

Nitrogen and Fluorine Incorporation in TiO₂

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1 Introduction

Various strategies have been pursued to make a typical semiconductor like Titanium dioxide(TiO₂, Anatase or Rutile) to be photo-active in visible region due to higher percentage component of this range in the solar radiation. Normally in the unsubstituted state, TiO₂ is active only in UV region with typical band gap values of 3.2 eV for anatase and 3.02 eV for the Rutile phase. Variety of strategies have been adopted to make TiO₂ active in the visible region like coupling semiconductors, doping with a variety of species and sensitization with molecular entities. In a recent publication, Scanlon et al., [1] have considered the band alignment of rutile and anatase and proposed that the electrons from the conduction band of rutile (obtained from the photo-excitation)are transferred to anatase and thus the life time of the exciton is increased. Thus they accounted for why the combination system is more active than the single polymorph of titanium dioxide. This possibly provides an explanation why P 25 Degussa sample of titanium dioxide is often taken as reference for evaluating the photo efficiency of semiconductors. In another recent publication C N R Rao et al [2] cosubstituted nitrogen and fluorine in TiO₂ and provided a variety of evidences both experimental and theoretical for the shift of the absorption edge to the visible region.

In recent times, substitution of hetero-atoms mostly N, C, B. and S in semi-conducting oxides has been reported as a means of extending the wavelength of photon absorption to the visible region[3]. UV light accounts about 5 % of solar energy while 45% of its energy falls within visible region [4]. Therefore attempts have been made for activating photo-catalysts in the visible light[5]. One such attempt is the substitution of Ti ions by means of metal ions like Fe,Mn, Au, Ag and Cr [6,7] and also by doping TiO₂ with non metal species such as nitrogen and other atoms mentioned above [8-11]. These studies have been repeated in literature a few times to demonstrate the reproducibility

of the observations[12]. This situation has also been recently reviewed with doubts on the nature of the substitution especially that of nitrogen either cationic or anionic, though most of the available literature assumes it to be anionic in place of oxide ions in the lattice[13]. There are various arguments for the shifting of the absorption wavelength to the visible region by doping with nitrogen, the two essential postulates are, that the 2p wave functions of nitrogen mix with the 2p wave functions of oxygen thus raising the top of the valence band or isolated narrow band is placed above the valence band which could be the reason for the response in visible region.[14] Even though in reference 13, the authors have raised doubts about the valence state of incorporated nitrogen in oxide lattice, the evidences available so far seem to favour anionic state for the incorporated nitrogen atoms in the lattice. The points in favour of this postulate are:

1. The relative size of oxide anions and nitride anion.
2. The possibility of highest occupied states of nitride species overlapping with the valence band of the oxide ions thereby altering energetically the top of the valence band thus extending the photon absorption wavelength towards visible range.
3. The corresponding cationic vacancies can give rise to allowed energy states in the band gap thus accounting for the shift of the photon absorption wavelength.

It is therefore necessary to compare the band positions of pure semiconductor and nitrogen doped semiconductor. One such schematic diagram is shown in Fig.1. The essential features of this band diagram is that the top of the valence band is shifted to less positive value (in electro-chemical scale) or to less energy in absolute energy scale. Possibly the bottom of the conduction band is not altered significantly and it is at the same energy value of the pure semiconductor. The cationic vacancy states are now have allowed energy states in the band gap. A simple pictorial representation of this is given in Fig.1. The possible supports for this model are as follows:

1. Nitrogen incorporated semiconductors showed photo absorption to longer wavelengths compared to the pure semiconductor.
2. Diffuse Reflectance Spectrum (DRS) of these samples showed enhanced absorption at higher wavelengths compared to the band gap excitation.

In Fig 2 the DRS spectrum of Nitrogen incorporated TiO_2 is shown and it is seen that above the conventional band gap which is usually identified by the gradient changes, there is absorption in longer wavelengths as compared to pure TiO_2 lending support that there are additional energy levels present in the band gap and this accounts for higher absorption in nitrogen doped semiconductors at higher wavelengths. It may be appropriate to consider in detail the results recently reported by Rao et al [2] for substitution of N and

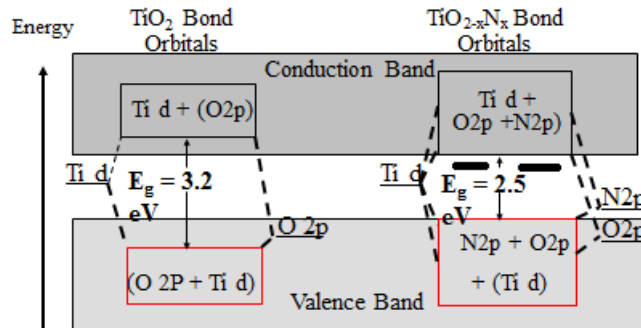


Figure 1: (A) represent the band positions for the pure semiconductor and B that for nitrogen doped semiconductor. Note the top of the valence band is shifted with respect to the pure semiconductor upwards(!)and additional energy states are introduced in the band gap

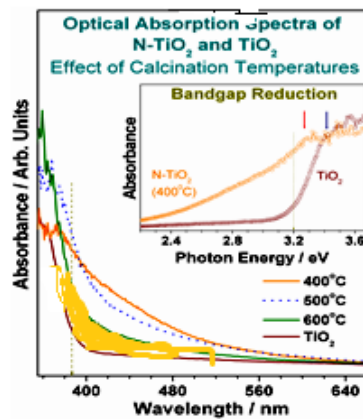


Figure 2: DRS spectrum of nitrogen doped TiO_2 and one can see not only the band gap value is changed but also the photon absorption for doped semiconductors are higher at higher wavelengths as compared to Pure TiO_2 . This observation may be true of most of the DRS reported in literature for nitrogen doped semiconductor **Note**: the yellow shaded region

F in TiO₂. Certainly their DRS spectrum reproduced in Fig.3 shows that the N and F substitution in TiO₂ shifts the absorption edge to longer wavelength. However, their extensive XPS data identifies three nitrogen species (nitrogen atom directly bonded to Ti, interstitial nitrogen atom and NH species) and two fluorine species (TiOF₂ and fluorine substituted in oxygen site). The stoichiometry computed by them also shows that the substituted system may be non-stoichiometric. The larger shift of the absorption band to longer wavelength for the co-doped system has also not been accounted for. They have provided theoretical justification for the formation of N2p-derived sub band above the valence band but possibly this may not account for the greater absorption for the codoped system experimentally observed. From the calculation of bond effective charges, they have concluded that the mixed ionic-covalent and ionic nature of the Ti-N and Ti-F bonds respectively. It may be some interest that similar concept on the extent of ionicity and covalency of the metal anion bond has been proposed as a selection criterion for the choice of materials for photoelectrochemical behaviour of semiconductors [15]. It would be interesting to examine how these two concepts can be coupled and used for the formulation of new semiconducting materials for higher photocatalytic activity and also for the photoelectrochemical decomposition of water.

2 Alternate Model

The results considered in this presentation can also be treated in terms of another model. In the case of nano-state due to high surface, there will always be segregation of one phase over another phase as a result of surface free energy differences. This situation can be present in substituted systems since the substituents can segregate and thus give rise to core shell configuration such that the photon is absorbed in the shell and the exciton is transported to the core where the charge transfer reaction takes place. This situation may also be possible in nitrogen incorporated semiconducting oxides and thus one can also account for the observed enhanced photo-catalytic behaviour of substituted systems on this model. The band alignment concept put forth by Scanlon et al[1] may also be accountable by such a model.

The possible message that one seems to draw is that the selection of materials for photo-electro-chemical applications can be based on a configuration system with core and shell so that in one part the photon absorption takes place and the excited charge carriers move over to the other part thus increasing the life time of the charge carriers thus reducing the probability of recombination which is otherwise the predominant route for the charge

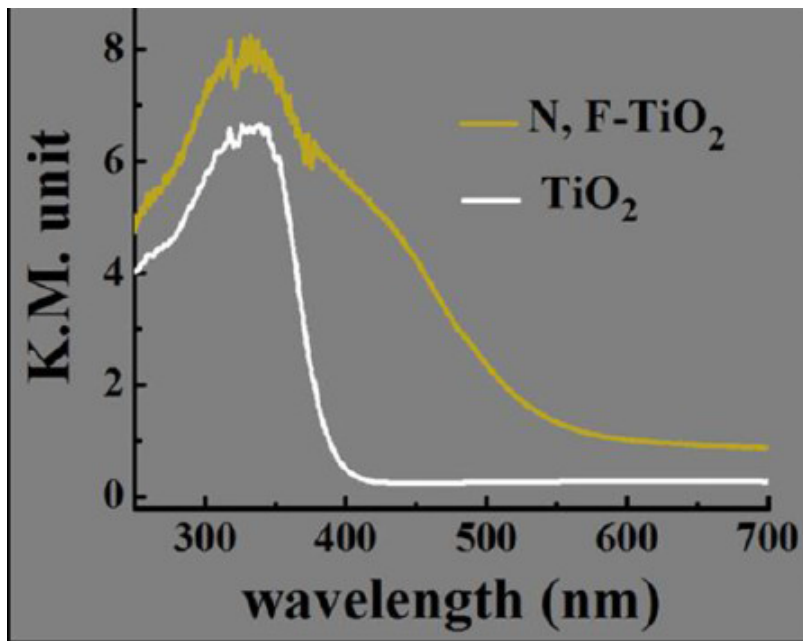


Figure 3: DRS spectrum of nitrogen doped TiO₂ and one can see not only the band gap value is changed but also the photon absorption for doped semiconductors are higher at higher wavelengths as compared to Pure TiO₂. This observation may be true of most of the DRS reported in literature for nitrogen doped semiconductor

carriers generated.

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