

# Titanium dioxide is Preferred for Photo-catalytic and PEC Applications: Why?

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## Abstract

Titanium dioxide-based systems are the preferred photo-catalytic materials. Among this the commercial P25 has been consistently employed for Photo-catalytic and PEC applications. This system (~20% Rutile and ~80% anatase) possibly crystallizes in a core shell configuration and the relevance of this 10 patterning for the observed photo-catalytic or Photo-electrochemical (PEC) activity is examined.

## Introduction

The extensive exploitation of Degussa P25 (TiO<sub>2</sub>) for studies in photo-electrochemical splitting of water and photo-catalysis has to be rationalized even though, the objective of its use in reported studies is mainly for comparison purpose. Its remarkable reproducibility has to be recognized. It is presumed that P25 is a model core-shell system with anatase and rutile (4:1 weight ratio) and possibly the relative 15 thickness of the core and shell of this system is most appropriate for its behaviour as a photocatalyst. It is necessary that one recognizes the relative values of surface energy of the polymorphs of TiO<sub>2</sub> in order to recognize the type of core shell configuration this system can adopt. The values of the surface energies of the three polymorphs of TiO<sub>2</sub> are given in Table 1.

Table 1. Values of Surface energies of the three polymorphs of TiO<sub>2</sub>

Polymorphs of TiO <sub>2</sub>	Surface energy/J/m <sup>2</sup>
TiO <sub>2</sub> (Rutile)	2.2 ± 0.2
TiO <sub>2</sub> (Brookite)	1.0 ± 0.2
TiO <sub>2</sub> (Anatase)	0.4 ± 0.1

## Core/shell model

20 A few remarks on this system are appropriate. These are:

- (1) The core shell structure possibly alters the relative electronic structure of the system so as to be facile for photo-catalytic reaction and for charge separation and transfer.
- (2) The thickness of the shell (Anatase) may be optimum so as to provide adequate amount of surface adsorption and activation sites.
- (3) There are two possible routes for the electron transfer either from anatase core conduction band to Rutile conduction band or Rutile 25 conduction band to Anatase trap states. The correct electron transfer route has to be established..

The readers are referred to the following publications in this connection<sup>1-6</sup> wherein the superior photo-catalytic activity of hetero-junctions has been demonstrated over that of pure anatase or rutile in different reactions. Shi et al., have stated that the combination of anatase and rutile “demonstrates magic effects on carrier transfer in photo-catalytic application”<sup>7</sup>.

Another aspect of the studies on TiO<sub>2</sub> deals with doping with hetero atoms like C, N, S and others, in these studies it has been reported 30 that the reason for doping with these elements is to shift the photon absorption to visible region. This aspect has been examined recently in a review<sup>8</sup>. These studies must be considered in the light of the observations recorded that the coexistence of Rutile and Anatase phases and the depth of Rutile core and Anatase shell can be tuned by adjusting the “thickness of TiO<sub>x</sub>C<sub>y</sub> (x < y) and TiO<sub>x</sub>C<sub>y</sub> (x > y) in the precursor composite by a change of the calcinations temperature”<sup>9</sup>. It is necessary that one recalls the repeated reports in literature on the improvement of photo-catalytic activity due to metallization of TiO<sub>2</sub><sup>9</sup>.

35 In a recent publication, Wu et al<sup>10</sup> reported studies on TiO<sub>2</sub> single crystals with different percentages of {001} facets and have shown the higher is the percentage of {001} facets, the higher photo-oxidation reactivity and possibly also dependent of the size of the crystal. They postulate that this may be one of the important criterion for many of the oxides in photo-catalytic processes.

## The Energetics of Hetero-junction of Titania

The energetics of this hetero-junction has been considered by Deak et al<sup>11</sup>. They postulate on the basis of their computations that both 40 the bands (VB and CB) lie higher than those of Anatase and in this situation, the electrons accumulate in the anatase phase and holes are concentrated in the Rutile phase. This kind of charge separation can have the following consequences:

- (i) This configured system can possibly facilitate the hydrogen (reduction reaction) evolution from water decomposition
- (ii) The effective of charge separation may account for the unusual photo activity for water decomposition especially for hydrogen evolution so far reported on TiO<sub>2</sub> system

(iii) The holes accumulated on Rutile core may facilitate oxygen evolution and possibly account for the non-stoichiometric amount of oxygen evolution observed experimentally.

These authors have also proposed that the patterning of the photo-catalytic systems can selectively tune the properties of one of the components of the multi-component system by the various modes of sensitization (doping, metallization and other means of sensitization) and the structured configurations may also facilitate directional transfer of charges.

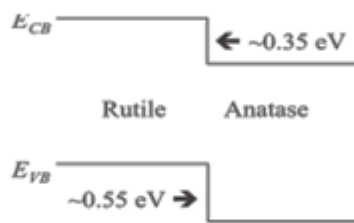


Fig.1 Schematic representation of the band line up between rutile and anatase reproduced from ref<sup>11</sup>.

A few other remarks are appropriate at this stage. Even though in this short presentation only titania system is considered, it may be equally applicable to other photo-catalytic and PEC systems. The generation of core shell configuration in titania systems have been attempted in a number of ways, like vapour phase hydrolysis<sup>7</sup>, as well as in caramelized sucrose (organic or inorganic) matrix followed by hydrothermal process generating capped systems which ultimately yields the core shell configuration of the same component namely titania in this case. Since the introduction of these hetero atoms favours core shell configuration, it is natural systems prepared using the precursors containing hetero-atoms will exhibit increased photo-catalytic and PEC activity. Liu et al.<sup>1</sup> have also claimed that the depth of the rutile core in the Anatase shell can be tuned by adjusting the thickness of  $\text{TiO}_x\text{X}_y$  (X being the hetero/metal atom and  $x < \text{ or } > y$ ). There can be alternate methods of generating core shell configurations. It may be possible that the presence of hetero atoms or metallic species may be inducing/retarding the phase transformation of anatase to rutile<sup>12-14</sup> and the extent of these species inducing the phase transformation and the conditions employed may be responsible for this core shell configuration being formed in  $\text{TiO}_2$ .

### PEC and Photo-catalytic Activity

The core shell configuration together with the inducing species may be providing the necessary energetics for the charge transfer. It has been claimed in a recent communication<sup>15</sup> that at the interface the metallic species absorbs photons to undergo Plasmon excitations and these energized charges are responsible for effective transfer to the substrate at the contact site. It is possible that the interface sites are appropriate for photo catalytic behaviour for charge transfer including hydrogen evolution from water splitting by PEC. As stated earlier, it is possible that in this core shell configuration one may have alternate charge transfer routes in addition to possibly increasing the life time of the exciton which may be responsible for the observed changes in photo-catalytic or PEC applications. The charge transfer routes can be from rutile to anatase or to the trap states in anatase with or without the involvement of the phase transferring agent.

It is possible that many of the photo-catalysts or the materials employed in PEC applications have this patterned configuration. Those systems that do not fit to the patterned configurations may not exhibit perceptible photo-catalytic activity or may not find use in PEC application. Further studies alone will provide answer to this important aspect.

It is necessary to understand how these dopants promote the phase transformation and how the patterned configuration is generated in titania system. This aspect requires an understanding of the crystal structure of both anatase and Rutile forms. Even though both the forms have titanium ions in six fold coordination of oxide ions the arrangements of the oxide ions are different as shown in Fig.2.

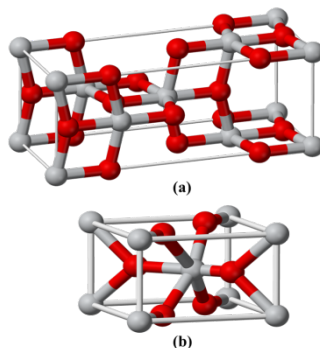


Fig.2 The atomic arrangement in a). Anatase, b). Rutile

Accordingly, the unit cell parameters also differ. At this stage a few remarks may be appropriate. Normally, depending on the magnitude of rearrangement of atoms required for phase transitions, the conventional variables of temperature and pressure are fixed. However, it is known that certain additives also can induce the phase transition possibly by inclusion in the lattice such that lattice

contraction or alteration can be easily achieved. In the case of Anatase to Rutile transformation, the inclusion of hetero-atoms or even possibly certain metallic species may favour this phase transition in a facile manner. This could be one of the reasons that titanium dioxide samples prepared in the presence of hetero-atom containing precursors especially C or N could have both the phases.

There are still some questions which have to be answered. These include:

- 5 (i) Is there a possibility of controlling the extent (in terms of %) of simultaneous phases present in a given sample of Titania?
- (ii) How the core shell model generate active sites for the photo-electrochemical decomposition of water?
- (iii) Why these sites are more active than the active sites normally present on single phase materials? These aspects need careful consideration in future.

In order to elucidate further, DFT calculations have been carried out on typical units representing pure anatase, pure rutile and anatase-rutile combination in an assumed configuration as shown in Fig. 3(a) The configuration shown in the combination may be considered as representing a core shell model. The density of states per unit of building block is considered and the results obtained is shown in Fig.3(b). It is seen that the valence band density of states for the core shell configuration is particularly altered with respect to that of either pure anatase or pure rutile. Wu et al.<sup>10</sup> have shown that the absorption edge has red shifted as the crystal size is decreased. They have postulated that the band gap of anatase is nearly independent with different percentage of reactive facets while the band gap is narrower with smaller particle size. The width of the valence band is the same for uniform particle size with different percentage of facets ( of the order of 6.42 eV) while systems with varying particle size with the same percentage of facets showed decreasing band width. They concluded that the crystal size is an important factor for the electronic and band structure of anatase. However, there are no reports on the effect on these parameters by the presence of another phase along with anatase. It is generally known that the added phase can alter the phase transfer characteristics of the original anatase phase. It is also possible that the size control that will inherently take place in the core shell model can also alter the wave functions of both valence and conduction band of the resulting system and also create additional active sites at the interface. Against these results, the calculations lead to the following points:

1. Pure anatase shows higher density of states at the valence band as compared to pure rutile or anatase-rutile combination. This will have implications for the observed photo-activity of anatase phase as compared to other phases.
2. The valence band width (~2.5 eV) appears to be greater for the rutile-anatase combination rather than the other two pure phases.
- 25 This could be the reason why the combination system exhibits higher photo-activity. This can result in higher photon absorption cross section and thus facilitate facile electron hole pair formation.

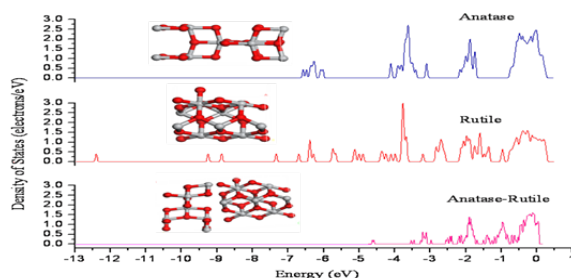
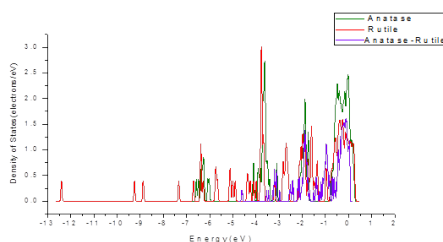


Fig 3 (a) Density of states for pure anatase, rutile and anatase-rutile combination calculations on representative cluster size of M9O18 for both systems.



30 Fig.3 (b) - Density of states for three systems anatase, rutile and anatase-rutile combination

3. The observation certain facets of titania is more active as compared to other facets may imply that in the presence of both polymorphs may induce these active phases to be predominant in the combined system.
4. It is also possible that the interface sites (anatase-rutile) may be differently active, and their electronic structure of the interface may be favourable for the combined system to be better photoactive.
- 35 It is necessary that the postulates presented need further experimental verification and it is hoped that not only core shell model, but other combination configurations may be also similarly active.

## Computational Details

All the calculations have been carried out in the CASTEP 5.5 implemented in materials studio package 5.5. A molecular unit of  $Ti_9O_{18}$  cluster is used for the model of anatase and rutile. The Density functional theory electronic structure calculations were performed in Generalised Gradient Approximation (GGA) method employing the exchange correlation function of PW91, with default spin. Cluster is

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treated with plane wave method with the energy cut-off value 300eV and the k points of  $5 \times 3 \times 1$ . For single point energy and Density of States Calculations (DOS) the self-consistent field convergence window is set to be  $2.0e^{-6}$ eV/atom along with  $48 \times 48 \times 48$  FFT grid with the augmentation density scaling factor of 1. The pseudopotentials were treated as Ultra soft in the real space system. The calculated DOS is plotted with smearing of 0.2 eV.

## 5 Acknowledgment

The authors thank Department of Science and Technology, Government of India for their generous support.

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