Chapter 3

Melting and Diffusion Co-efficient of Metal and non-Metal Diffused TiO₂ Nanoparticles

3.1 Introduction

TiO₂ (titanium dioxide) is a promising photocatalyst material, its low photocatalytic efficiency calls for the modification of TiO₂. The metal and non-metal doping of TiO₂ nanoparticles have been proved to be effective ways to enhance photocatalytic properties. This chapter provides a deep insight into the understanding of the metal and nonmetal diffused TiO₂ nanoparticle photocatalysts. This chapter also discusses the introduction and shortcoming of solar cells, and includes use of TiO₂ in dye sensitized solar cell and methods available to increase the efficiency of solar cells. Further, chapter includes results of our work to find diffusion coefficient and diffusion time of the doped-TiO₂ system in two categories: (1) metal-doped TiO₂ and (2) nonmetal-doped TiO₂ photocatalyst systems. Every section of the present chapter ends with a concise conclusion and outlook of new trends in the development of TiO₂ based photocatalysts.

A solar cell is a device that converts photons from light into electricity. Fundamentally, the device needs to fulfill two functions: photogeneration of charge carriers (electrons and holes) in a light-absorbing material, and separation of the charge carriers to a conductive contact that will transmit the electricity. This conversion is called the photovoltaic effect, and the field of research related to solar cells is known as
photovoltaics. Due to the nature of photovoltaics, the light-absorbing material will only absorb certain energy level from photon. For example, silicon has a band gap of 1.14 eV, which means 1.14 eV energy can excite the electron into conduction band. If photon has energy more than 1.14 eV, excess energy will generate heat instead of generating more electron-hole pairs. This phenomenon limits the overall efficiency of the conventional semiconductor photovoltaic device. Shockley and Queisser [1] have calculated that the maximum thermodynamic efficiency for the single threshold absorber is around 31%. Thus, several approaches to increase the efficiency have been investigated. TiO$_2$ is very close to being an ideal photocatalyst, but unfortunately not, like all the other things in the world, perfect photocatalyst seems not to exist. Despite those outstanding properties which TiO$_2$ displays, there are many shortcomings of TiO$_2$ as photocatalysts. Furthermore, many applications of TiO$_2$ nanomaterials are closely related to its optical properties. However, the highly efficient use of TiO$_2$ nanomaterials is sometimes prevented due to some problems. The main problems are (1) The major drawback of TiO$_2$ is its wide band gap. The bandgap of bulk TiO$_2$ lies in the UV regime 3.0 eV for the rutile phase and 3.2 eV for the anatase phases, which is only a small fraction of the sun’s energy (<10%), as shown in Fig. 3.1.

Thus, efficient absorption of the visible light which constitutes the major part of solar spectrum is prevented and the photocatalytic efficiency of TiO$_2$ is hindered. (2) The recombination rate of photogenerated electron-hole carriers is rapid. The lifespan of photogenerated electron-hole carriers are approximately 10 ns. The rapid recombination rate of photogenerated electron-hole carriers decreases photo quantum efficiency of TiO$_2$. (3) At the initial stage of the study of photocatalysis, TiO$_2$ was used in the form of
powders. After photocatalytic reaction, a filtration step was requested. Thus, one of the goals for improvement of the performance of TiO₂ nanomaterials is to increase their optical activity by shifting the onset of the response from the UV to the visible region. There are several ways to achieve this goal. First, doping or diffusing certain element like metal or non-metal in TiO₂ [2].

![Solar spectrum at sea level with the sun at its zenith.](image)

**Fig. 3.1:** Solar spectrum at sea level with the sun at its zenith.

Nanomaterials can narrow the electronic properties and thus alter the optical properties of TiO₂ nanomaterials. This may be due to the formation of new $d$-bands as a consequence of the interaction of interstitial metal ions in the TiO₂ lattice with host material. Second, sensitizing TiO₂ with other colorful organic or inorganic compounds can improve its optical activity in the visible light region. Third, coupling collective oscillations of the electron in the conduction band of TiO₂ nanomaterials in metal-TiO₂ nanocomposite can improve the performance. In addition, the modification of the TiO₂ nanomaterial surface with other semiconductors can alter the charge-transfer properties between TiO₂ and surrounding environment, thus improving the performance of TiO₂ nanomaterials based devices.
The optical response of any material is largely determined by its underlying electronic structure. The electronic properties of a material are closely related to its chemical composition (chemical nature of bonds between the atoms or ions), its atomic arrangement and its physical dimension (confinement of carriers) for nanometer-sized materials. The chemical composition of TiO$_2$ can be altered by doping/diffusing. Specially, the metal (titanium) or nonmetal (oxygen) component can be replaced in order to alter the material’s optical properties. It is desirable to maintain the integrity of the crystal structure of photocatalytic host material and to produce favorable changes in electronic structure. It appears easier to substitute the Ti$^{4+}$ cation in TiO$_2$ with other transition metals and it is more difficult to replace the O$^{2-}$ anion with other anions due to difference in charge states for the modification of the chemical composition of TiO$_2$ due to higher tolerance of the structural distortion than that of bulk induced by the inherent lattice strain in nanomaterials [3].

**Diffusion** is an important process to spread the particles through random motion from regions of higher concentration to regions of lower concentration. It is an efficient process which shifts the optical response of TiO$_2$ from the UV to the visible spectral range i.e. to longer wavelength and gives maximum utilization of the solar induced photocatalytic properties of this material. Further, the diffusion for any TiO$_2$ photocatalytic system helps in controlling electron-hole transport which may be hindered by any material interfaces, and hence it may lead to great interest in TiO$_2$ based electronics [4-6]. However, our aim limits to the study theoretically the effect of size and shape on diffusion process using a simple empirical method within thermodynamical limit. In order to understand the effect of diffusion of metal/ non-metal in TiO$_2$, diffusion
activation energy, diffusion time and diffusion coefficient are also calculated at the nanoscale in undiffused and diffused TiO$_2$. The size effect on the diffusion activation energy is analyzed through the size effect on the melting temperature. Further, it is well known that the diffusion activation energy decreases, which results into an increase in the diffusion coefficient of atoms in nanocrystals than its bulk counterpart [7-10]. The band gap of TiO$_2$ can be narrowed by doping it with non-metals like O [11], C [12-14] and N [15, 16], which can replace the lattice oxygen atoms.

The size and shape dependent diffusion coefficient function is an important parameter for any phase transition process, and is related to the thermodynamical properties of material. The understanding of this kind of scientific problem is a challenge particularly in the field of nanotechnology. Until now, to the best of our knowledge there is no study with consideration of shape and size on diffusion coefficient in the case of metal and non-metal doped TiO$_2$ nanocrystals particularly to see the effect of diffusion of any metal/non-metal nanoparticles in the TiO$_2$ nanocrystal. In the present work, we consider the diffusion of nitrogen and platinum in the TiO$_2$ nanoparticles.

3.2 Modification Methods of TiO$_2$ Photocatalysts

Many methods have been proposed to overcome those shortcomings which constrain the wide usage of TiO$_2$ photocatalysts. Here, we briefly focus on some recent progress in the preparation of metal and non-metal doped TiO$_2$ nanomaterials. In discussing briefly, the methods involve in the preparation of doped TiO$_2$ nanomaterials, we present a typical procedure and representative application and development of the TiO$_2$ photocatalyst.
3.2.1 Surface Sensitization

If the sensitizers are absorbed (either chemisorbed or physisorbed) on the surface of TiO$_2$, they can be much more easily excited than TiO$_2$. Hence, the excitation process can be efficiently improved [17-20]. The sensitizers can extend the range of excitation energies of the TiO$_2$ into visible region. However, the sensitizers themselves can degrade. Thereby, there is a need to add more sensitizers in reaction systems. Because of this reason, the publication of this kind of modification method has diminished these years.

3.2.2 Metal and Nonmetal-Doped TiO$_2$

Doping has been proven to be a great method to enhance the photocatalytic activity. Metal-doping has long been used [21-24]. In recent years, nonmetal-doping has demonstrated great potential to be applied in the photocatalytic field [25-28]. However, controversial experimental results have been reported in literature, and different theoretical models have been proposed to analyze these phenomena. Yet, the mechanisms of the optical and photocatalytic properties of nonmetal-doped semiconductors are still open to discuss.

3.2.3 Coupling of Different Kinds of Semiconductor Photocatalysts With Different Energy Levels

This method is beneficial over others as the absorption spectrum can be expanded and the carrier separation is effective [29-35]. The wide band-gap semiconductor can be photoactivated by narrow band-gap semiconductors. In addition, the charge injection from the conduction band of the narrow band-gap semiconductor to that of TiO$_2$ can lead to efficient charge separation by reducing the electron-hole recombination rate. The
synergetic effect of composite semiconductor of anatase and rutile on the photocatalytic activity has also been reported [36].

**Fig.3.2:** Energy diagram for the heterogeneous anatase/rutile TiO$_2$ films at pH7

Fig. 3.2 shows the energy diagram for the heterogeneous anatase/rutile TiO$_2$ films at pH 7. The transfer of photogenerated electrons from the anatase to rutile phase may reduce the electron-hole recombination rate. Hence, the composite semiconductor of anatase and rutile shows better photocatalytic activity than pure anatase phase.

### 3.2.4 Doped TiO$_2$ Nanomaterials

Many applications of TiO$_2$ nanomaterials are closely related to its optical properties and hence band gap engineering. Diffusion/doping of TiO$_2$ have been an important approach in band gap engineering and hence modifying electrical and optical as well as other properties. The main objective of diffusion/doping is to induce a bathochromic shift, i.e. a decrease of the band gap or introduction of intra-band gap states, which results in the
absorption of more visible light. Diffusion may lead to photocatalytic system that exhibit enhanced efficiency.

Doped- TiO\textsubscript{2} photocatalysts (either with metal ions or nonmetal ions) have been proven to enhance the photocatalytic activity by red-shifting the absorption edge to lower energies direction. Hence, these doped- TiO\textsubscript{2} photocatalysts have been widely prepared and discussed for years. Choi and co-workers [21] systematically studied the role of metal-doping in quantum-sized TiO\textsubscript{2} nanoparticles using photochemical and photophysical experiments. The ionic radii of the dopant metal ions they choose were similar to that of Ti\textsuperscript{4+}, thus making easier for the substitution of the metal ions into the lattice of TiO\textsubscript{2} matrix. All dopants showed that an optimum concentration existed in the degradation of CHCl\textsubscript{3}. According to their work, doping with Fe\textsuperscript{3+}, Mo\textsuperscript{5+}, Ru\textsuperscript{3+}, Os\textsuperscript{3+}, Re\textsuperscript{5+}, V\textsuperscript{4+}, and Rh\textsuperscript{3+} at 0.1{0.5 at. pct} could significantly increase the photoactivity. For Co\textsuperscript{3+} and Al\textsuperscript{3+} doping, the photoreactivity would decrease. The most important factor that influenced the photoactivity of metal-doped TiO\textsubscript{2} was the enhanced interfacial charge transfer in the presence of effective dopants. Fe\textsuperscript{3+} doped TiO\textsubscript{2} has been reported to be efficient in the degradation of many kinds of organic pollutants. The introduction of iron cations can exert strong influence on the charge carrier recombination time, and extend the absorption edge of TiO\textsubscript{2} into the visible light region [21]. Similarly, Brezov et al. investigated the photocatalytic decomposition of phenol using metal-doped TiO\textsubscript{2} photocatalysts supported by the sol-gel method on glass fibers [23, 37]. Their study demonstrated that the photoactivity of doped TiO\textsubscript{2} was strongly dependent on the character and concentration of dopant ions. The best results in terms of phenol decomposition were obtained for dopant-free TiO\textsubscript{2}, Li\textsuperscript{+}, Zn\textsuperscript{2+}, and Pt- doped
TiO₂. Further, the transition metal doping has been extensively studied to extend the optical absorption of TiO₂ to visible light. However, the metal-doping of TiO₂ photocatalysts also has some drawbacks, such as thermal instability and increase in the carrier-recombination centers. Whereas, the nonmetal-doped TiO₂ seems to be more promising photocatalysts candidates. The vast research of nonmetal-doped TiO₂ photocatalysts has been widely carried out since the early 1990s [38-51]. Among all the nonmetal-doped TiO₂ photocatalysts, nitrogen-doped TiO₂ is the most studied system [25, 26, 38, 39]. Subsequently, several other visible-light active materials, such as B-[40, 41], C-[27, 42], F-[43-45], P-[46, 47], S-[28, 48], I-[49-51] doped TiO₂ were reported.

According to Fick’s law, current density of any material is directly proportional to its diffusion coefficient. In order to increase the photocatalytic efficiency of TiO₂ nanoparticles researchers, have calculated different properties of TiO₂ nanoparticles like self diffusity, electron diffusion co-efficient, ambipolar diffusion etc. as a function of pressure, temperature etc. [52-54]. **However, the obtained results are inconsistent and unclear.** Further, the diffusion coefficient of TiO₂ nanoparticles with and without doping as a function of size as well as dimension is yet to be calculated. Motivated, from the above fact we have performed a systematic study of the diffusion coefficient of metal and non-metal doped TiO₂ as a function of size and dimension [55].

To investigate the size and shape dependent diffusion coefficient and melting temperature of undoped TiO₂ and nitrogen and platinum doped TiO₂ nanoparticles, we have used the formula developed in chapter 2. It is clear from the Eq. (34) of chapter 2, that the size and shape dependency of diffusion coefficient of the material can be calculated using the shape and size dependent melting temperature. The melting, a first
order phase transition is an important indication of thermal stability requires melting enthalpy and molar volume to be not equal to zero. The melting enthalpy is mainly produced by the internal energy change of atoms and can be related to melting temperature by relation $H_m = T_m S_m$. Here, $S_m$ is induced by a structural change. As a variable for the melting thermodynamics, the size effect has been studied in recent years only due to rapid progress in nanoscience and nanotechnology [56, 57]. It is observed that while $T_m$ of a free nanocrystal decreases as size decreases, nanocrystals embedded in a matrix can melt below or above the corresponding $T_m (\infty)$, the bulk melting temperature depending on interface structure between embedded nanocrystals and matrix.

3.3 Results and Discussion

3.3.1 Shape and Size Dependent Melting Temperature of TiO$_2$ Nanoparticles

The calculated melting temperature of anatase TiO$_2$ nanoparticles as a function of size and shape is presented in Fig. 3.3. The Fig. 3.3 reveals that the melting temperature of TiO$_2$ nanoparticles decreases as the size of the particle decreases, similar to earlier results on metal nanoparticles [58-60]. There is a considerable difference in the behavior of melting temperature of nanoparticles of different dimension for the particles of smaller sizes. As the particle size increases, melting temperature increases and approaches to the melting temperature 1160 K of bulk irrespective of the shape. There is a rapid drop of the melting temperature below 5 nm which is consistent with earlier findings [58-60]. The melting temperature, which decreases with size, is minimum for 0-D structure and maximum for 2-D structure, for the same size. This is due to the fact that the size of nanoparticles decreases, surface to volume ratio increases, so there are more
number of surface atoms which are loosely bound and are responsible for the melting of nanoparticles. A remarkable feature is observed that the melting for 0-D structure is faster than the other structured (Dimension) material.

![Graph showing melting temperature of anatase TiO₂](image)

**Fig 3.3:** Melting temperature of anatase TiO₂

### 3.3.2 Diffusion Coefficient of TiO₂ Nanoparticles

The diffusion coefficient of undiffused nanoparticles for different shapes and size is presented in Fig. 3.4. The Figure reveals that the diffusion coefficient of TiO₂ nanoparticles (spherical) is maximum than the nanostructure of other dimensions such as one dimensional wire or two dimensional thin films due to the fact that the activation energy as well as melting temperature for TiO₂ spherical nanoparticle is lesser than the corresponding cylindrical (1-D) and thin film (2-D) nanostructures. This suggests that the reaction or diffusion can be made faster in the case of spherical nanoparticles. The size and shape dependent activation energy shows the same behavior as of melting temperature. The diffusion coefficient is nearly same for 0-D and 1-D structures of size below 2.5 nm. This may be due to the shape instability effect arising from the thermal fluctuation [61]. The present results on the size and shape dependent diffusion
Results and Discussion

A coefficient could not be compared with any experimental data due to their unavailability. However, an experimental diffusion coefficient at 453 K is available [61]. Therefore, to check the accuracy of the present approach, we have included the temperature effect in the calculation of size dependent diffusion coefficient and compared with experimental data at temperature 453 K in the inset of Fig. 3.4. The figure shows a reasonably good agreement between calculated and only available experimental size dependent diffusion coefficient in case of 2-D for 14 nm and 19 nm [62]. Since the considered size is only several nanometers, this decrease is induced not only by the contribution of surface, but also by the increase of internal energy of atoms within the nanocrystals. This indicates that the activity needed for diffusion is much smaller than the corresponding bulk. Further, this remarkable enhancement of diffusion ability due to reduced grain size leads to the possibility of surface chemical treatment of TiO$_2$ at much lower temperature than the usual treatment temperature. We also present the calculated diffusion time for TiO$_2$ nanostructures in Fig. 3.5 and observed that the variation of diffusion time with size shows a reverse behavior than the diffusion coefficient.

![Fig. 3.4: Diffusion coefficient of undiffused TiO$_2$](image1)

![Fig. 3.5: Diffusion time of TiO$_2$](image2)
3.3.3 Diffusion Coefficient of Nitrogen Diffused TiO$_2$ Nanoparticles

It is known that the diffusion or doping of metal and non-metal ions are widely used as it could better satisfy the property requirement for different applications especially when the optical or photocatalytic properties are mainly considered. The bandgap of TiO$_2$ nanocrystal is narrowed due to doping of both metal and non-metal. This is due to fact that the electron density around dopant is expected to be large in valance band and small in the conduction band compared to the undoped TiO$_2$. We have calculated the diffusion coefficient of diffused TiO$_2$ using the methodology discussed in chapter 2. The Fig. 3.6 presents the size and dimension variation for diffusion coefficient of nitrogen diffused TiO$_2$ nanostructures. Nitrogen doping seems to be more attractive among all of these anionic elements because of its comparable atomic size with oxygen, small ionization energy, metastable center formation and stability [3, 63]. The Fig. 3.6 shows that the diffusion coefficient depends on dimension and increases with the decrease in the size of TiO$_2$ nanoparticles. However, there is a remarkable increase in the diffusion coefficient of nitrogen diffused TiO$_2$. This increase in diffusion coefficient of nitrogen-diffused TiO$_2$ is the consequence of the decrease in melting temperature and activation energy due to the decrease in band gap of TiO$_2$ [64]. Fig. 3.7 presents the calculated electronic density of states of undoped, nitrogen doped, and platinum doped TiO$_2$ nanoparticles, using the plane wave pseudopotential method in the framework of local density approximation of density functional theory [64, 65]. It is observed from the figure that the N-doping introduces some states at the valance band edge and resulting into the narrowing of bandgap of TiO$_2$ nanoparticles. The details are however not discussed here.
The nitrogen octet rule is satisfied without inducing any significant structural change as the nitrogen occupies the oxygen sites.

**Fig 3.6**: Diffusion coefficient of N-doped TiO$_2$

**Fig. 3.7**: Density of states of undoped, N and Pt-doped TiO$_2$ (Fermi level $E_f$ set to zero)
3.3.4 Diffusion Coefficient of Platinum Diffused TiO$_2$ Nanoparticles

The Fig. 3.8, we present size variation of diffusion coefficient of platinum, of different shapes diffused in TiO$_2$ nanoparticles. We use entropy and pre-exponential factor for different shapes of Pt nanoparticles from experimental work of Narayana et al. [66]. Fig. 3.8 reveals that the diffusion coefficient in the case of diffused cubic Pt nanoparticles increases rapidly below 4 nm. The diffusion coefficient in the case of tetrahedral shape Pt nanoparticles doped TiO$_2$ does not show any variation with size. This may be due to the fact that the tetrahedral particle has sharp edges and corners corresponding to either very high or very low value of activation energy [66]. In the case of cubic nanoparticles most of its atoms are at the surface located on (100) facet. These surface atoms are not tightly bound and give rise to high value of activation energy and entropy of activation.

Fig. 3.8: Diffusion coefficient of Pt-doped TiO$_2$

Similarly, in the case of spherical nanoparticles most of the atoms are located on (111) and (100) facets with edges at the interface of these facets [66]. A remarkable feature observed in Fig. 3.8 that the diffusion coefficient for spherical shape Pt nanoparticles lies
between cylindrical and tetrahedral shape is due to the fact that the activation energy of spherical nanoparticles follows the similar trend. The calculated diffusion coefficient of platinum diffused TiO$_2$ for 0-D, 1-D and 2-D is presented in Fig. 3.9 and shows similar behavior as observed for nitrogen diffused TiO$_2$ nanostructures. However, we note that the diffusion coefficient of platinum diffused TiO$_2$ is more than the nitrogen diffused TiO$_2$ i.e. activation energy of platinum is lesser than nitrogen which corresponds to higher value of diffusion coefficient of platinum diffused TiO$_2$ as compared to the nitrogen diffused TiO$_2$, which is in good agreement with available data [66].
References


