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Research Article

Role of fluorine doping on the electron transport layer of F-doped TiO_2 (Titanium dioxide) for photovoltaic systems and its environmental impact

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Abstract
Photovoltaic (PV) systems are regarded as clean and sustainable energy sources and exhibit minimal pollution during their lifetime. The production of hazardous contaminants contaminating water resources, emissions of air pollutants during the manufacturing process, and the impact of PV installations on land use are important environmental factors to consider. The present study aimed to synthesise the F-doped Titanium dioxide (TiO_2) thin films on a glass substrate employing spin coating followed by the sol-gel process ETL application purpose. Fluorine-doped TiO_2 thin films were prepared using the sol-gel spin coating technique. The X-ray diffraction (XRD) results confirmed that the most intense peak was observed at 25.37° corresponding to the crystallographic plane (101) for anatase TiO_2. The average transparency of TiO_2 was increased by adding the doping level of fluorine and increment in the optical bandgap. The thickness of the thin film was kept at about 300 nm. The resistance of nanocrystalline thin films of different F doped TiO_2 was decreased from $1.322\times10^{12}\ \Omega$, $9.728\times10^{11}\ \Omega$, as the F doping concentration was increased from pristine to 7 at. %. Based on electrical measurements, it was observed that a suitable electron transport layer (ETL) of F-doped TiO_2 can be synthesized for photovoltaic applications. The present study offers a synthesis and analysis of F-doped TiO_2 that can be used to improve the sustainability of PV manufacturing processes, improve its economic value, and mitigate its negative impact on the environment.

Keywords: Electron transport layer, Environmental impact, F-doped TiO_2, Optical properties, Sol-gel preparation, Thin films

INTRODUCTION

The increase in the global population places heavy demands on the food, water, and energy sectors. Energy generation processes face major challenges such as sustainability, cost, security, and market price fluctuations. In addition, the increase in environmental awareness and the application of more stringent discharge regulations has directed the scientific community to work on developing alternative, sustainable, and renewable energy sources. With such implications, the transformation of energy systems has also received much attention, from focusing more on biofuels and solar cells. Hybrid and sustainable energy systems such as solar, wind, geothermal, and biomass are key technologies in the renewable revolution phase. Organic-inorganic hybrid perovskite solar cells (PSCs) based on halide perovskite material have proficient, unrivalled advancement in the last few years, showing appreciable potential for large-scale commercialization and ap-

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plications (Xiang *et al*., 2017). Titanium dioxide (TiO_2), as the most known electron transport layer (ETL) material, has been extensively adopted in PSCs due to its high transparency, carrier charge separation performance and environmental stability (Yang *et al*., 2019).

TiO_2 is an interesting material due to its different technological properties and ultimate applications involving energy-conversion applications such as photo-catalysis, fuel generation, CO_2 reduction, electrochromic devices and solar cells (Singh *et al*., 2019). The non-toxicity, environmental compatibility and low price are other practical advantages of TiO_2 (Karthikeyan *et al*., 2020). After so many applications, there is still a problem in commercial use, i.e., its wide band gap 3.2 eV; this large band gap makes it difficult to use in photocatalysis, solar cells, and other applications(Asemi *et al*., 2017). There are a number of ways through which researchers have tried to reduce the band gap, such as doping, dye anchoring, heterogeneous composites (WO_3, SiO_2, Al_2O_3, etc.) and hybridization with nanomaterials (Mathankumar *et al*., 2020; Mishra *et al*., 2020; Yahya *et al*., 2018). Using non-metallic materials as dopants is a method to reduce band gaps with exceeding electrons coming from dopants. Nitrogen doping has always been the most attractive way to reduce the band gap(L. Tian *et al*., 2013). Further, fluorine is another suitable candidate for doping in TiO_2 due to its effectiveness in generating more charge carriers, resulting in enhanced conductivity of the TiO_2 (Che *et al*., 2017). In fact, phases such as anatase and rutile are present in TiO_2 nanocrystals, depending on preparation conditions. If the temperature is less than ~450°C), it may be an anatase phase; increasing temperature would lead to rutile phase (Upadhyay *et al*. 2021). Therefore, according application, researchers have been focused on optimum phase of TiO_2. The anatase phase is more stable as compared to rutile phase which is not good in different applications except photovoltaic application(Davis *et al*., 2019).

Various deposition techniques are available to fabricate doped and undoped TiO_2 thin films like sol- gel spin coating technique, chemical vapour deposition, electrophoretic, screen printing, sputtering and electron beam deposition(Choudhary *et al*., 2021). Among these, the sol-gel process is the most convenient as it is a low-cost, effective method for coating the films. The present study aimed to synthesize undoped and F-doped TiO_2 thin films by sol-gel spin coating technique for ETL application and to determine the effect of doping concentration on the structural, morphological, electrical, and optical properties of F-doped TiO_2 thin films.

MATERIALS AND METHODS

Thin films of undoped and F-doped TiO_2 were prepared on a glass substrate using the sol-gel spin coating technique (Rajput *et al*., 2018). The precursor solutions were prepared using titanium tetra isopropoxide (TTIP), and tri fluoroacitic acid as a source of Ti and F, respectively, while 2-methoxy ethanol was used as solvent. The TiO_2 solutions with F doping, such as 0, 1, 3, 5, and 7 at.%. were prepared separately and stirred 2 h at room temperature. After 24 h, the coating process on the glass substrate was started at the constant 2500 rate per minute for 30 s, dried at 200°C for 10 min with 10 layers, and annealed at 450°C for 60 min.

The crystalline properties of prepared thin films were analyzed by an X-ray diffractometer (Philips X'pert Pro-diffractometer) using CuK_α radiations (λ=0.15406 nm) (Upadhyay *et al*., 2020). The optical property was analysed by UV-Vis-NIR spectrophotometer (Shimadzu, UV-3600) and electrical properties by two probe electrometers (Keithley-4200-SCS) at bias voltage in the range of -4 to +4 volt (Larumbe *et al*., 2015).

RESULTS AND DISCUSSION

X-ray diffraction

The crystallinity of the F doped and undoped TiO_2 thin films using X-ray diffraction (XRD) pattern revealed the crystalline behavior of anatase TiO_2 as shown in Fig.1. The observed peaks exhibited the anatase TiO_2 phase (JCPDS No:-21-1272) and situated at 25.48°, 37.89°, 48.21°, 53.98°, and 55.23°, 62.98°, 69.05° correspond to the (101), (004), (200), (105), (211), (204) and (116) planes, respectively (Essalhi *et al*., 2017). Fig.1 shows that the crystal structure of F doped TiO_2 thin films did not transform compared to undoped TiO_2 thin films (Sharma *et al*., 2024). However, the intensities of the peaks along all (hkl) planes decreased as F doping content increased. Consequently, peaks were broadened also for higher doping content i.e. 7 at.%, which revealed that the crystallite size decreased with higher values of F. This might be due to the mismatch radius of F ion (0.136 nm) and Ti^{+4} (0.068 nm), and the crystallite size decreased due to the replacement of O_2 with F ions in the lattice site. Generally, X-rays reflect different angles from each plane and cause a broadening in the XRD peak (Kazeminezhad *et al*., 2016). Although, there was no extra peak of any impurity in the form of Florine oxide, which revealed about successful doping in the TiO_2 lattice sites. The average crystallite size of thin films was calculated by using the well-known Debye-Scherrer's formula in equation (1) as follows (Panwar *et al*., 2022):

$$D = \frac{0.9\,\lambda}{\beta\ Cos\theta} \quad (1)$$

where, D refers average crystallite Size, β is full width at half maxima (FWHM) of the peak, λ is for X-ray wavelength (1.5406 Å) and q refers as diffraction an-

Table 1. Structural parameters of undoped and F-doped TiO_2 thin films

Sample (hkl):(101)	d-spacing (nm)	FWHM (degree)	Crystallite size (nm)	Strain e $x10^{-2}$
Pristine TiO_2	0.3519	0.24512	33.2	6.03
F(1%)	0.3521	0.32764	24.8	8.05
F(3%)	0.3523	0.34753	23.4	8.54
F(5%)	0.3520	0.35323	23.0	8.68
F(7%)	0.3532	0.43856	18.6	10.78

gle. The average crystallite size of the pristine and F-doped TiO_2 thin films is mentioned in Table 1.

Surface morphology analysis

The surface morphology of the synthesized thin films of F-doped and undoped TiO_2 was examined via *Scanning Electron Microscope* (SEM) micrographs as shown in Fig. 2. SEM images (Fig. 2 a-c) showed that thin film formation was uniform or in-homogeneous by medium flaky nature morphology for undoped TiO_2 thin film and these flakes may be formed during the drying process in furnace due to surface tension between film and the air (Jeantelot *et al*., 2018). However, the flaky nature decreases in F(5%)-doped TiO_2 thin films and could exhibit better conductivity for this formation, as seen in Fig. 2 (d-f). Generally, capillary forces are generated during the drying process, which is responsible for the cracks in the film prepared by the spin coating technique.

Afterwards, the elemental composition of the prepared F-doped TiO_2 thin films determined using EDX is shown in Fig. 2 g and h. The EDX spectrum for pristine TiO_2 thin film is shown in Fig. 2 (g), while Fig. 2 (h) shows the elemental composition for F(5%)-doped TiO_2 thin film sample, which confirmed the presence of Ti, O and F owing to the successful doping during the

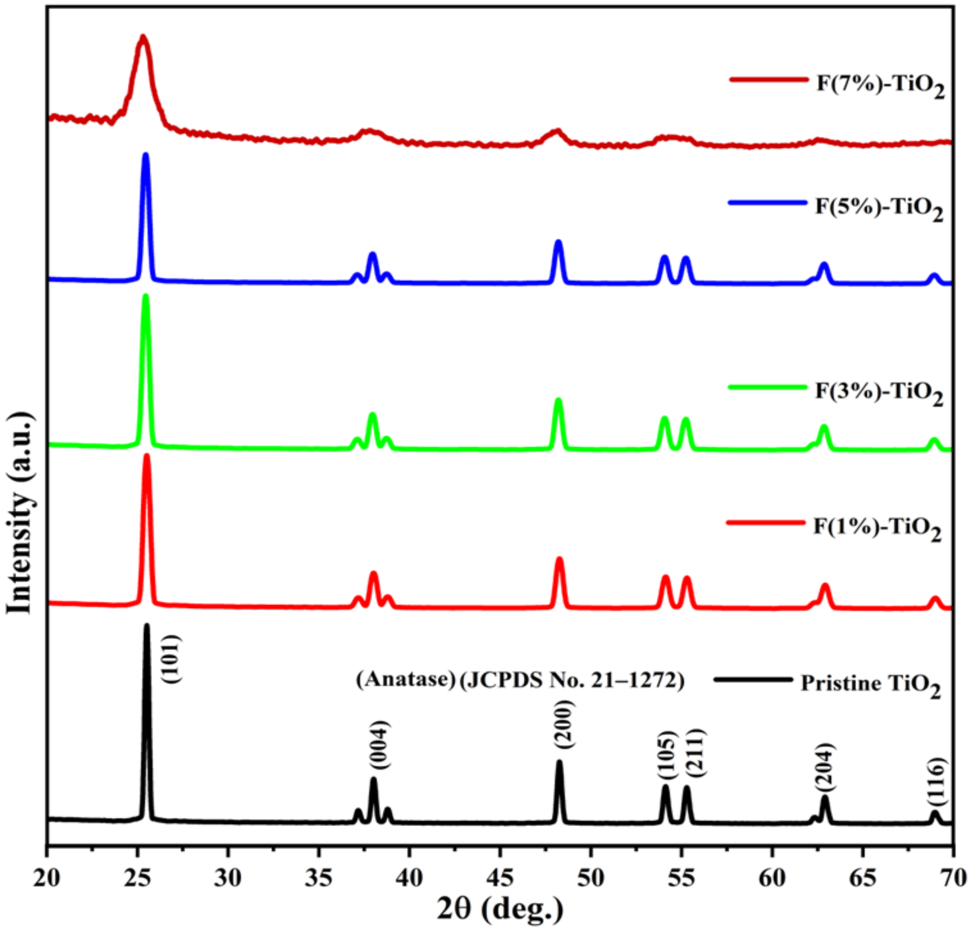

Fig.1. *X-ray diffraction patterns shows the corresponding planes of undoped and F doped TiO_2 thin films matched with JCPDS card No. 21-1271*

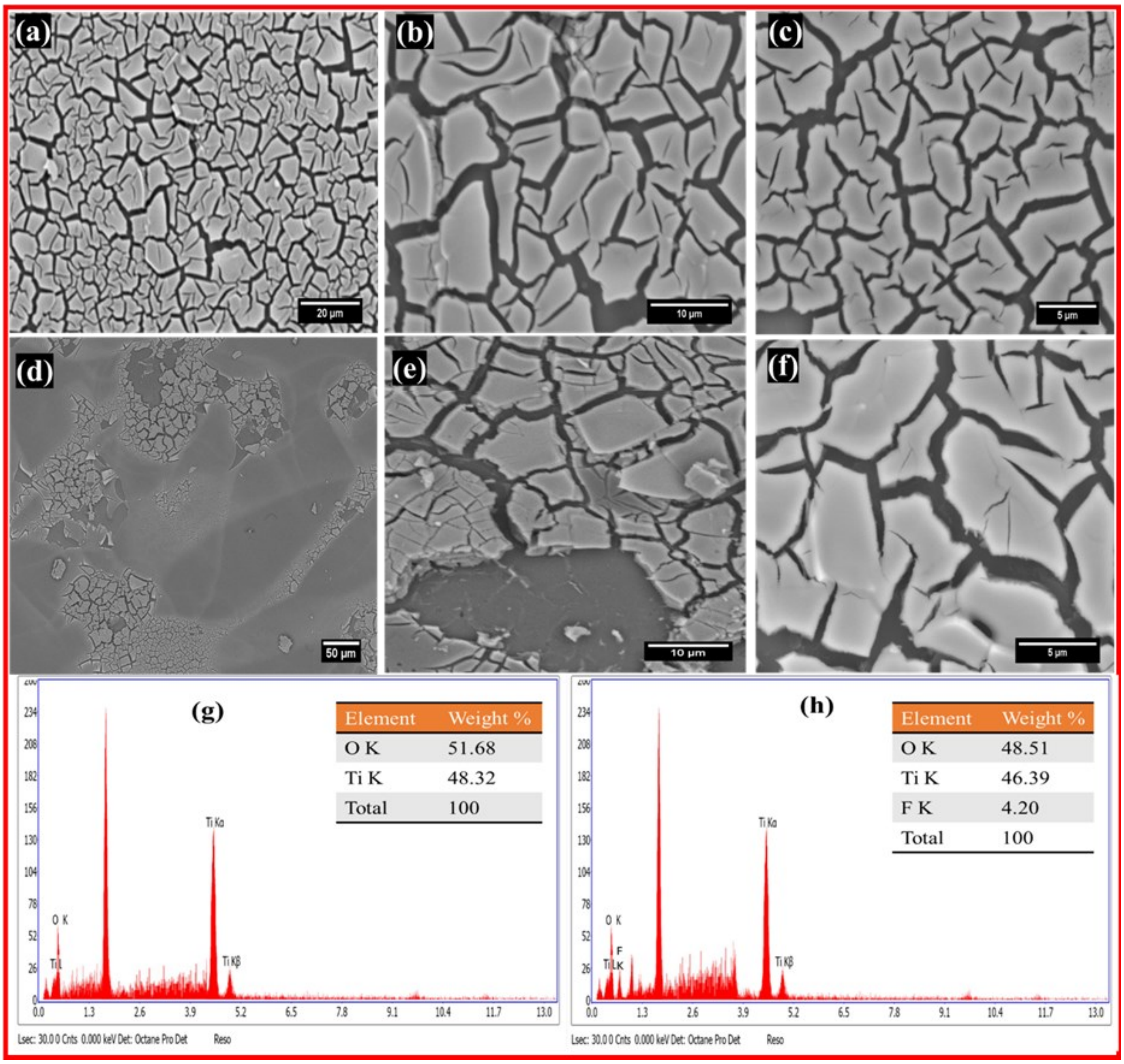

Fig.2. *Scanning Electron Microscope (SEM) micrographs of undoped TiO_2 thin films at* ***(a)*** *20 µm, (b) 10 µm, (c) 5 µm scale and F(5%)-doped TiO_2 at (d) 50 µm, (e) 10 µm, (f) 5 µm scales, (g) chemical elemental spectra for TiO_2 and (h) chemical elemental spectra for F(5%)-doped TiO_2 thin films*

synthetization process. Therefore, doping TiO2 with F can help reduce defects and recombination losses, improving solar cells' stability and longevity. Longer-lasting solar cells mean less frequent replacement and lower material waste and resource consumption.

Electrical measurements

The resistance of nanocrystalline thin films deposited on the glass substrate with various doping concentrations such as 0 at.%, 1 at.%, 3 at.%, 5 at.% and 7 at.% was found to be 1.322×10^{12} Ω, 2.112×10^{11} Ω, 5.807×10^{10} Ω, 3.328×10^{9} Ω and 9.728×10^{11} Ω, respectively. As doping concentration was increased, an augmentation was observed in the resistance of F-doped TiO_2 thin films owing the lowest resistance with better conductivity as compared to pristine TiO_2 thin films (Wang *et al*., 2021) as shown in Fig. 3(a). Therefore, the minimum resistivity was observed for 5 at. % F doped TiO_2 thin films while maximum for pristine sample. This can be explained by SEM results because maximum oxygen vacancies formed by adding F in TiO_2 which were seen by white reflection in SEM as shown in Fig. 2 (f). Hence, the obtained minimum resistive thin films were further used to fabricate ETL for PV devices to provide maximum light-to-energy conversion. This could provide a sustainable and cheap PV device. F-doped TiO_2 ETLs can significantly enhance the efficiency of photovoltaic devices. Higher efficiency means more electricity is generated per unit area, potentially reducing the land and materials needed for solar power generation.

Ultraviolet-Vis study

The transmittance spectra were analyzed in the 300-

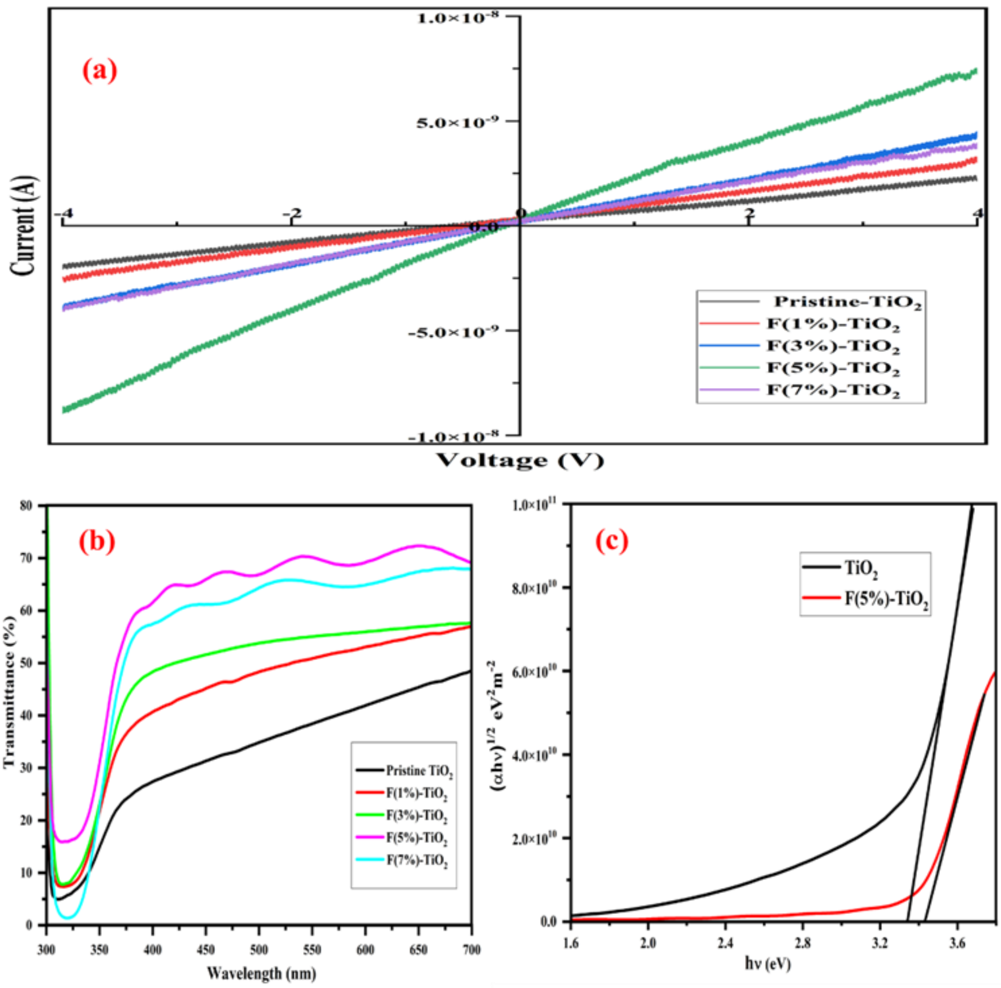

Fig.3. *(a) I-V characteristics curve of F-doped TiO_2 thin films, (b) Transmittance of pristine and F-doped TiO_2 thin films within 300-700 nm and (c) Tauc's plot for pristine and F(5%)-doped TiO_2 thin films*

700 nm wavelength range for all samples, as seen in Fig. 3(b). It is observed that the average transmittance was 35-70 % in the visible region for all samples. Moreover, the minimum transmittance value was found for TiO_2 films while the maximum for F-doped TiO_2 (5%). Thus 5% doping of fluorine in TiO_2 can be suitable for higher transmittance-based application (Al-Shomar, 2020). The absorption coefficient α is related to the direct band gap, which is function of frequency of light is indicated by the following formula (Tian *et al*., 2013);

$$(\alpha h\nu) = A(h\nu - Eg)^{1/2} \quad (2)$$

where, E_g is the optical band gap, hν is the photon energy, *A* is a constant independent of photon energy. Plotting the $(\alpha hn)^2$ versus *hn*, E_g was obtained by extrapolation method. The band gap of the fabricated thin films of pristine TiO_2 and F-doped TiO_2 is shown in Fig.3 (c). The band gap was increased with augmentation in F doping into TiO_2, which was calculated to be 3.32 eV and 3.56 eV, respectively which is suitable for ETL to manufacture PV devices. This blue shift was observed in the absorption edge with increasing the doping concentration of F into TiO_2. This may be related to particle size, surface morphology, and variation with the increase in the doping concentration of F. This blue shift causes variation in the Fermi level of TiO_2 nanoparticles, leading to increased energy bandgap (Sharma *et al*., 2021). Therefore, PV energy is a clean energy source, and its impact on air quality and climate change is significantly lower than that of any other traditional power generation system. Hence, it can assist in eliminating numerous environmental issues that result from utilizing fossil fuels. PV systems have zero emissions of carbon dioxide, methane, sulfur oxides, and nitrogen oxides during operation, which has negligible effects on air pollution and global warming.

Conclusion

TiO_2 thin films with different F-doping concentrations were prepared using the spin coating technique on glass substrates. It was observed that the crystallite size decreased as F doping content increased. Consequently, the flakiness of the films reduces and the film becomes more intact on the substrate surface. Through the optical analysis of the TiO_2 and F-doped TiO_2 thin films, the transmittance increased as the F doping concentration increased. However, maximum transmittance was observed with 5 at.% doping of F and the band gap increased to 3.56 eV, making it appropriate to use F-doped TiO_2 as ETL in solar cells. The widespread solar energy facilities combined with efficient utilization promise to increase the energy supply and reduce the dependence on fossil fuels. However, the contribution of solar energy to the energy demand is still at the minimum level, and several economic and environmental challenges are faced.

Conflict of interest

The authors declare that they have no conflict of interest.

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