge and it lies around 3.3 eV which is consistent with reported value.

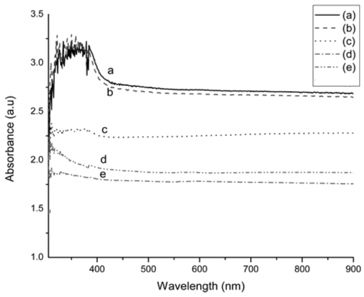

Figure. 1 UV – Visible absorbance spectra of TiO_2 thin films

B. Fourier – Transform Infra-red spectroscopy

Figure. 2 shows FT- IR spectra of synthesized TiO_2 films of different mol concentration of TTIP. The peaks below 1000 cm^{-1} are due to the Ti-O-Ti stretching and bending vibrational modes and the peak at 1614 cm^{-1} shows the presence of hydroxyl groups. The well-defined peaks about 400–800 cm^{-1} with increasing intensity with increase of the mol concentration due to direct Ti-O bonding[14].

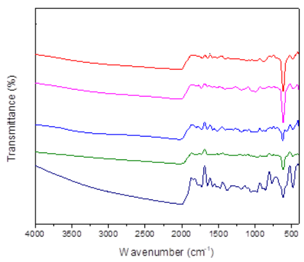

Figure 2. FT-IR spectra of synthesized TiO_2 thin films from 0.2, 0.4, 0.6, 0.8 and 1mol concentration of TTIP (top to bottom).

C. X-Ray Diffraction

Figure 3 shows XRD pattern of TiO_2 thin film. According to standard pattern (JCPDS. NO. 21-1272), the TiO_2 film has pure anatase structure with good crystalline nature. The peaks at 26.50°, 38.95°, 49.17°, 55°, 56.17°, 63.61° and 71.35° are (101), (004), (200), (105), (211), (204), and (116) planes of anatase titania respectively[15]. The crystallite size is calculated by scherr's equation D=0.9 λ / β cos (θ) at the characteristic peak 26.50° and it is found to be 24 nm.

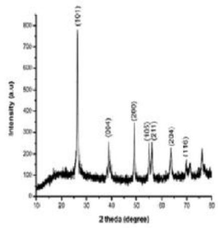

Figure 3. XRD pattern of TiO_2 thin film

D. DC electrical conductivity

Electrical conductivity of the pristine and protonated PDMA/TiO_2 thin film coated on a glass substrate was measured in room temperature. Voltage, current and resistance of the thin films have been measured. The specific resistivity of the samples was calculated using the equation $\rho = \frac{RA}{l}$ where R, A and l are the resistance measured, cross sectional area and the thickness of the film (~1 μm) respectively. The DC electrical conductivity found to be increasing with the Titanium isopropoxide mol concentration of 0.2, 0.4 and 0.6 mol. The EB PDMA shows the value of 1.45×10^{-7} S/cm. The DC electrical conductivity are found to be 2.7×10^{-7} S/cm, $3.8\ 10^{-6}$ S/cm and $5.6\ 10^{-4}$ S/cm for 0.2, 0.4 and 0.6 mol respectively. Due to the elongation of conjugation length of the polymer and the interaction of TiO_2 withdraws electron due to inductive effect on the polymer backbone leads to increase in conductivity[16][17].

IV. CONCLUSION

In the present work TiO_2 has been synthesized for different mol concentration of Titanium isopropoxide. Different mol solutions has been blend with CSA protonated PDMA and cast as thin film by dip coating. The DC electrical conductivity was measured for dip coated thin film. UV- Vis absorption spectra shows better absorption for 0.6 mol concentration and also better crystalline nature from XRD pattern analysis. The DC conductivity value found to be high for 0.6 mol concentration of TTIP.

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