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# Modification of Physical and Chemical Properties of Titanium Dioxide (TiO<sub>2</sub>) by Ion Implantation for Dye Sensitized Solar Cells

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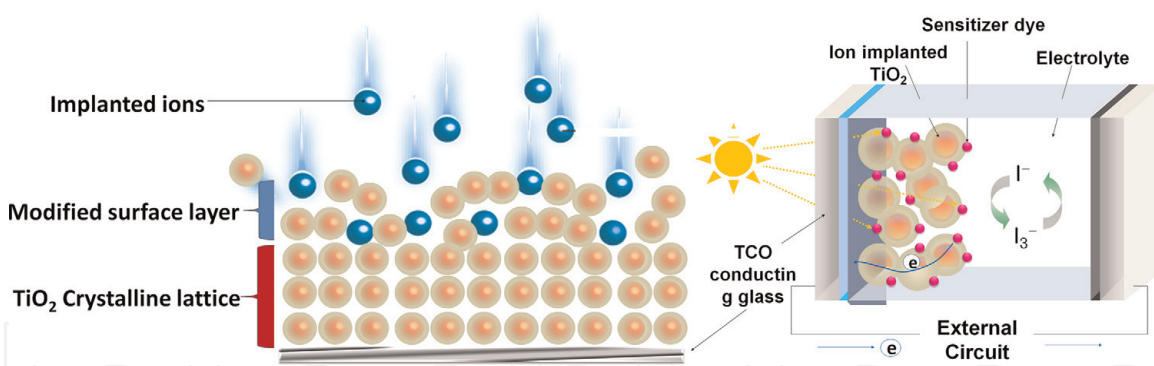
## Abstract

Nowadays, ion implantation is used as a leading technique for doping. In spite of generating lattice distortions it is preferred over other techniques due to its large range of doses, extremely accurate dose control and low temperature process. This chapter deals with the modification of physical-chemical properties of titanium dioxide (TiO<sub>2</sub>) through ion implantation method. The TiO<sub>2</sub> material is tested in many fields, e.g., nano-catalysts, light harvesting, magnetic data storage and Optics. Various synthesis routes have been reported for the preparation of TiO<sub>2</sub> nano-micro structures (particulate solids). Further, implanting these particulate solids revealed anisotropic ferromagnetism at room temperature. On the other hand, noble ion implantation opens up the horizon for fabrication of plasmonic and optical composites. Here in this chapter, TiO<sub>2</sub> based photoanodes have been extensively examined for dye sensitized solar cells (DSSC) with metallic and non-metallic ion implantation to realize TiO<sub>2</sub> with specific properties.

**Keywords:** ion implantation, doping, TiO<sub>2</sub>, dye sensitized solar cells, photoanode

## 1. Introduction

The growing energy demand of the society has engaged scientific community over the last decade in a search to enhance the light harvesting applications by utilizing nanostructured materials [1, 2]. The situation is quite obvious that the enlargement of solar cell efficiency through nanostructured materials is very important in the future. After the year 1991, a major breakthrough has come in the area of photovoltaics as dye sensitized solar cells (DSSCs) which possess modest functioning along with their advantageous features such as flexibility in device handling, low toxicity and respectable performance in diverse light conditions [3–7]. So far, TiO<sub>2</sub> is a well-known material as photoelectrode having tremendous performance in DSSC device application [6–10]. However, despite of the outstanding performance, TiO<sub>2</sub> tends to suffer from high recombination center of electrons and holes coupled with wide band gap (i.e., 3.2 eV) [11]. Thus, lot of research is being carried out with the aim to enhance device performance by reducing the



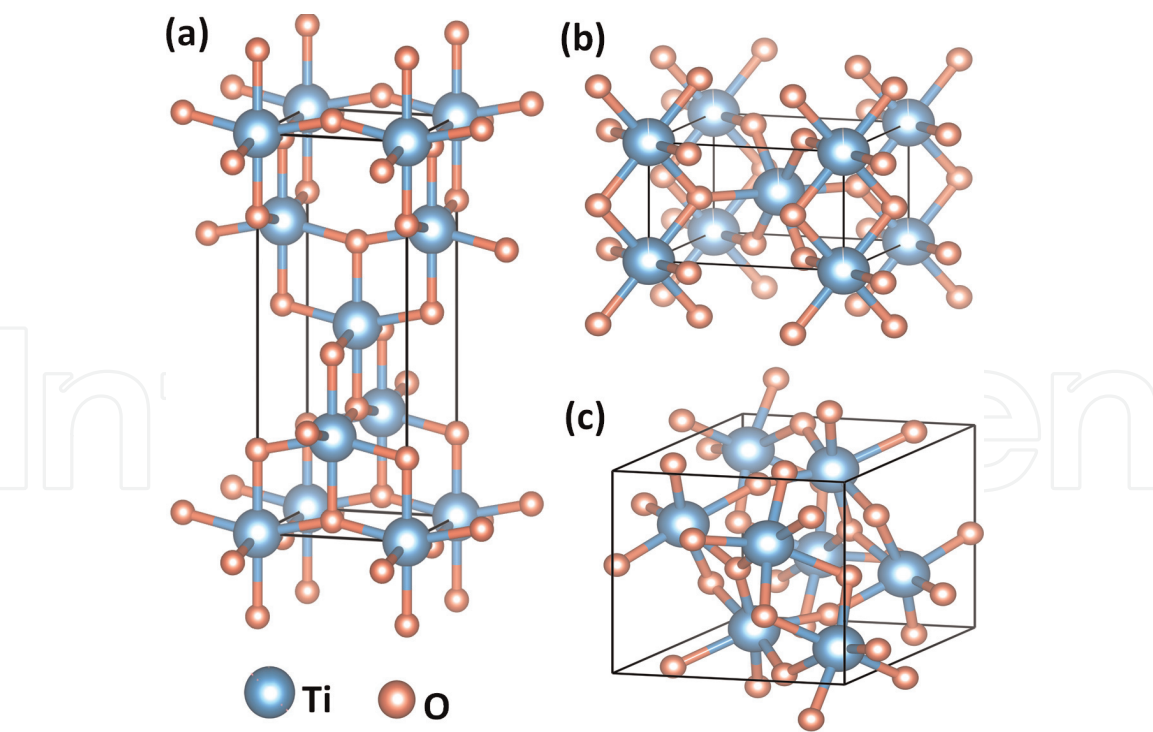
**Figure 1.**  
*Ion-implanted  $\text{TiO}_2$  photoanode for dye-sensitized solar cells.*

charge carrier recombination and improving electrical/optical performance of  $\text{TiO}_2$  photoelectrode [4–13]. In this regard, elemental doping is the most advantageous approach to modify its properties. Much work has been reported on synthesis processes adopted for preparation of  $\text{TiO}_2$ . The chemical synthesis methods involve the complexity of chemical reactions and reproducibility is often problematic [14]. Physical doping, e.g., high-energy beam modifications have an adept of post-treatment produced titania films for further precisions, were essentially ignored and less effort was conducted in this direction for doping in photoanodes of DSSC [15–20]. The author have gone through the literature carefully and after keenly analyzing the reported results, proposed the better applicability of the ion implantation system and extensively examined the ion implanted  $\text{TiO}_2$  as photoanode in DSSC application.

The present piece of work is mainly focused on the ion implantation technique for the modification of photo-physical properties of titanium dioxide ( $\text{TiO}_2$ ) thin films for application as efficient photoelectrode material in dye sensitized solar cell application (**Figure 1**). The work focuses the finding towards the power conversion efficiency enhancement in DSSCs through ion implanted  $\text{TiO}_2$  and also discusses in detail the reported results and extensively examines the effects of ion implementation on the performance of dye sensitized solar cell. This chapter imparts knowledge in the field of ion implantation and its application in dye-sensitized solar cells. The fabrication technique adopted here is compatible with currently utilized fabrication techniques for the same and is of great interest to the readers working in the area of ion implantation for optoelectronic device application.

## 2. Crystal structure of $\text{TiO}_2$

$\text{TiO}_2$  is an n-type wide bandgap semiconductor and has four polymorphs as tetragonal (anatase and rutile), orthorhombic (brookite) and monoclinic  $\text{TiO}_2$  (B) phases (**Figure 2**), apart from these polymorphs the  $\text{PbO}_2$  structure ( $\text{TiO}_2$  (II)) and hollandite structure  $\text{TiO}_2$  (H) are also synthesized from the rutile phase under high-pressure [21]. In DSSC application, both anatase and rutile phases are highly appreciated as they are stable and possesses good photoreactive properties. Brookite  $\text{TiO}_2$  has complicated phase with high unite cell volume with minimum density that makes it not suitable for device application [21]. The anatase  $\text{TiO}_2$  is most stable phase at nanoscale, however the energy difference between anatase and rutile is very small ( $2\text{--}10 \text{ kJ.mol}^{-1}$ ). The crystal structure, lattice parameters, optical band gap values and related parameters of different phase  $\text{TiO}_2$  are tabulated in **Table 1**.



**Figure 2.**  
Crystal structures of TiO<sub>2</sub> (a) anatase (tetragonal), (b) rutile (tetragonal), and (c) brookite (orthorhombic) polymorphs [21].

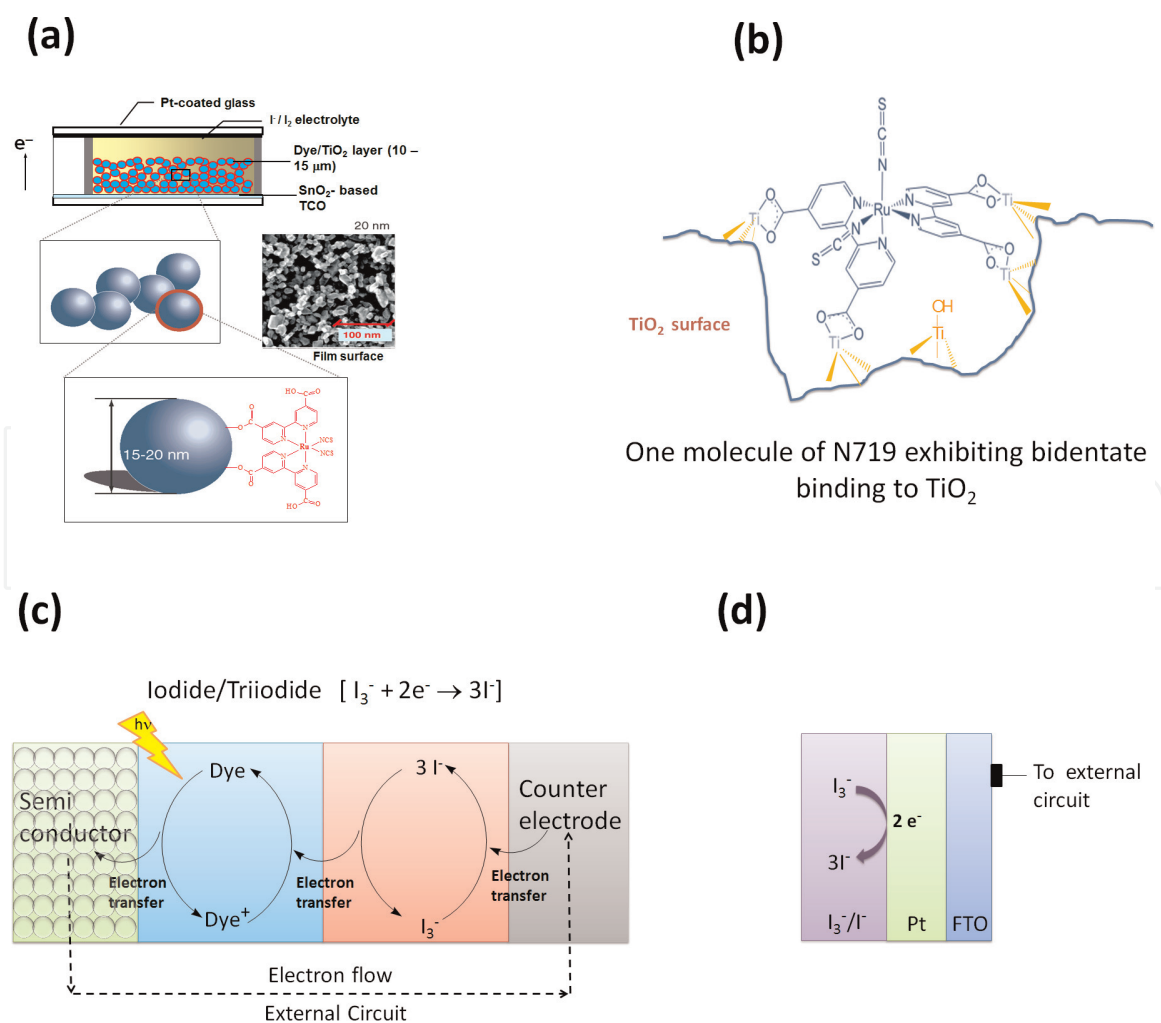
Crystal structure	Anatase TiO <sub>2</sub>	Rutile TiO <sub>2</sub>	Brookite TiO <sub>2</sub>
Form. Wt.	79.890	79.890	79.890
Crystal system	Tetragonal	Tetragonal	Orthorhombic
Point group	4/mmm	4/mmm	mmm
Space group	I4 <sub>1</sub> /amd	P4 <sub>2</sub> /mm	Pbca
Unit cell			
a (Å)	3.7842	4.5845	9.184
b (Å)			5.447
c (Å)	9.5146	2.9533	5.145
Volume (Å <sup>3</sup> )	136.25	62.07	257.38
Molar volume	20.156	18.693	19.377
Density	3.895	4.2743	4.123
Thermal expansion (volumetric)			
Alpha		28.9	
a <sub>0</sub>		0.2890	
Density	3.2 eV	3.0 eV	4.123

**Table 1.**  
Structural properties of crystalline structures of TiO<sub>2</sub> Ref. [21].

TiO<sub>2</sub> is more stable as compared to other metal oxides in DSSC, because it has suitable Fermi level to accept electrons from photoexcited dye, and its internal network structure (mesoporous structure) plays an important role in achieving high charge collection efficiency and more electron transportation.

### 3. Dye-sensitized solar cells

The basic idea of dye-sensitization technique was given by Vogel and Berlin in 1873 [7] and the well understood sensitization was perfect in early 1960s and 1970s, with the pervasive photoelectrochemical examination of dye-sensitized single-crystal electrodes. However, as compared to silicon based photovoltaic devices, the performance of these early DSSCs was poor (efficiency <1%). The major obstacle was the low light harvesting efficiencies of these single-crystal cells by a dye monolayer adsorbed onto a planar TiO<sub>2</sub> surface. Some improvements in efficiency were achieved by coating a thick layer of dye onto the planar TiO<sub>2</sub> surface; the efficiency was still limited to <2% due to less proficiency in charge-collection from the faraway dye molecules [14]. A breakthrough in DSSC performance was achieved in early 1990s by the research group of Grätzel who creatively demonstrated that a practical DSSC which consists of ruthenium sensitizer dye-adsorbed mesoporous titanium dioxide (thin ~10 µm) layer on fluorine doped tin oxide glass substrate serving as a photoanode (PA), a platinum-coated counter electrode (CE) and a redox couple liquid electrolyte introduced in between the two electrodes [3]. The main parts of DSSC are shown in **Figure 3** [22–25]. Considerable developments in DSSC efficiency have been reached since then, and the record A.M. 1.5 conversion efficiency for a DSSC presently touched at 14.3%, making it comparable to the conventional *p-n* junction silicon solar cells in terms of efficiency and cost-effectiveness [7]. Despite intense study of DSSCs over the past two decades, the



**Figure 3.** (a) Semiconductor (photoanode, PA), (b) sensitizer dye, (c) redox couple/electrolyte, and (d) counter electrode [22–25].

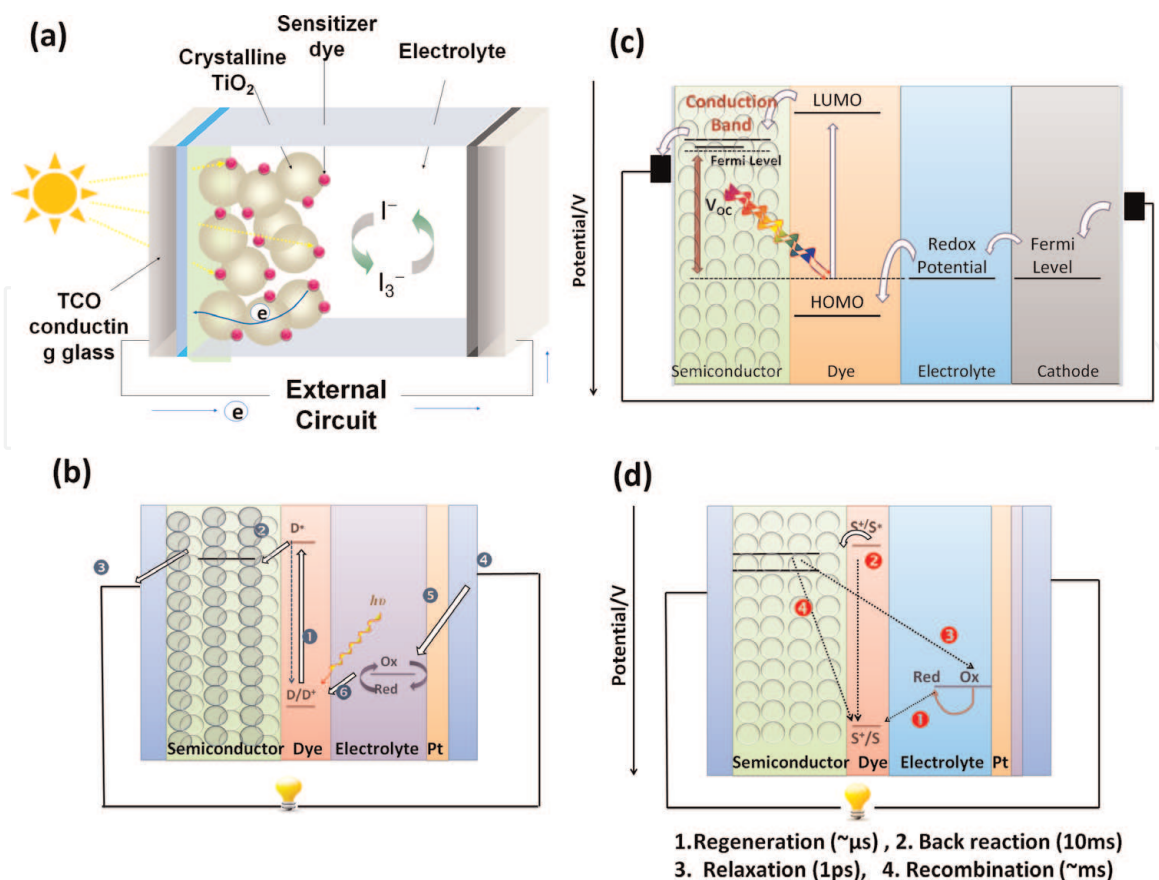


increase in conversion efficiency has been insignificant and several aspects of the physics and chemistry of the DSSC stay uncertain or debated. If further progress is to be made in device optimization of DSSCs for use in the photovoltaic market, scientists should understand the full mechanism of electron transport in the photoanodes, dye sensitization kinetics and electron recombination at the substrate/TiO<sub>2</sub>/electrolyte interface. The ion implantation method lays emphasis on the modification of photoanode, e.g., [16–18]:

- The ion implanted TiO<sub>2</sub> have high surface area for dye adsorption and avoid absorbing visible light to cover high amount of light harvesting.
- The energy level of the ion implanted TiO<sub>2</sub> is matched with that of the excited dye molecules for smooth electron (e<sup>-</sup>) injection.
- The ion implanted TiO<sub>2</sub> has large charge carrier mobility, for collecting the photoelectrons competently.
- The ion implanted TiO<sub>2</sub> is easy to synthesize, stable, cheap and environmentally friendly.

### 3.1 Basic principles of DSSCs

**Figure 4** depicts typical structure of a DSSC and its operational principle [22–25]. In DSSC the photo-excitation of electrons from lowest unoccupied molecular orbital (LUMO) of dye molecules takes place with the external light irradiance, by choosing sufficient energy, electron reaches highest occupied molecular orbital



**Figure 4.**  
 (a) Schematic of a typical DSSC. (b) The basic sequence of events in a DSSC. (c) Electron transfer in dye sensitized solar cell. (d) Electrical losses in DSSCs [22–25].

(HOMO) of dye molecule, which is further injected into the conduction band (CB) of the  $\text{TiO}_2$  and fast transferred to the external circuit through the CE, generating an electrical current. The inserted electrolyte here plays a vital role in donating an electron back to the unusual state of dye molecule and serves as a redox couple. The CE proceeds charge from the external circuit back to the cycling circuit in the cell [6–8]. Nevertheless, the device performance depends on the photoelectrode material as well. The voltage produced under irradiance shows resemblance to the potential difference between the electrolyte redox couple ( $\text{I}^-/\text{I}_3^-$ ) and the quasi-Fermi level of the electron in  $\text{TiO}_2$ . The net outcome is the conversion from light to electricity without any permanent chemical transformation. DSSC is thus a regenerative type photo-electrochemical cell [9, 10]. The sequence of the charge transfer processes responsible for the operation of a dye sensitized solar cell is given in the following Eqs. (1)–(7) [26]: The charge transfer processes and the unwanted loss mechanisms presented below are well discussed in details in Ref. [8].



In addition to the forward electron transfer and ionic transport processes, several electron loss pathways could be analysed as shown in **Figure 4(d)**, which gives the electron transfer losses occurred at the dye-sensitized heterojunction. The earlier studies clearly indicate that the main losses in DSSC were due to the potential drop in the dye regeneration and recombination losses between electrons in the  $\text{TiO}_2$  and acceptor species in the electrolyte [26].

- Fall off the electron from dye excited state to the ground state



- Recombination of the vaccinated electron with the dye cations



- Recombination of the vaccinated electron with the ( $3\text{I}^-$ ) redox mediator



- At CE, the electron decreases the redox mediator situated in the electrolyte of the DSSC.
- Redox mediator diffuses to meet and regenerate oxidized dye molecules.

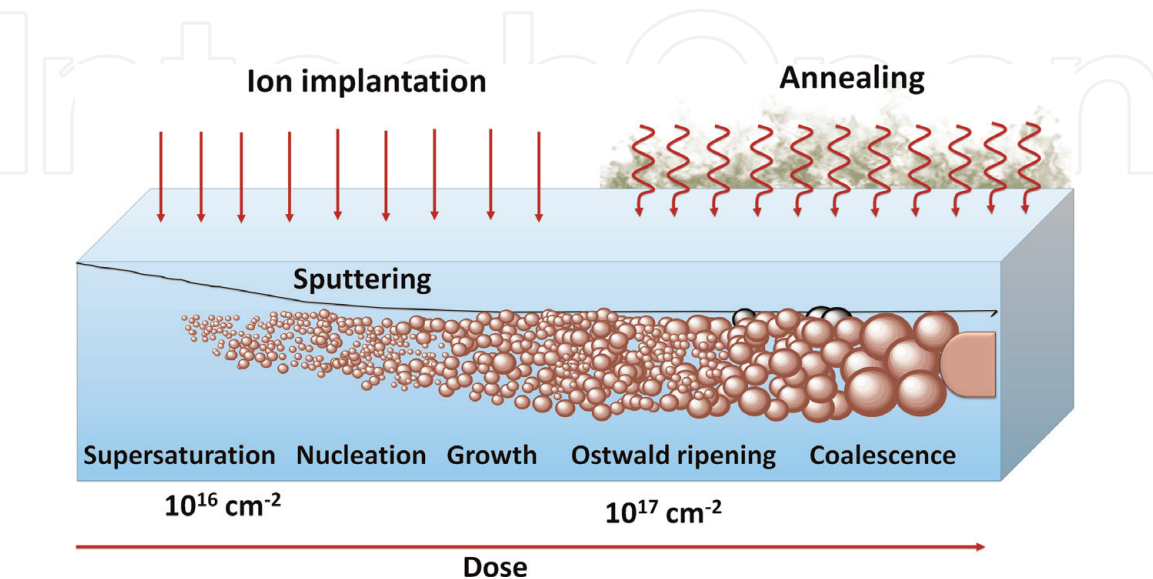
Hence, the challenge is to effectively regenerate the oxidized dye molecules with efficient charge transport through the ion implanted  $\text{TiO}_2$  matrix followed by the decrease in recombination which can happen at the  $\text{TiO}_2/\text{dye}/\text{electrolyte}$

boundaries. The morphology and structure of the ion implanted TiO<sub>2</sub> photoanode depends on the absorption of dye, electron injection, transportation and the recombination.

#### 4. Ion implantation

The basic information of nucleation and growth mechanisms of TiO<sub>2</sub> thin film is essential to understand microstructure and properties for DSSC [4, 16]. The TiO<sub>2</sub> nanoparticle with anatase and rutile phases has been synthesized by ion implantation technique, where the degree of surface modification is significantly influenced by various implantation parameters, e.g., current density of ion beam, substrate temperature, and energy of an implant ions [17], etc. In ion implantation technique, ion dose (denoted by  $F_0$ ) is the key factor to determine the total implant ions. TiO<sub>2</sub> implantation can be categorized as low-dose and high-dose under conditional surface modification. Low-dose irradiation, e.g.,  $\sim F_0 \leq 5.0 \times 10^{14}$  ion/cm<sup>2</sup> (energy of the implant is transported to the matrix by electron shell excitation and nuclear collisions [27]), causes the radiation-induced defects, which may in turn become reversible or irreversible modification of the material structure. Several types of defects are present in TiO<sub>2</sub> crystal such as point defects, line defects, stacking faults defects, local crystallization, etc. The range of high-dose implantation can be classified into two sub-ranges, e.g.,  $10^{15} \leq \sim F_0 \leq 10^{17}$  ion/cm<sup>2</sup>.

**Figure 5** depicts the cross-section view of nucleation and growth of nanoparticles. Once the concentration of doped ions over does the solubility limit of TiO<sub>2</sub> atoms in matrices and the system relaxes [19]. The threshold dose values which nucleate the TiO<sub>2</sub> nanoparticles are dependent on the sort of the implant and dielectric matrix. Therefore, the ion implantation method delivers a suitable way to alter physical and chemical properties of materials. Still there is rare information or literature available on improvement of photovoltaic properties for DSSCs with ion implantation [15–18].



**Figure 5.**  
Basic physical stages of TiO<sub>2</sub> nanoparticle synthesis by ion implantation in dependence on ion dose [27].



5. Recent progress in DSSCs

Till date, the record efficiency of DSSCs is exclusively achieved on TiO<sub>2</sub> nanoparticles. Optimized photoelectrode films usually contain two layers: the bottom layer is a 12-μm thick transparent layer made of 10–20 nm TiO<sub>2</sub> nanoparticles which has efficiently high surface area for dye adsorption; the top layer is a 4-μm thick film made of much larger TiO<sub>2</sub> particles (~400 nm in diameter) to scatter light back into the bottom layer and enhance near-IR light harvesting [3]. The highest efficiency achieved based on the different architecture of DSSCs is summarized in **Table 2**. Despite the excellent performance of TiO<sub>2</sub> nanoparticle films in conventional DSSCs, they are still incapable to contribute suitable efficiency as compared to silicon based solar cells. Thus there is a need to realize a higher access rate of the photogenerated electrons from dye to the photoanode, to extend the efficiency at suitable level.

5.1 Important results

The TiO<sub>2</sub> photoanode prepared via the ion implantation method has active paths to expand the DSSC performance [19]. Ion implantation permits the incorporation of Ti<sup>4+</sup> ion species at accelerated high-energy into the raw surface under high applied power for short time duration. On the other hand, it can improve the properties of TiO<sub>2</sub> like enhanced resistance to oxidization, little interfacial fault and respectable optical properties [17]. But till date the reported work on ion implanted TiO<sub>2</sub> served as photoanode in DSSC are very limited (available reports are summarized in **Table 3**). The implanted ions may act as intermediaries for charge transfer and centers for electron-hole recombination, and this dual characters affect the performance of the DSSC. The true impact should be conceded by both the effects, and also depend on the doses of the implanted ions. It has been found that the annealing state also play a key to explaining the charge transfer dynamics on ion implantation, because annealing state regulates the activation and the diffusion profile of the dopant. The beginning part of the annealing is more precarious since the in-activated dopants act as recombination sites, which reduces the minority carrier lifetime and decreases the performance of DSSCs. Luo et al. and Low et al. has found that minimum temperature annealing of ion implantation TiO<sub>2</sub>

Author	Year	Dye	η (%)	Ref.
Kenji et al.	2015	ADEKA-1 and LEG4	14.3	[28]
Simon et al.	2014	SM315 with cobalt (II/III) redox	13.0	[29]
Liyuan et.al.	2012	N3	11.4	[5]
Yella et al.	2011	YD2-o-C8	12.3	[11]
Kim et al.	2010	Black dye	11.2	[30]
Qingjiang et al.	2010	Ruthenium	12.1	[31]
Chen et al.	2009	CYC-B11 dye	11.5	[32]
Feifei et al.	2008	C101 and C102	11.3	[33]
Yasuo et al.	2006	Black dye with YD2-o-C8	11.1	[34]

**Table 2.**  
*Photovoltaic parameters of the DSSCs under an illumination of 100 mW/cm<sup>2</sup> (AM 1.5G).*

Dopant/Modifier	Strategies	$\eta$ (%)	Ref.
Ag-ion	Tri-layer titania films has been doped with Ag ions using metal vapor vacuum arc ion-implantation.	5.85	[15]
Ti	Ti ion implantation has been used to modify the reduced graphene oxide nanosheet by incorporating the Ti <sup>4+</sup> ion at various applied powers ranging from 50 to 250 W	8.51	[16]
Ruthenium-iron	The anatase TiO <sub>2</sub> electrode has been prepared via a sol-gel process and deposited onto ITO. The deposited TiO <sub>2</sub> films have been subjected to MPII at 20 keV in order to incorporate ruthenium Ru and Fe atoms into the TiO <sub>2</sub> surface layer.	8.0	[17]
Carbon	The optimal concentration of ions implantation for C-implanted cells is $1 \times 10^{15}$ atom*cm <sup>2</sup>	5.32	[18]
Nitrogen	TiO <sub>2</sub> layer has been uniformly implanted with 100 keV nitrogen (N) ions of fluence $1 \times 10^{16}$ ions cm <sup>2</sup> .	1.64	[19]
Iron	Fe-doped TiO <sub>2</sub> electrodes with the illumination of $6 \times 10^{15}$ atom/cm <sup>2</sup>	4.86	[20]

**Table 3.**  
*Doped/surface modified through ion implanted TiO<sub>2</sub> based DSSCs.*

photoanode was due to shallow emitter which can enhance the quantum efficiency at short wavelengths [15, 16].

6. Conclusions

In the future, dye-sensitized solar cells will be used in many fields, such as mobile commerce, building-integrated photovoltaics (BIPVs), and vehicles. Moreover, DSSCs are essential in the Smart Grid, which are utilized in our daily lives. To apply solar energy in the Smart Grid, DSSCs are required to have transparency, flexibility, lightweight, low cost, and high power conversion efficiency. In terms of low cost and lightweight, organics, inorganics, and hybrid materials have brighter prospects than the semiconductors. In hybrid materials, photovoltaic cells have been prepared with the advantages of organics or inorganics selectively. However, it is not easy to increase the power conversion efficiency. One potential solution presented in this study is to use ion implanted TiO<sub>2</sub> nanostructures in DSSCs. The slow progress of ion-implanted TiO<sub>2</sub>-based DSSCs in the past 7 years has demanded to realize the reliable and practical commercialization of DSSCs. It is expected that ion-implanted TiO<sub>2</sub> can efficiently separate photoexcited charge carriers and generate higher photocurrent in DSSCs. In comparison to untreated cell, the implant ion can act as mediators for electron transport that reduces charge transfer resistance and enhance the dye loading resulting in boost of PCE [15]. One way of achieving the better light-harvesting ability is to grow the various low dimensional nanoparticles on the ion-implanted TiO<sub>2</sub> thin film, which is presently the active field of study [17]. Thus, the future prospects of material and ideas revealed in the present chapter can be better applied to efficient visible light-activated material to boost the performance of DSSCs.

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