Structural, Optical, Functional, Morphological and Compositional Analysis of Ni-doped TiO2 Nanofibers Prepared by Electrospinning Technique

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Abstract. In the present work, three different concentration of Nickel is doped with TiO2/PVA nanofibers by electrospinning method which can be used as photoanode in DSSC applications. The samples are annealed at 200°C for one hour. XRD results show the anatase phase of the prepared samples. FESEM images of different concentration of nanofibers show that diameter of nanofibers depends on the concentration of Ni. Large concentrations of nanofibers show fewer diameters of nanofibers. The EDX spectrum clearly confirmed that the TiO2 composite nanofibers are consists of nickel, titanium and oxygen elements. From UV-DRS studies, redshift is observed with the increase in dopant concentration. The transitions are direct and indirect allowed and the calculated bandgap finds to be decreasing with increase in dopant concentration. PL spectra of Ni-doped samples show less intensity, which indicates the low recombination rate and intensity decreases with increase in dopant concentration. It is concluded that Ni is doped with TiO2/PVA gives better energy conversion efficiency in DSSC compare to undoped TiO2.

1. Introduction
DSSC, a third generation solar cells have many advantages compared to convention devices such as low-cost material, high stability, negligible negative environmental effect and ability to work at wider angles and low light [1]. TiO2 nanoparticle coated with dye shows, low light adsorption, due to the scattered effects and charge trapping at grain boundaries. These results in the very slow transportation rate of photoelectrons through the TiO2 nanoparticle that leads to low efficiency. The efficiency of DSSC will be enhanced by improving the light scattering of photoanode [2] and it can be attained by increasing the specific surface area and porosity of TiO2 nanoparticles, which results in the expansion of the contact area between the adsorbed surface area of dye and solar power. One of the methods to improve the efficiency of DSSC is using a one-dimensional material such as nanowires, nanorods, nanotubes and nanofibers which have many advantages like good light scattering and electron transportation rate [3]. Also, photoanodes with suitable dopants (metals or non-metals ions) can be used, which can provide additional reactive part on the surface, for the adsorption of the dye molecule, for better light absorption by reducing the band gap, improving the charge carrier collection in the conduction band [4]. According to literature survey, Ni-doped TiO2 nanofibers, the resistance of charge transport is very low, recombination rate is low and enhances electron lifetime compared to the undoped nanofibers. Also, DSSC with Ni-doped TiO2 nanofibers show enhanced efficiency, short-circuit current density and charge mobility more than undoped nanofibers [5]. In the present work Nickel (Ni) doped TiO2 nanofibers are prepared at the different amount (0.2, 0.5 and 0.8g) of nickel by electrospinning technique [6-8] and the structural, optical, morphological characteristics are analyzed to find its suitability as
photoanode in DSSC. Large surface area to volume ratio, large surface area, and small pore size, greater mechanical properties and adaptability in surface functionalities are advantages of electrospinning techniques. Therefore electrospinning technique is used for preparing nanofibers.

2. Experimental

2.1. Preparation of TiO$_2$ Nanofibers
Poly (vinyl alcohol) (PVA, 86.09 g/mol) and Nickel Nitrate hexahydrate purchased from NICE chemicals and TiO$_2$ from Hi-Media and Double deionized water is used for the preparation of nanofibers. All these materials were used without any further purification. Polyvinyl alcohol (PVA) solutions were prepared by dissolving 1g of PVA (Mw=8000) into 10ml of distilled water and stirred at 50°C for 4 hours. TiO$_2$/PVA nanoparticle solution was prepared by adding 0.05g of TiO$_2$ into PVA solution and stirred at room temperature for one hour. Different concentration of Ni-doped TiO$_2$/PVA nanoparticle is prepared by adding 0.2g (sample 1), 0.5g (sample 2) and 0.8g (sample 3) of nickel nitrate (Ni(NO$_3$)$_2$) to TiO$_2$/PVA and stirred for 4hrs at room temperature. The solution prepared was put into a syringe for electrospinning (as shown in figure 1 [9]) 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 a flow rate of 0.4ml/h. The prepared samples are annealed at 200°C for one hour.

2.2. Characterisation Techniques
The samples were subjected to Powder X-ray diffraction analysis using Shimadzu XRD 6000 diffractometer with CuK$_\alpha$ radiation of wavelength 1.541 Å. The functional group was analyzed by FTIR using Perkin-Elmer spectrometer by KBr pellet technique in the range of 4000-400 cm$^{-1}$. The percentage of reflectance was characterized by UV-DRS spectrophotometer (UV 2600 ISR). The morphology and compositional analysis of the prepared samples are assessed by Field Emission Scanning Electron microscopy (FESEM – ZEISS EGIMA). The Photoluminescence (PL) measurement were carried out using a spectrophotometer of RF 6000.

3. Results and Discussion

3.1. Structural Analysis
XRD spectra (figure 2) of different concentration of Ni-doped TiO$_2$ nanofibers were observed in the 20 range from 100 to 900. The peaks viewed at 25.40 and 48.20 were assigned to (101) and (200) plane of TiO$_2$ anatase phase with the tetragonal structure (JCPDS card no. 04-0850). For differently doped samples showed the minor shifts in the peak position and broadening of peaks is noticed in the diffraction spectra and allowed to the anatase phase of TiO$_2$. The substitution of Ni$^{2+}$ for Ti$^{4+}$ results in
peak shift in the XRD showing the formation of solid solution between the dopant and the host matrix. As a result of the average crystallite size and strain affected by doping. [10]

The average crystallite size of doped TiO$_2$ nanoparticles are determined using the Scherrer equation [11]

$$D = \frac{K \lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

Where $\lambda$ is CuKα radiation of X-rays with wavelength 1.541 Å, K is shape factor. The stress ($\varepsilon$) and the dislocation density ($\delta$) is calculated using the equations [11]

$$\delta = \frac{1}{D^2} \left( \frac{\text{lines}}{\text{m}^2} \right)$$  \hspace{1cm} (2)

$$\varepsilon = \frac{\beta \cos \theta}{4}$$  \hspace{1cm} (3)

Microstructural parameters are shown in table 1. It is noted that the average crystallite size improves when the concentration of the Ni increases and the decreased FWHM shows the improved crystallinity of the doped samples. This is attributed to substitution of the higher ionic radius of the Ni$^{2+}$(0.79Å) in the place smaller radius of the Ti$^{4+}$(0.605 Å). The grain size and the dislocation density are inversely proportional and in the present study, it reduces with the increase in the crystallite size. It is concluded that the crystallite size increases with the Ni concentration and the defects such as strain and dislocation density decreases. The variation in the c/a ratio confirms the incorporation of dopant with the TiO$_2$ lattice. It is noted that the values increases and the c value decreases and then increases when the amount of Ni dopant increases which shows that the nonuniform expansion with respect to c axis of the unit cell. It is due to the fact the there is the more directional substitution of dopant atoms in one axis than in the other axis [12].

![Figure 2. XRD Pattern of Ni-TiO$_2$ nanofibers for different concentration](image-url)
Table 1: Microstructural Parameters of Ni doped TiO$_2$ nanofibers at different concentration

| Samples  | Average Crystallite Size (nm) | Lattice constant | Dislocation Density ($\times 10^{15}$ lines/m$^2$) | Microstrain |
|----------|-------------------------------|------------------|----------------------------------|-------------|
| Sample 1 | 5                             | a= 3.772         | 3.99                             | 0.1622      |
|          |                               | b= 9.794         |                                  |             |
| Sample 2 | 27                            | a=3.7732         | 1.37                             | 0.0304      |
|          |                               | b= 9.425         |                                  |             |
| Sample 3 | 13                            | a=3.7754         | 0.69                             | 0.0214      |
|          |                               | b=9.617          |                                  |             |

3.2. Optical Analysis

The change in the properties of the doped TiO$_2$ is, because of two causes (1) capacity to absorb lesser energy photons to create larger recombination rate. This process is helped by the introduction of further energy levels, by the dopant ions below the conduction band and/or above the valence band. (2) Reduction in different PL peak intensities which leads to a reduction in recombination loss of produced electron-hole pair. The properties of a sample, compared to excitation of electrons throughout the bandgap are determined firstly by the electronic structure of lower states of the conduction band and upper states of the valence band. The anatase phase of the TiO$_2$ is a wide bandgap semiconductor with bandgap energy of 3.2eV. Based on the theoretical calculations [13] the lower states of the TiO$_2$ conduction band arises from the 3d orbital of titanium and valence states from 2p orbitals of the oxygen atom. In the case of Ni-doped TiO$_2$ nanofibers, the electron densities around the dopant are large in the valence band and less in the conduction band as compared with undoped sample [14].

![Figure 3. % of Reflectance of Ni-TiO$_2$ nanofibers for different concentration.](image-url)
The optical reflectance properties of the prepared samples are deliberated by UV-DRS which is shown in the figure 3. The reflectance is observed at 480, 310 and 320 nm for sample 1, 2 and 3. A redshift is noticed with increase in the concentration of Ni. The main reason for redshift is resulting from the change of s p-d exchange interaction between band electrons and localized d-electrons of the Ni$^{2+}$ ions. Kubelka-Munk relation is used for analyzing the reflectance spectra. This relation to converting the reflectance into a Kubelka-Munk function (equivalent to the absorption coefficient), F(R$_\alpha$), using the relation[11]:

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

Where R$_\alpha$ is the reflectance, with respect to each wavelength. Bandgap energies of the prepared samples were calculated from the change of the Kubelka-Munk function with photon energy and the transition are found to be both direct and indirect. The direct and indirect bandgap was decreased with increase in the concentration of dopant. This can be assigned to the introduction of new electron states in the band structure of Ni-doped TiO$_2$ nanofibers [15]. In this work, Ni-doped samples at different amount of doping show 4.2 to 3.5eV for direct transitions and 4.1 to 2.75 eV for indirect transitions [figure. 4 to 9 and table 2]. Similar observations are noted for Ni-doped TiO$_2$ samples [16]. Also, a large change in the optical gap for TiO$_2$ films prepared by Sol-gel technique is also noted by Yen et al. [17]. The decrease in the bandgap is due to increase in the concentration of Ni doping leads to in the valance band delocalized electrons are found, thus significantly adding to the p and 3d electrons into valance band, which results a less reduction of the bandgap in Ni-doped samples [15, 18].
### Table 2. Optical Bandgap values of Ni-TiO$_2$ nanofibers for Different concentration

| Samples  | Direct Band Gap (eV) | Indirect band Gap (eV) |
|----------|----------------------|------------------------|
| Sample 1 | 4.2                  | 4.1                    |
| Sample 2 | 3.6                  | 3.25                   |
| Sample 3 | 3.5                  | 2.004, 2.75            |

#### 3.3. Functional Group Analysis

Figure 10 shows the FTIR spectra of Ni-doped 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 [19]. 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 [20].

![Figure 10. FTIR Spectra of Ni-TiO$_2$ nanofibers for different concentration](image)

#### 3.4. Photoluminescence Analysis

The Photoluminescence (PL) spectra of doped samples excited at 320 nm are shown in the figure 11 to 13. The resolved peaks at 377, 467, 490, 494, 517 and 543 nm showed the wide emission spectra have been founded in the PL spectra of different concentration of Ni-doped samples. Due to Ni doping the PL peaks are found at 517 and 543 nm, this demonstrates the two peaks at 494 and 543 nm are achieved while peaks at 377, 467 and 490 nm are eliminated as a conclusion of Ni-doped samples. Band edge luminous of the TiO$_2$ particle can be founded from the high energy peaks, oxygen vacancies can be allowed by low energy peaks [13, 21]. If oxygen vacancy is more, the recombination rate will be high. Less intensity indicates the low recombination rate. Where the incorporation of Ni in TiO$_2$ nanofibers leads to drastically decreased the PL intensity [22]. From PL studies get the change in recombination processes due to Ni doping [10].
3.5. Morphological Analysis

Figure 14 to 16 shows the FESEM images of Ni-TiO$_2$ nanofibers after annealed for one hour at 200°C. The morphology of the as-spun Ni-TiO$_2$/PVA nanofibers after annealed at 200 °C for 1 h is noticed to be even and uniform with the average diameter of sample 1 (0.2 g of Ni-doped TiO$_2$ nanofibers) is 426 nm, sample 2 (0.5 g of Ni-doped TiO$_2$ nanofibers) is 226 nm and sample 3(0.8 g of Ni-doped TiO$_2$ nanofibers) is 170 nm. The Ni-doped TiO$_2$ nanofibers showed a surface free from roughness and uniform diameter. The reasonable diameter reduction could be assigned to the decay of the precursor and degeneration of polymer. Due to the densification of the morphology outward of nanofibers will extend the incorporation of NPs. Differently, there was no such projection was showed in the case of Ni-doped TiO$_2$/PVA nanofibers after calcination process. So, we can clearly understand that these projections are due to the addition of Ni in the prepared sample. According to FESEM images, Ni-doped nanofibers range the diameter of 0.2 g of Ni-doped TiO$_2$ nanofibers is large.0.5 g of Ni-doped TiO$_2$ nanofibers diameter compare to 0.2 g of Ni-doped TiO$_2$ nanofibers is less and 0.8 g of Ni-doped TiO$_2$ nanofibers is very less compare to others. The diameter of nanofibers depends on the concentration of Ni. A large concentration of nanofibers indicates the fewer diameters of nanofibers.

3.6. Compositional Analysis

Figure 17-19 shows the energy dispersive X-ray spectroscopy (EDX) analysis of annealed Ni-TiO$_2$ nanofibers. The EDX spectrum certainly concluded that the Ni-doped TiO$_2$ samples contain nickel,
titanium and oxygen elements, as shown in figure 20. This result proved the successful mixing of nickel with TiO$_2$ nanofibers that give a good accordance with that of XRD data.

**Figure 17.** EDS Spectrum of Ni-TiO$_2$ Nanofibers for the Sample 1

**Figure 18.** EDS Spectrum of Ni-TiO$_2$ Nanofibers for the Sample 2

**Figure 19.** EDS Spectrum of Ni-TiO$_2$ Nanofibers for the Sample 3

**Figure 20.** Atomic Wt. % of Ni-TiO$_2$ Nanofibers for different concentration

4. Conclusion

For Dye-Sensitized Solar Cells (DSSC) application, highly efficient photoanode based on nickel doped TiO$_2$/PVA nanofibers was synthesized by electrospinning method. The sample was annealed at 200°C. The effect of Ni on the morphology, crystal structure, compositional analysis and optical behavior of TiO$_2$ nanofibers were studied by several advanced techniques. XRD shows the anatase phase and grain size increases with decrease dislocation density. The FESEM images exhibit Ni-doped TiO$_2$ nanofibers with a surface free from roughness and uniform diameters. The diameter of nanofibers depends on the concentration of Ni. A large concentration of nanofibers indicates the fewer diameters of nanofibers. The EDX spectrum certainly concluded that the Ni-doped TiO$_2$ nanofibers are contained nickel, titanium and oxygen elements. The reflectance is observed at 480 nm for 0.2 g of Ni-doped TiO$_2$ nanofibers, 320nm for 0.5 g of Ni-doped TiO$_2$ nanofibers and 480nm for 0.8 g of TiO$_2$ nanofibers from UV-DRS studies. A redshift is observed with the increase in dopant concentration. The direct and indirect bandgap finds decreasing with increase in dopant concentration. This can be assigned to the introduction of new
electron states in the band structure of Ni doped TiO$_2$ nanofibers. The resolved peaks at 377, 393, 419, 494 and 543 nm showed the wide emission spectra have been founded in the PL spectra of different concentration of Ni-doped samples. Less intensity indicates the low recombination rate and intensity decreases with increase in dopant concentration. From PL studies get the change in recombination processes due to Ni doping. Accordingly, incorporation of TiO$_2$ nanofibers by nickel can be considered a productive action to increase the efficiency of DSSC.

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