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Preparation and Characterisation of PVA+TiO₂ Nanofiber by **Electrospinning Technique**

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Abstract. In the present work PVA+TiO₂ nanofibers were prepared by electrospinning technique. Structural and Functional groups were carried out by X-Ray diffraction and FTIR technique. The optical analysis was analysed by UV-DRS and Photoluminscence studies. Morphology and compositional were characterized by FESEM and EDS analysis. From Structural analysis shows PVA+TiO₂ anatase crystal structure and crystallite size are nanometers. The FTIR technique was used to find out the functional groups present in the prepared set of samples. The optical analysis shows above 70% transparency in the visible region. From the PL analysis titanium and oxygen vacancies are found to be 375 and 526 nm. FESEM analysis of the annealed samples shows the uniformity of nanofibers without any beads which is attributed to the interaction of TiO_2 particles with the PVA matrix. From the compositional analysis, the atomic weight percentage of Ti and O increases with the TiO₂ loading in PVA.

1. Introduction

Solar cells are one among the energy conversion device that can meet the requirements of future world. unlike other conventional devices DSSC has got a low cost material component, high stability, economically solar energy conversion and imperceptible negative environmental effect. Typical DSSC cell is a combination of semiconductor (TiO₂) photoanode, counter electrode and electrolyte. In a single layer DSSC anode, TiO_2 is generally used as a base material for the high photon absorptivity of the dye [1]. The properties of dye coated TiO_2 photoanode in DSSC: 1. visible light scattering effects, 2. charge trapping at grain boundaries are the promising one that exhibit low light absorption of the dye, this leads to a remarkable loss of the incident light and reduction in the power generated. Among above mentioned, development of light scattering at the photoanode is relevant for enhancing the DSSC efficiency. One dimensional material such as nano wires, nano rods, nano tubes and nano fibers differ from bulk materials due to their good electron transport and light scattering property. Nano fiber layers are better absorption in the visible light range due to light scattering effect [2]. PVA (polyvinyl alcohol) has got a very good film forming ability and certain physical properties like processibility, biocompatibility and good chemical resistance. It is a water soluble synthetic polymer, suitable for chemical cross linking due to its high density functional -OH groups. Cross linked polymer offer better chemical stability than the blend polymer. Due to its excellent physical and chemical properties PVA can be used for the fabrication of polymeric fiber. Also it is nontoxic; offer good chemical resistance ant is biocompatible [3-5]. The best method to synthesis nanofiber is electrospinning technique. The property of the fiber depends on the parameter such as type of polymer used, polymer solution concentration, viscosity, surface tension, electrical Conductivity, electrical field strength, fluid flow rate and environmental humidity [6-8]. Cost

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efficient and environment friendly nano composites can be synthesized using semi crystalline PVA as polymer matrix as it has easy processibility and optical transparency. It has many applications like air filtration, tissue engineering, water purification, textile industry, paper coating due to its flexibility and good thermal and chemical stability. In the present work $PVA+TiO_2$ nanofibers are being prepared by electro spinning technique. The electro spun nanofibers are having several advantages such as high specific surface area, small pore size, superior mechanical properties and flexibility in surface functionalities. Also it is relatively easier to fabricate and economically. It lacks elementary assembling, and is suitable step-up production for generating ultra-fine fibers which is not that easier to achieve by using other conventional fiber forming techniques [6].

2. Experimental Technique

2.1. Working of Electrospinning

PVA(Mw=80000) solutions were prepared by dissolving 1g of PVA into10ml of distilled water at 80°C, and well mixed at room temperature till clear solution is obtained and 0.025g of TiO₂ particles are added and mixed well. The solution prepared was put into a syringe for electrospinning at room temperature and solution solidified on the plate in the form nanofibrous structure. The distance between the syringe needle and collecting plate is kept at 15cm and voltage is maintained at 15kV with rate of 0.4ml/h. The process is repeated with 0.05 and 0.1g of TiO₂ keeping the distance and voltage constant. The prepared samples are annealed at 200°C for one hour. The as prepared samples with 0.025, 0.05 and 0.1g of TiO₂ with 1 g of PVA are named as A, B and C and the annealed samples are named as D, E and F. Figure 1 shows the schematic diagram of electrospinning technique [9].



2.2. Characterisation Techniques

The crystallite size and phase of the fibers were recognized by X-ray diffraction analysis by RIGAKU ULTIMA IV diffractometer with CuKα radiation wavelength of 1.541 Å. The functional groups are confirmed by FTIR using Perkin-Elmer spectrophotometer by KBr pellet technique in the range of 4000-400 cm⁻¹. The percentage of reflectance and transmission was characterized by UV-DRS spectrophotometer (UV 2600 ISR). The PL spectral measurements were carried out using a spectrometer of RF 6000. Morphology and size of as-prepared PVA nanofibers and TiO₂/PVA fibers were noticed by Field Emission Scanning Electron Microscope (FESEM) by ZEISS EGMIA.

3. Results and Discussion

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3.1. Structural Analysis

The structural analysis of as prepared PVA+TiO₂ nanofibers were studied by XRD with X-ray source of Cu-K α radiation of 1.541A° at the diffraction angle (2 θ) 10° to 90° (figure 2). It is noted that as prepared PVA+TiO₂ nanofibers with 0.025 g of TiO₂ shows amorphous nature and the 0.05 and 0.01g loaded TiO2 in PVA shows crystalline nature with tetragonal phase of TiO₂. Also the peaks corresponding to the planes (101), (004), (200) and (211) matches with the JCPDS data of anatase TiO₂ (84-1286). It is noted that the sample with 0.1g of TiO₂ loading with PVA shows three additional peaks $(2\theta = 37.76^{\circ}, 47.75^{\circ})$ and 54.86°) which is due the higher percentages of TiO₂. During Electrospinning with high electrostatic field which results that the TiO₂ nanoparticles loaded in the PVA nano-fibers maintained their crystalline structure [10]. Figure 3 depicts the XRD analysis of annealed samples. It is noted that the intensity of the peaks increases which shows the improved crystallinity during annealing process. The observed peaks, corresponding to the planes (101) and (004) matches with the JCPDS data for the anatase TiO_2 nanoparticles. The peak corresponding to the plane (004) is only seen in the 0.1g TiO₂ loaded with PVA. From the observations it is noted that PVA+TiO₂ nanocomposite fibers with and without annealing of the samples with lower loading amounts the peak corresponding to (19.8°) of PVA appeared, indicating that the presence of the nanoparticle didn't interfere in the crystallization path of the PVA phase [11]. It is observed that for the sample A with 0.025g of TiO₂ loading with PVA (with and without annealing) only a small peak for anatase appeared at $2\theta = 25.280$ but in the sample with 0.05 and 0.1 g of TiO₂ loading with PVA (with and without annealing) the peaks of anatase phase appeared clearly with maximum intensity ($2\theta = 25.28^{\circ}$) and there are no peaks corresponding to rutile phase are noted. Microstructural analysis calculated for the prominent anatase peak (101) is shown in the table 1. The average crystallite size is calculated using the Scherrer equation [12]

$$D = \frac{K\lambda}{\beta\cos\theta} \tag{1}$$

Where λ is CuK α radiation of X-rays with wavelength 1.541 Å, K is shape factor. The stress (ϵ) and the dislocation density (δ) is calculated using the equations.

$$\delta = \frac{1}{D^2} \left(\frac{lines}{m^2}\right) \tag{2}$$
$$\epsilon = \frac{\beta \cos \theta}{4} \tag{3}$$

Microstructural analysis of the as prepared $PVA+TiO_2$ is listed in the table1. It is noted that the grain size decreases with the increase in the amount of TiO_2 loading on PVA. The strain and dislocation density increases with the decrease in the crystallite size. The lattice constant 'a' is found to increase and 'c' found to be decrease when the amount of TiO2 loaded with PVA, which may be attributed to the strain subjected by the surface of the anatase material. Similar type of observations is noted for increased grain size by W. Li et al [13]. From the table 2 it is noted that the average crystallite size decreases with the increase in the loading of TiO_2 in PVA in the annealing process. When compared with the as prepared films the corresponding average crystallite size is found to decrease which may be due to the removal of defects that may occur during the deposition process. The stress and dislocation density is directly proportional and in the present case it decreases with increasing in the quantity of TiO_2 loaded in the PVA matrix. The lattice constant 'a' is found to decrease and the constant 'c' found to increase with the decrease in the crystallite size is attributed to the stress occur on the surface of the anatase structure.



Table 1: Microstructural Parameters PVA+TiO₂ nanofibers Without Annealing

Samples	2theta (deg.)	Grain Size (nm)	Dislocation Density 10 ¹⁴ (l/m ²)	Microstrain 10 ⁻⁶
А	Amor.			
В	24.9	37.71	7.0319	0.0212
С	25.1	33.19	9.0735	0.0243

Table 2: Microstructural Parameters of PVA+TiO₂ nanofibers With Annealing

Sample	2theta (deg.)	Grain Size (nm)	Dislocation Density 10 ¹⁴ (l/m ²)	Microstrain 10 ⁻⁶
D	25.2	85.60	13.647	0.0094
E	25.6	30.87	10.490	0.0266
F	25.2	37.78	7.0051	0.0214

3.2. Optical Analysis

Normally high transparency and UV- light absorption is necessary for the photo degradation. Figure 4 and 5 shows the UV- Vis transmission spectra of all the samples and it is noted that the all the samples show above 70% transparency in the visible region. This suggests that TiO₂ is homogeneously dispersed in the PVA matrix which is evident from FESEM analysis. For both the as prepared and annealed samples, the % of transmission and corresponding band gap values are gradually increased with increasing the wt% of TiO₂ in the PVA matrix. The good transparency results shown in the visible light region are due to the uniform dispersion of TiO₂ nanoparticles in the matrix. The uniform dispersion of nanoparticles into a polymer matrix is the important for successful synthesis of transparent PVA/TiO₂. Normally, the uniform dispersion is difficult due to Van der Waals forces between the nanoparticles resulting in agglomeration. The formation of hybrid nanocomposite agglomerates of the organic and inorganic nanocomposite leads to optical scattering, resulting transparency of the material [14]. The bandgap calculations for the as prepared and annealed PVA+TiO₂ composites are listed in the table 3. It is noted that the bandgap increases from 3.2 eV to 4.31 eV and 2.48 eV to 4.07 eV for as deposited and annealed samples. The absorbance that appeared at energies below the band gap energy is attributed

to the result of interference fringes [15]. The reflectance is converted into Kubelka-munk function by analyzing the reflectance spectra using Kubelka-Munk relation (equivalent to the absorption coefficient), $F(R\alpha)$, given below [16]

$$F(R_{\alpha}) = \left(\frac{(1-R_{\alpha})^2}{2R_{\alpha}}\right) \tag{4}$$

 $R\alpha$ indicates the reflectance at each wavelength of infinitely thick samples, with respect to the reference. Bandgap energies of the prepared samples were calculated from the variation of the Kubelka-Munk function with photon energy. The transition was also found to be direct (figures 6 to 11).



Figure 4. UV Transmission Spectra PVA+TiO₂ nanofibers without annealing

Figure 5. UV Transmission Spectra of PVA+TiO₂ nanofibers with annealing



Figure 6. Optical Direct Band gap of PVA+TiO₂ nanofibers for the Sample A

Figure 7. Optical Direct BandFigure gapgap of PVA+TiO2 nanofibersgapfor the Sample Bfor the

Figure 8. Optical Direct Band gap of PVA+TiO₂ nanofibers for the Sample C



Without Annealing			With Anne	With Annealing		
Samples	% of Transmission	Band gap values (eV)	Samples	% of Transmission	Band gap Values (eV)	
А	70.66	3.26eV	D	80.66	2.48eV	
В	81.22	3.8eV	E	84.16	3.8eV	
С	87.11	4.31eV	F	97.08	4.07eV	

Table 3. Optical Direct Bandgap values of PVA+TiO₂ nanofibers with and without Annealing

3.3. Functional Group Analysis

Figure 12 shows the FTIR spectra of $PVA+TiO_2$ nanofibers for different concentration. The wideband at 3336 cm⁻¹ which are attributed to symmetric stretching vibrations of a single-bond functional group of OH bond. The peaks observed at 2900 and 2200 cm⁻¹ indicate the CH antisymmetric and symmetric stretching and C=C stretching vibration. The strong peaks between from 1900 – 1700 cm⁻¹ is due to the Bending vibrations of the hydroxyl functional group (H–O–H). A strong peak around 438 cm⁻¹ corresponds to the Ti–O–Ti bonding [16].



3.4. Photoluminscence Analysis

The PL spectra can be used for perceptive the electronic structure of nanocomposite materials, the transfer nature of the photoexcited electron-hole pairs in semiconductors and the rate of recombination [17 - 19]. Figure 13 and 14 shows the PL spectrum of PVA-TiO₂ of as prepared and annealed. From the PL studies, the wavelength at 375 nm shows that the excitonic emission band and the peaks at 466nm and 526 nm are due to O₂⁻ vacancies. The initial peak in the PL spectra between 320–400 nm represents the recombination between electrons in the conduction band and holes in the valence band. Therefore, the hybrid samples show shift in the higher wavelength region of the absorption edge. The strong PL spectrum of TiO₂ shows that the oxygen vacancies, related to the kex = Eg, occurs from bound free excitons and impurity-related centers. The band for kex\Eg may be free excitons, and the shift with variation of excitation energy is due to the change in clusters size. Therefore, the crystallite size has an enormous issue on the peak of the PL intensity, because of the interaction of TiO₂ particles with the PVA matrix. The observations made are: 1.as the particle size decreases the band gap seen to be increasing, 2.the absorption shift is observed to move towards a higher energy (blue shift) as the crystallite size decreases. The blue shift absorption position from the bulk TiO₂ samples can be due to the direct transition of electrons to the TiO₂ hybrid composites [20].



3.5. Morphological Analysis

Figure 14 to 16 shows the FESEM images of the PVA+TiO₂ by varying the amount of TiO₂ to 0.05 and 0.1 gram with annealed samples. It is noted that the sample E and F shows the fibrous structure and there is no agglomeration that shows that TiO₂ nanoparticles are well dispersed in the PVA matrix. The presence of PVA causes to decrease the solution's viscosity, and then it forms thinner nanofibers. Beads on the nanofiber decrease by adding TiO₂ nanoparticles into the electrospun solution and diameter of nanofiber also decreases but not significant. It happened because by loading TiO₂ nanoparticles into the electrospun solution, viscosity, and conductivity of electrospun solution increases [21]. Most of the samples maintained cross-sectional uniformity throughout their length. It can be seen that the morphology was similar in each sample. From the samples E and F, there is no bead, probably due to some instability in the initial drop caused by the large loading amounts. It was not possible to determine the length of fibers, but apparently they were in the order of microns. Also, there wasn't visual segregation of phases, probably indicating a good distribution of the loaded TiO₂ nanoparticles [11].

Image:	2m Bf = 100 W BmB to +272 Sgw4 A 5E2 De 310x297 2m Bf = 100 W BmB to +272 Sgw4 A 5E2 De 310x297	Pire Birl - 18.0V VD - 8.8m Res/Rs 5273 Birls - 5273 Dec 8.ax 784 Mg + 558.33 Tm + 1539
Figure 14. FESEM Images of PVA+TiO ₂ nanofibers for the Sample D	Figure 15. FESEM Images of PVA+TiO ₂ nanofibers for the Sample E	Figure 16. FESEM Images of PVA+TiO ₂ nanofibers for the Sample F



Table 4. Average Diameter	values of PVA+TiO ₂ nano	fibers for the sample D, E and F
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Samples	Beads	TiO ₂	Avg. diameter
		(g)	(nm)
Sample D	No	0.025	109
Sample E	No	0.05	347
Sample F	No	0.1	352

The average of resulting PVA nanofibers for Sample E and F was 347.38 nm and 352.35 nm (Figures 17 to 19). From the above figures and table 4 the diameter of nanofiber decreases as the concentration of TiO₂ solution with PVA decreases (i.e.) the higher concentration of the solution tends to increases the diameter, this concentration of TiO₂ solution is very low, the polymer chains may not aggregate enough to construct stable nanofiber. However, TiO₂ nanoparticles show well distribution in PVA nanofiber matrix. From the histograms, the diameter is found to be in the range in the range of 200 to 400 in Sample F for 0.1g is higher than that of the Sample E (0.05g). However, TiO₂ nanoparticles show well distribution in PVA nanofibrous matrix. The reasons of TiO₂ nanoparticles without coagulation in the matrix may be (1) interaction between PVA and TiO₂ nanoparticles and (2) strong electric field during electrospinning. The interaction caused by hydrogen bonding between hydroxide groups in PVA and oxygen in TiO₂ may avoids the aggregation of TiO₂ nanoparticles. Nanoparticles pulled by strong electric field can be sprayed evenly on collecting plate, because of strong shear stress [20].

3.6. Compositional Analysis



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Compositional analysis shows that the atomic weight percentage of TiO_2 in the prepared samples. Figures 20 to 22 shows that EDS profile of PVA+ TiO_2 . From the results it is noted that TiO_2 nanoparticles were loaded onto the PVA surface and was dispersed linearly along the fiber direction, which is generated as a result of polarization and orientation caused by the high electric field during electrospinning method. It is concluded that TiO_2 nano-particles were successfully loaded into the PVA nanofibers.

4. Conclusion

In the present work TiO₂ nanofibers with uniform diameters were successfully obtained from as prepared electrospun TiO₂/PVA composite nanofibers and annealed nanofibers at 200°C for 1 hr. Structural analysis shows that The structure of the PVA+TiO₂ composite shows tetragonal with the planes (101), (004), (200) and (211) matches with the JCPDS data (84-1286). There are no peaks corresponding to rutile phase are noted. This result confirmed that even in the high electrostatic field used during electrospinning also TiO₂ nano-particles loaded in the PVA nano-fibers retained their crystalline structure. From the UV-Vis transmission spectra we can conclude that, the good transparency results shown in the visible light region are due to the uniform dispersion of TiO₂ nanoparticles in the matrix. Particle size has a great effect on the intensities of the photoluminescence peak, due to the interaction of TiO_2 particles with the PVA matrix. We can conclude that the particle size is inversely proportional to band gap and it is found that the absorption edge is shifted to the blue shift region. Morphological analysis of samples by varying the amount of TiO₂ shown fibrous structure in the diameter range of 200-400nm. Samples maintained cross sectional uniformity and smooth nature throughout their length. From the compositional analysis also concluded that TiO2 nano particles were successfully loaded into the PVA nano fibers. In this present work, an attempt has been made for the developing of TiO₂ photoanode for DSSC by varying the concentration of TiO₂. The thriving claim for energy in the near future is confront with the help of DSSC materials which are inexpensive and also ecofriendly.

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