Effect of various types of Dyes and N-doping in supporting performance of TiO_2 based Dye Sensitized Solar Cells

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Abstract

Dye Sensitised Solar Cell (DSSC) have piqued both practical and theoretical attention since they emerged as low-cost alternative to conventional silicon based solar cell [1][2]. TiO_2 nanoparticles are abundant, stable, and nontoxic and they are widely employed for a variety of applications [3]. The band gap of TiO_2 is determined to be about 3.2 eV for the anatase phase, which restricts the visible light absorption. Here we have analysed the absorption spectra for the pure TiO_2 and compared it with that of N-doped TiO_2 using a UV-visible spectrophotometer. Absorption spectra were also observed for composites of TiO_2 made by varying the concentration of Nitrogen [7]. Synthesis of TiO_2 and N-doped TiO_2 was done using Sol-gel method [4][5][6]. Particle size for TiO_2 was confirmed using X-Ray Diffraction.

It was observed that Nitrogen doping reduces the band gap leading to increase in the absorption of light in visible range. Further studies were carried out by adding four different Azo dyes as a sensitizer for N-doped TiO_2. I-V Characterizations of the samples was examined to determine their effectiveness. The best result was found with Methylene Blue.

Keywords: *Dye Sensitised Solar Cell (DSSC), Azo Dye, TiO_2 Nano-particles, N-doped TiO_2, Energy band gap.*

Introduction:

O'Regan and Grätzel reported that the Dye-Synthesized Solar Cell (DSSC) is a promising alternative to silicon and multi-junction solar cells [8]. DSSC is a device that converts photons into electrons [1][9]. The Dye used as a photosensitizer has a significant impact on the DSSC's performance [10]. This is because it absorbs lighter than TiO_2 alone and converts photons to electrons, resulting in a higher photon to electron conversion efficiency [7].

The advantages of Azo dyes include their availability and low cost. For a dye to efficiently convert light to electricity in DSSC, the Lowest Unoccupied Molecular Orbital (LUMO) must have a more negative potential than TiO_2's conduction band edge, allowing the injection process to be thermodynamically favorable. Furthermore, the dye must be in a good electrical and chemical contact with TiO_2 for electron injection to be efficient. The Highest Occupied Molecular Orbital (HOMO) of the dye must be more positive. Finally, the band gap of the dye must be as small as possible [2][11][12].

Experimental:

Synthesis of TiO_2 and Nitrogen doped TiO_2 Nanoparticles by Sol-Gel method

By using the Sol-Gel method, we have prepared samples of TiO_2 nanoparticles, pure TiO_2 and Nitrogen doped TiO_2[4][6][13]. Four different Azo dyes were obtained from Loba Chemicals: Methyl Orange, Methylene Blue, Eriochrome Black T and Alizarin Red. Titanium butoxide ($C_{16}H_{36}O_4Ti$) precursor used for TiO_2 nanoparticles synthesis, Ethanol (C_2H_5OH), De-ionized water, and Nitric acid (HNO_3) are taken in the ratio 1/20/0.5/0.1 respectively [13]. It was maintained at 450ºC for annealing. N-doped TiO_2 is obtained using TiO_2 nanoparticles and Tri-ethylamine (Nitrogen source) taken in equal ratios. Composites were also prepared with TiO_2 and 4 different Azo dyes taken in a ratio of 1:1 and also N-doped TiO_2 with Azo dyes taken in a ratio of 1:1.

Characterization of the Composites

Size of the TiO_2 Nanoparticles using XRD

X-Ray Powder Diffraction (XRD) patterns for the pure TiO_2 sample were collected and the crystal size of samples was calculated from peak broadening by the Scherrer equation.

Absorption Spectra of the composites

The absorption Spectra was studied using UV visible spectrophotometer first with pure TiO_2 and N-doped TiO_2, composites of TiO_2 with all four dyes taken in the ratio of 1:1, composites of N-Doped TiO_2 with all four dyes taken in ratio 1:1.

Result and Discussion:

X-Ray Diffraction (XRD)

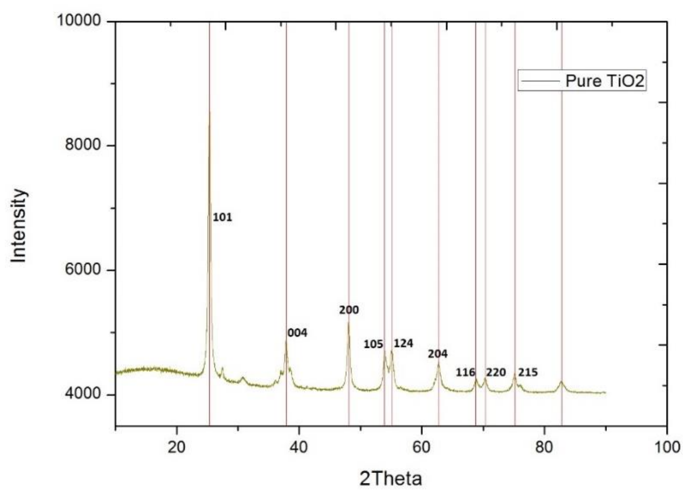

***Fig. 1**: XRD of Pure TiO_2*

Figure 1 shows the X-Ray Diffraction pattern of Pure TiO_2. Diffraction peaks of Pure TiO_2 were obtained at 25.320, 37.870, 48.0560, 53.910, 55.080, 62.70, 68.760, 70.310, and 75.120. These can be assigned to crystal planes (101), (004), (200), (105), (211), (204), (116), (220) and (215) that correspond to the anatase phase of titania and agree with JCPDS card np.21-1272.

The average crystalline particle size is calculated by applying Sherer expressions in equation (1)

$$D = \frac{0.9\,\lambda}{\beta . COS\theta} - - - - (1)$$

Sample	2θ	FWHM (Full Width Half Maxima)	Average particle size(nm)
Pure TiO_2	25.302	0.6177	13

Table 1: *The average particle size of the sample*

The λ is X-Ray wavelength of 1.5406 Å of Cu kα radiation. β is the line broadening at maximum intensity (FWHM) and θ is the Bragg angle. The particle size is recorded in the table.

UV-Visible Spectroscopy

The Optical measurement was made using UV-VIS Spectrophotometer for the dyes and the composites of dyes with Pure TiO_2 and N-doped TiO_2 for the mixing ratio (1:1). The absorption Spectra showed the presence of distinct absorption peaks in the visible region for each type of dye.

Image1: *Azo Dyes At 1000 PPM*

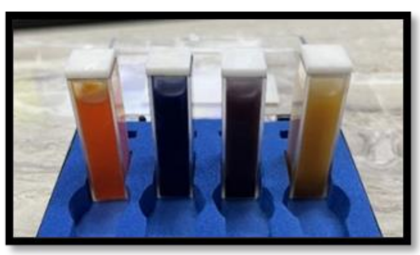

***Image2**: Dyes with Pure* TiO_2

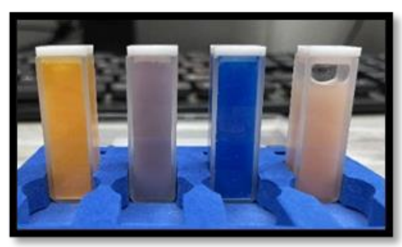

Image3: *Dyes with N-Doped* TiO_2

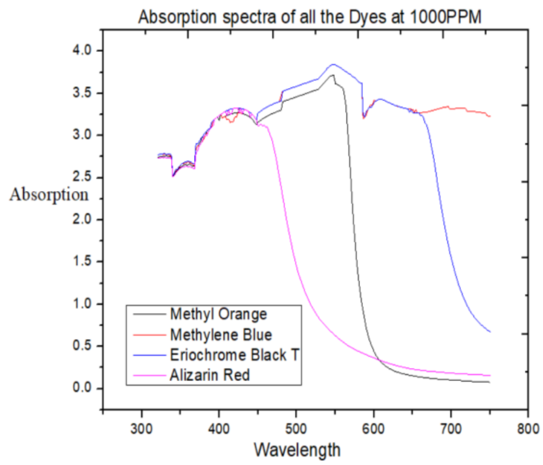

Fig.2: Absorption Specta of all the 4 dyes

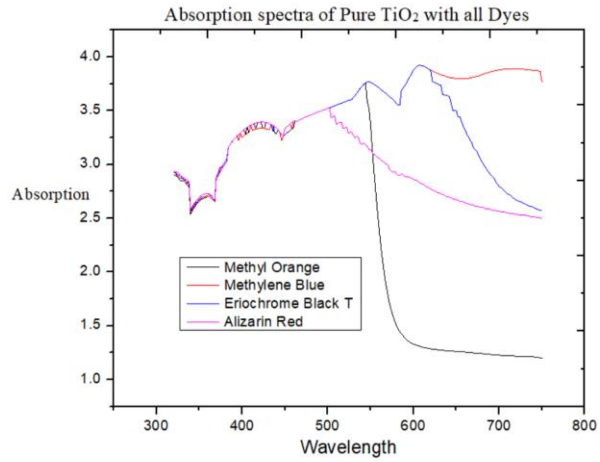

Fig.3: Absorption Spectra of Pure TiO_2 with all 4 dyes (1:1 Ratio)

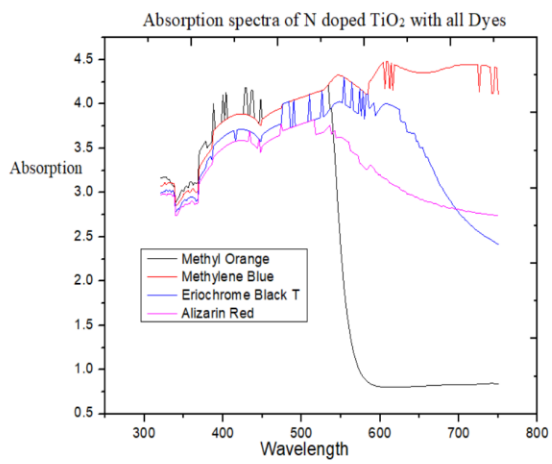

Fig.4: Absorption Spectra of N-doped TiO_2 with all 4 dyes (1:1 Ratio)

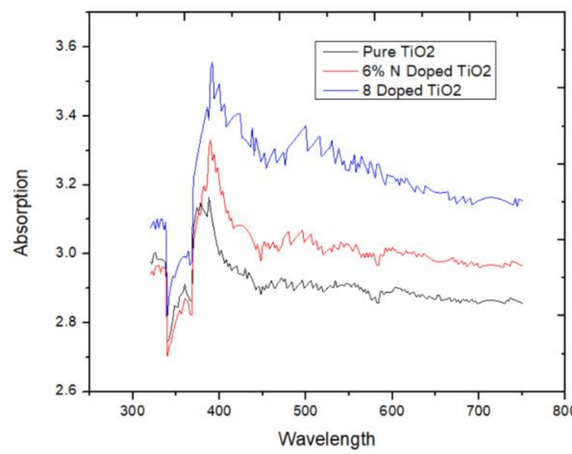

Fig.5: Absorption Spectra of Pure TiO_2 and N-doped TiO_2

It is evident from the characterization that as nitrogen is introduced, the absorbance edge shifts, resulting in a smaller band gap. As a result, the N-doped TiO_2 sample had a greater absorption of visible light. Similarly, narrowing the band gap of TiO_2 leads to less charge recombination as compared to pure TiO_2. Using the Kubelka-Munk formula[14] from equation (2), UV-Visible Spectra are transformed into Tauc plots to determine the band gap of the doped sample.

$$\alpha h\nu = A(h\nu - E_g)^2 ----(2)$$

where α is absorbance coefficient, h is the Plank's constant ($4.136*10^{-15}$eV), A is constant (~1), ν is frequency and E_g is band gap.

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Band Gap

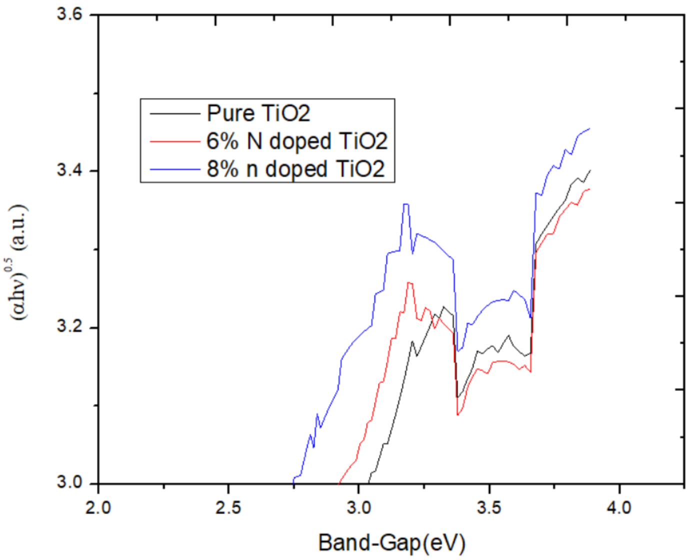

Fig. 6: *Band-Gap of Pure and N-doped TiO_2*

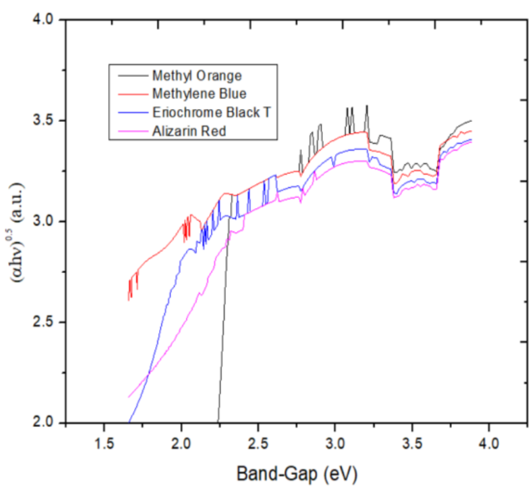

Fig.7: *Bandgap of Pure TiO_2 with all 4 Dyes*

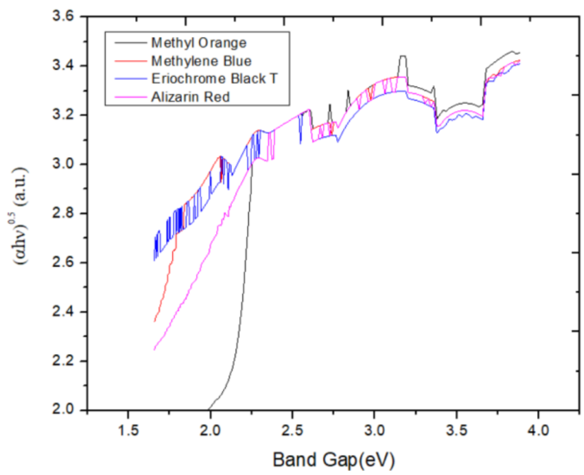

Fig.8: *Bandgap of 8% N-doped TiO_2 with all 4 Dyes*

Sample	Band Gap (eV)
Pure TiO_2	3.05
6% doped TiO_2	2.92
8% doped TiO_2	2.73
8% doped TiO_2 with Methylene Blue	1.63

Table 2: *Bandgap energy for all samples*

Figure 6 shows the narrowing of the band-gap for N-doped TiO_2. Figure 7 and 8 show that TiO_2 with all the four dyes has enhanced absorption in visible region and narrowed band-gap maximum absorption was observed for Methylene Blue.

Conclusion:

By examining the optical characteristics, it is observed that composites of dye with pure TiO_2 and N-doped TiO_2 enhance the performance of DSSC. Doping of TiO_2 with Nitrogen lowered its band gap. The composite of N-doped TiO_2 with Methylene Blue was found to have maximum absorption.

Conflict of Interest:

The authors declared that they have no conflict of interest.

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