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# Effect of fluorine-doped $TiO_2$ photoanode on electron transport, recombination dynamics and improved DSSC efficiency

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ABSTRACT

Fluorine doped $TiO_2$ (F-$TiO_2$) nanocuboids were synthesized using a simple template-free hydrothermal method and the XRD studies confirms that the nanoparticles are crystallized in anatase phase. Both HRSEM and HRTEM examinations reveal the formation of nanocuboids with nanovoids/pores morphology by corrosive fluorine action in hydrothermal container and such porous morphological feature can increase the surface area for high level dye adsorption. BET studies confirm the F-$TiO_2$ exhibits a higher surface area than that of pure $TiO_2$. The dye adsorption–desorption study confirms high dye-loading capacity in F-$TiO_2$. XPS result confirms the existence of $Ti^{3+}$ trap states and Ti—F bonding is evidenced from FTIR results. The absorption spectra of pure and F-$TiO_2$ shows a broad absorption in ultraviolet range and increase in band gap energy with F doping is determined using Kubelka-Munk function. Raman analysis shows the increase in percentage of exposed high reactive (0 0 1) facet with increasing the fluorine doping concentration. A high carrier concentration by F doping is found to promote fast electron hopping and increase the electrical conductivity, verified using ac impedance spectroscopy and photoconductivity measurements. The interfacial charge transfer kinetics such as charge transfer resistance, chemical capacitance, diffusion length, electron recombination lifetime and charge collection efficiency of fabricated DSSCs are calculated using EIS measurements. Enhanced power conversion efficiency of ~7.46% was achieved in F-$TiO_2$ photoanode based DSSC by using AAA solar simulator under standard test condition (1sun intensity; 100 mW/$cm^2$ with AM 1.5G filter).

## 1. Introduction

Dye sensitized solar cell (DSSC) based photovoltaic research is in great attraction since its invention by Gratzel in 1991 because of low cost device materials and ease in fabrication (O'Regan and Gratzel, 1991); (Gratzel, 2001). Recently, high photoconversion efficiency of 13% was demonstrated in porphyrin organic dye sensitized $TiO_2$ photoanode (Mathew et al., 2014) based DSSC. The anatase titanium dioxide ($TiO_2$) has been used as efficient wide band gap semiconductor for DSSC photoanode fabrication owing to its high dye adsorption and matching energy level properties (Quintana et al., 2007). Several material modification strategies such as design of (i) porous $TiO_2$ to obtain high surface area and dye loading (Hwang et al., 2012) (Rui et al., 2016) and (ii) metal (Cu, Co, Ni, Cr and Ag) (Wijayarathna et al., 2008; Yacoubi et al., 2015; Archana et al., 2013; Xie et al., 2013; Luo et al., 2014) and non-metal (N, C, F and S) (Chu et al., 2008; Kang et al., 2010; Song et al., 2012; Zheng et al., 2011) ion doped $TiO_2$ to reduce recombination and enhance electron transfer to improve the overall performance of DSSC.

The metal ions are used as cationic dopant substitution for $Ti^{4+}$ cation of $TiO_2$ whereas the non-metal ions are used as anionic dopant substitution for $O^{2-}$ anion. The lower edge of the conduction band (CB) of $TiO_2$ consists of $Ti^{4+}$ *3d* bands and the upper edge of the valence band (VB) is formed with $O^{2-}$ *2p* bands. Therefore, metal ion doping strongly affects the CB structure of $TiO_2$ while non-metal ion doping influences the VB energy level. The metal ion doping could effectively tune the position of CB $TiO_2$, but it present deep trap states which act as charge recombination centers that will lead to an increased recombination rate (Shalan and Rashad, 2013). Since the dye molecules anchor with $Ti^{4+}$ cation, the metal ion doping also affects the dye adsorption owing to different coupling strengths between the dopant and dye molecules. Therefore, non-metal ion doping is preferred for not to impede electronic binding between Ti atoms and dye molecules, which can provide larger dye adsorption and efficient electron injection. Among the non-metal ions doping, fluorine (F) is a superior anionic dopant causing small disruption in the CB of $TiO_2$ and inhibits electron recombination by its strong electronegativity. Fluorine doping also induces $Ti^{3+}$ species through charge compensation between $F^-$ and $Ti^{4+}$

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ions, and the existence of $Ti^{3+}$ trap states facilitates the charge collection efficiency. Recent literatures report that F doping in $TiO_2$ is an effective approach to reduce recombination and improve power conversion efficiency of DSSC. Zhaogi et al. showed an improved power conversion efficiency of 6.3% in fluorine doped $TiO_2$ (F-$TiO_2$) photoanode based DSSC (Yang et al., 2015). Junling et al reported an efficiency of 6.31% in a DSSC based on F-$TiO_2$ hollow spheres that served as scattering layer (Song et al., 2012).

On the other hand, the morphology and porosity of photoanode material also plays crucial role in determining dye loading and light harvesting ability. Nanoscale $TiO_2$ with different morphologies such as mesoporous spheres (Deng and Li, 2016; Dadgostar et al., 2012), hierarchical nanostructures (Rui et al., 2016; Shao et al., 2011) and nanorods (Kang et al., 2008; Lee et al., 2009) have been employed to achieve highly efficient DSSCs. The one dimensional nanorod structures can offer fast electron transport, but it provides low surface area and reduces the dye loading. The hierarchical hollow spherical and mesoporous $TiO_2$ structures can provide high surface area for better dye adsorption and enhanced light scattering (Rui et al., 2016; Deng and Li, 2016). However, the $TiO_2$ hollow spheres limit the electron diffusion by its numerous grain boundaries. Recently, $TiO_2$ nanoparticles with cubical morphology with well-defined facets have been employed as efficient photoanode material because they can deliver rapid electron transport and increased dye adsorption. Jinho et al., demonstrated that cubic $TiO_2$ nanoparticles have enhanced charge transportation by its flat surface than spherical shaped $TiO_2$ nanoparticles which leads to improved photocurrent in cubic $TiO_2$ based DSSC (Chae and Kang, 2011). The quasi cubical $TiO_2$ nanoparticles prepared by Huei Siou Chen et al., resulted an efficient light harvesting and fast charge transportation (Chen et al., 2013). Vipin Amoli et al., showed that porous $TiO_2$ nanocubes have improved the dye adsorption and speedup the electron transport compared with commercial titania (P25) nanoparticles (Amoli et al., 2015). It is interesting to note that fluorine is used as morphology directing agent and provided $TiO_2$ nanocrystals with well faceted square-like (Ding et al., 2013); nanoparallelepiped (Amoli et al., 2015), truncated bipyramid (Yang et al., 2008) and nanocube morphologies (Yu et al., 2014).

This work focuses on the synthesis of F-$TiO_2$ nanocubes with nanovoid/pore morphology by a simple and inexpensive hydrothermal method in which $F^-$ ions acts as both n-type dopant and morphological control agent. This novel F-$TiO_2$ structure can favor enhanced dye loading, improved light confinement and efficient electron transfer. Effect of fluorine concentrations on the structural, morphological, optical and electrical properties of the F-$TiO_2$ nanocubes was systematically investigated for DSSC application. Present investigation demonstrated better power conversion efficiency (*PCE*) of 7.46% in F-$TiO_2$ photoanode based DSSC in comparison to similar works (Table S3 Supplementary information). The prepared F-$TiO_2$ nanocubes with nanovoids/pores can give high surface area and enhances dye loading as well as light harvesting by increased light trapping, which resulted in improved *PCE*. The formation of $Ti^{3+}$ trap states by F doping reduce the electron hole recombination and thereby increased the DSSC efficiency.

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.solener.2018.06.077.

## 2. Experimental procedure

### 2.1. Materials

Reagent grade titanium *iso*-propoxide [$Ti(OCH(CH_3)_2)_4$ or TTIP, 97% purity], urea ($CO(NH_2)_2$), ammonium fluoride ($NH_4F$), polyethylene glycol [PEG 200, $(C_2H_4O)_nH_2O$)], di-tetrabutyl ammonium cis-bis (isothiocyanato) bis (2,2′-bipyridyl-4,4′-dicarboxylato) ruthenium (II) (N719-dye) and fluorinated tin oxide (FTO) substrate ($\sim 7\,\Omega/cm^2$) were purchased from Sigma-Aldrich. Lithium iodide (LiI), iodine ($I_2$), acetonitrile, tert-butyl alcohol and ethanol were obtained from Fisher scientific for the preparation of redox electrolyte. Dyesol's platinum (Pt) counter electrode was procured for the fabrication of DSSC.

### 2.2. Synthesis of pure and F doped $TiO_2$

Pure and F-$TiO_2$ nanoparticles were synthesized by one pot hydrothermal method without using any structure directing templates. In a typical synthesis of pure $TiO_2$, 0.3 M of titanium isopropoxide (TTIP) and 1.5 M of urea ($CO(NH_2)_2$) were dissolved in 40 ml of distilled water followed by stirring for one hour to get homogeneous solution. The solution was transferred into stainless steel autoclave and maintained at 120 °C for 24 h. The precipitate was collected and washed with distilled water and ethanol for several times to remove the unwanted residuals and calcined at 350 °C. For the preparation of F-$TiO_2$ nanoparticles, ammonium fluoride ($NH_4F$) as a source for $F^-$ ions was initially added to starting materials at different (2, 4, 6 and 8 at%) atomic ratios.

### 2.3. Fabrication of DSSCs

Fluorinated tin oxide (FTO) substrates were cut into a small dimension of $15 \times 15\,mm^2$ and ultrasonically cleaned with distilled water, acetone and ethanol for 10 min. An active area of $4 \times 4\,mm^2$ was defined by masking the FTO substrates using scotch tape. The prepared $TiO_2$ and F-$TiO_2$ nanopowders were made as paste using polyethyleneglycol [PEG 200, $(C_2H_4O)_nH_2O$)] binder and coated on FTO glass plates by doctor blade technique. Then, the prepared films were air dried at 80 °C and subsequently calcined at 350 °C for 30 min to eliminate the polymer binder. After being cooled to room temperature, the pure and F-$TiO_2$ films were soaked in ethanolic solution containing 0.3 mM N719 dye complex for 12 h. The dye sensitized photoelectrode was then rinsed thoroughly with ethanol and dried to remove unanchored dye molecules. The thickness of the prepared pure and F doped $TiO_2$ film was about $-25\,\mu m$, measured using surface profilometer SJ-210 (Supplementary information-Fig. S5). In the present work, commercially available Pt-coated FTO substrate was used as the counter electrode. Iodide electrolyte solution with high redox potential was prepared by dissolving 0.3 M of LiI and 0.03 M of $I_2$ in a 1:1 solvent mixture of acetonitrile and tert-butyl alcohol. Finally, DSSCs were fabricated by injecting the electrolyte solution between the dye-sensitized photoanode and platinum counter electrode using binder clips.

### 2.4. Characterization and measurements

X-ray powder diffraction patterns of pure and F-$TiO_2$ nanoparticles were obtained using Bruker-D8 Advance diffractometer with *Cu* $K_{\alpha 1}$ radiation at an operating voltage ($V = 40\,kV$ and $I = 30\,mA$) in a scanning rate of $0.02^\circ\ s^{-1}$ over the $2\theta$ range of 10–90°. Raman spectra were recorded by Laser Raman microscope (Raman 11i) with excitation laser wavelength of 532 nm. Fourier transform infrared spectra of the synthesized samples were carried out using FTIR-Perkin Elmer Spectrum. The surface morphology of the nanoparticles was analyzed using High resolution scanning electron microscope (HRSEM; Hitachi S4800). The detailed morphological analyses were obtained from high resolution transmission electron microscope (HRTEM; Jeol/JEM 2100). Brunauer-Emmett-Teller (BET) analysis was done using Micromeritics ASAP 2020 Porosimeter to find the specific surface area of the synthesized F-$TiO_2$ nanoparticles. To explore the chemical state of pure and F-$TiO_2$ nanoparticles, X-ray photoelectron spectroscopy (XPS; Carl Zeiss equipped with an Ultra 55 FESEM with EDS) analysis was carried out with Al Kα excitation at 250 W under ultrahigh vacuum. The optical properties of prepared samples were analyzed using UV–VIS diffuse reflectance spectrometer (Jasco-V-650) and the dye adsorption–desorption studies were carried out using UV–Visible spectrometer (Analytik Jena, Specord 210 Plus-German). The electrical response of synthesized materials and interfacial charge transfer phenomena of the fabricated DSSC devices were respectively