Nitrogen and Fluorine Incorporation in Titanium dioxide

B. Viswanathan

National Centre for Catalysis Reseach

Indian Institute of Technology, Madras, Chennai 600 036

1. INTRODUCTION

Various strategies have been pursued to make a typical semiconductor like titanium dioxide (TiO2, Anatase or Rutile) to be photo-active in the visible region due to higher percentage component of this range in the solar spectrum. Normally in the unsubstituted form 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 of semiconductors, doping with a variety of species and sensitization with molecular entities. In a 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 and anatase and proposed that the electrons from the conduction band of rutile (obtained from photoexcitation) are transferred to the 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 evaluation the photo-efficiency of semiconductors. In another publication by some other authors [2] co-substituted 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-atom mostly N, C, N and S in semiconducting 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 the solar energy while nearly 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 substation of Ti ions by means of metal ions like Fe, Mn, Au, Ag and Cu [6, 7] and also by doping titanium dioxide with non-metal species like 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 been recently reviewed with doubts on the nature of the substation 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 the visible region [14]. Even though in reference [13] the authors have raised doubts on the valence state of incorporated nitrogen in oxide lattice, the evidences available so for 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 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 wave length.

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 are that the top of the valence band is shifted to less positive value (in electrochemical scale) or to less energy in absolute energy scale. Possibly, the bottom of the conduction band is not altered to any significant extent and it is at the same energy value of the pure semiconductor. The cationic vacancy states have now allowed energy states in the band gap. 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 bang gap excitation.

In Fig2. the DRS spectrum of nitrogen incorporated TiO2 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 TiO2 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.

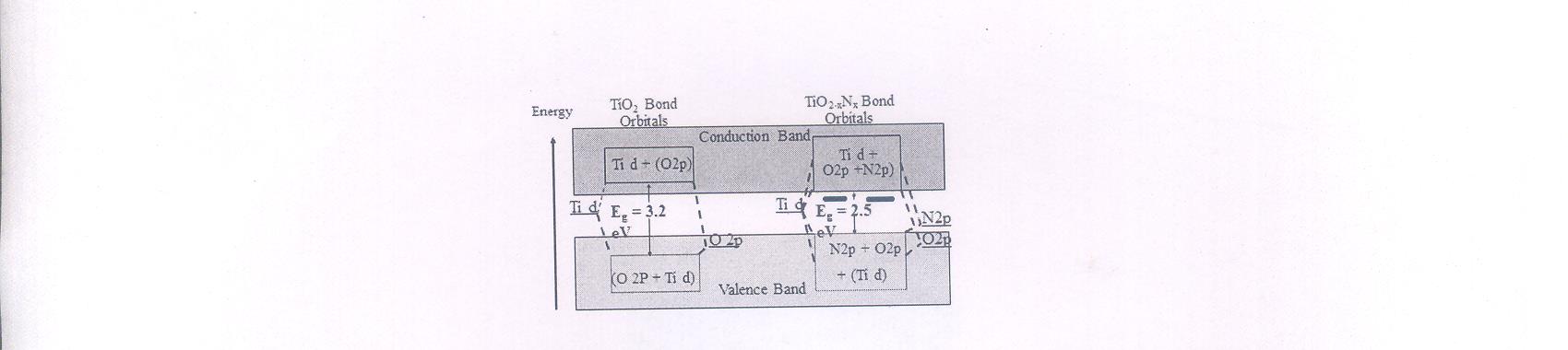


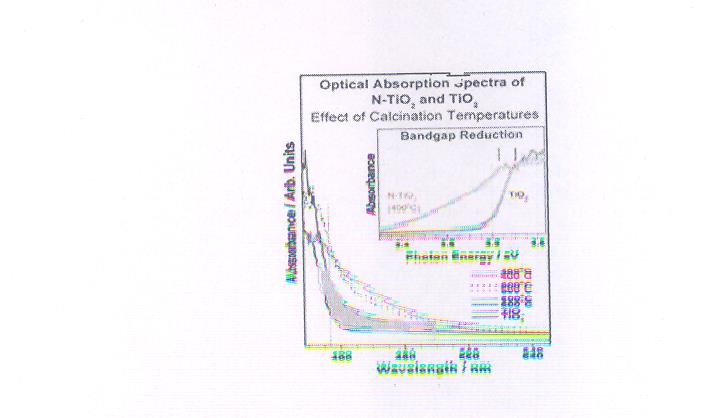
Fig.1. (a) Represent the band positions for the pure semiconductor and B that of nitrogen doped semiconductor. Note the top of the valence band is shifted with respect to pure semiconductor upwards (?) and additional energy states are introduced in the band gap.

Figure 2 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 semi-conductors are 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. Note the shaded region.

1. Alternate Model

The results considered in this presentation can also be treated in terms of alternate model. In thecae of non-state due to high surface, there will always be segregation of one phase over another phase due to surface free energy differences. This situation can be present in substituted systems since the substituents can segregate and this 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 this one can also account for the observed enhanced photo-catalytic behavior of the substituted systems. The band alignment model proposed by Scanlon et al., may also be accountable by this alternate model.

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

References

1. David O.Scanlon, Charles W.Dunnill, John Buckeridge, Stephen A.Shevlin, Andrew J.Logsdail, Scott M.Woodley, C.Richard A Catlow, Michael J.Powell, Robert G.Palgrave, Ivan P.Parkin, Grame W.Watson, Thomas W.Keal, Paul Sherwood, Aron Walsh and Alexey A.Sokoll, Band alignment of rutile and anatase, Nature Materials, 12, 798, (2013).
2. Nitesh Kumar, Vrmimala Maitra, Vinay I Hegde, Umesh V Waghmare, A. Sundaresan and C.N.R Rao, Inorg.Chem., Doi:org/10-121/IC401426g/inorg.chem.
3. M.Sathish, B.Viswanathan, R.P.Viswanath and C.S.Gopinath, Synthesis, characterization and electronic structure and Photo-catalytic activity of N-Doped TiO2 nanocatalyst, Chem.Mater., 17, (2005)6349.
4. S.Yin, H.Yamaki, M.Komatsu, Q.Zhang, J.Wang, Q.Tang, F.Saito, and T.Sato, Preparation of nitrogen doped titania with high visible light induced photocatalytic activity by mechanochemical reaction of titania and hexamethylenetetramine, J.Mater.Chem., 13, 29963001.
5. A.Khalilzadeh and S.Fatemi, Modification of nano-TiO2 by doping with nitrogen and fluorine and study of acetaldehyde removal under visible-light irradiation, Clean Techn.Envion Policy, DOI:10.1007/s10098-013-0666-7 22 nd August, 2013.
6. S.Klosek, and D.Raftery, Visible light driven V-doped TiO2 photocatalyst and its photooxidation of phenol, J.Phys.Chem., B105:28152819 (2001)
7. J C S Wu, and C H Chen, A visible light response vanadium-doped titania nanocatalyst by sol gel method, JPhotochem.Photobiol., A 163:509515 (2004)
8. C.Burda, Y.Lou, C.Chen, A C S Samia, J.Stout and J.Gole, Enhanced nitrogen doping in TiO2 nanoparticles, Nano Lett., 3:10491051 (2003).
9. S.Joung, T.Amemiya, M.Murabayashi and K.Itoh, Mechanistic studies of the photocatalytic oxidation of trichloroethylene with visible light driven N-Doped TiO2 catalyst, Chem Eur.J., 12:55265534 (2006).
10. T.Umebayashi, T.Yamake, H.Itoh and K.Asai, Band gap narrowing of titanium dioxide by Sulphur doping, Appl.Phys.Lett., 81:454456 (2002).
11. H A Le. L.T.Linh, S.Chin, J.Jurng, Photocatalytic degradation of methylene blue by a combination of TiO2 anatase and coconut shell activated carbon, Powder Technol., 225:167175 (2012)
12. X.Li, Z.Chen, Y.Shi and Y.Liu, Preparation of N, Fe co-doped TiO2 with visible light response, Powder Technol., 207:165169 (2011).
13. B.Viswanathan and K R Krishnamurthy, Nitrogen incorporation in TiO2 Does it make it a visible active photoactive material? International Journal of photoenergy, DOI:10.1155/2012/269654
14. H.Irie, Y.Watanabe, and K.Hashimoto, Nitrogen concentration dependence on photocatalytic activity of TiO2-xNx powders, J.Phys.Chem., 107:54835486 (2003).