Band gap narrowing for visible light active photocatalysts:
Is it really narrowing?

Suresh Pillai

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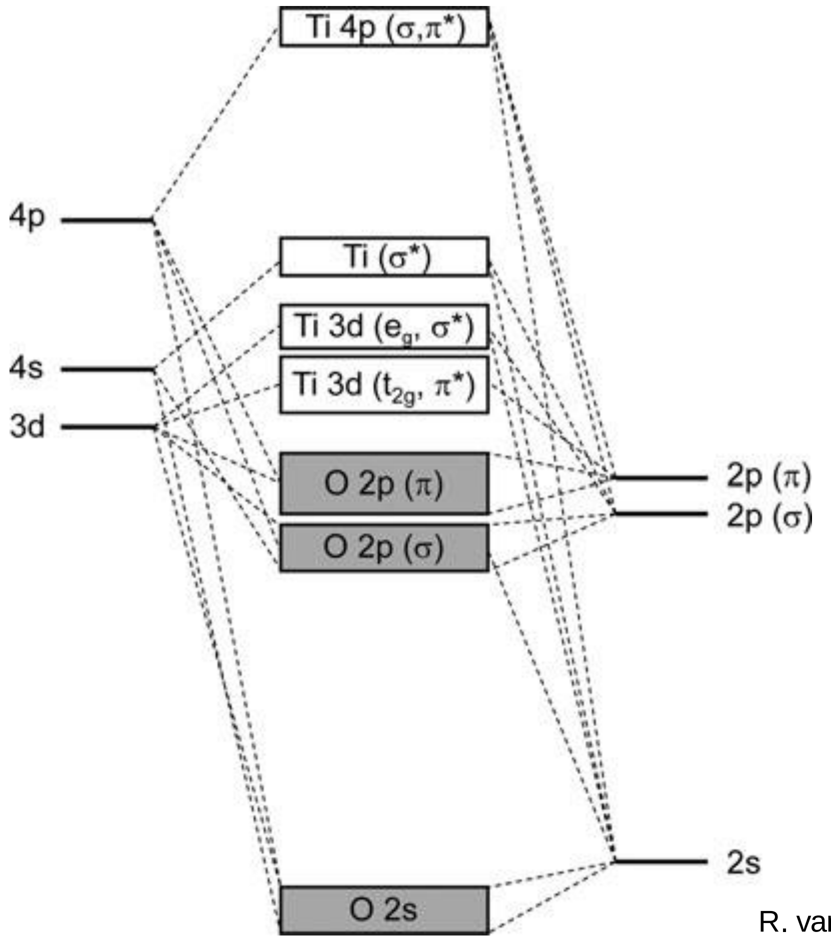
16/06/2015

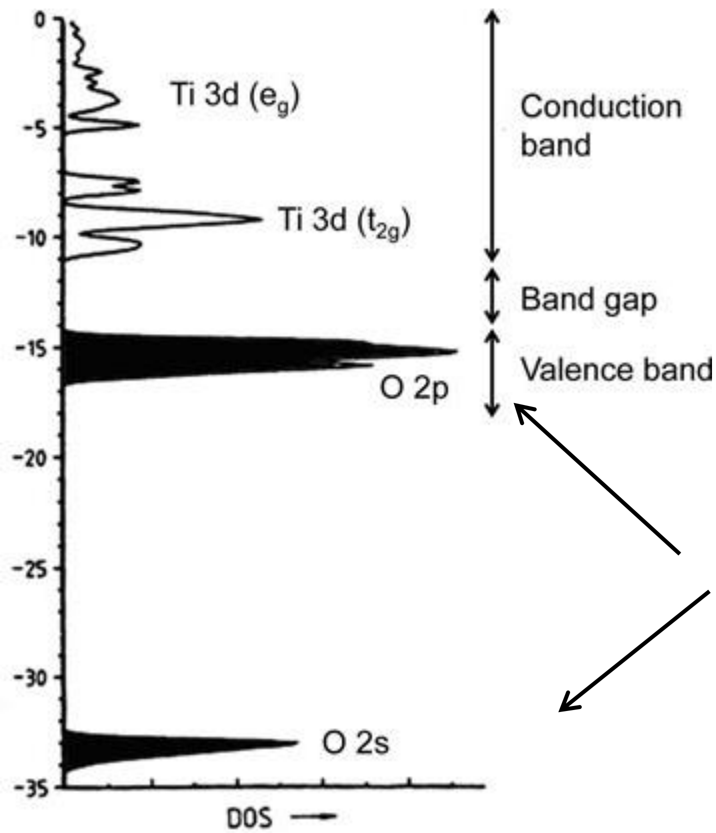
A Chemist's view of band-gap structure



Molecular orbital diagram of TiO2

R. van de Krol and M. Gra¨tzel (eds.), Photoelectrochemical Hydrogen Production,
Electronic Materials: Science & Technology 102, DOI 10.1007/978-1-4614-1380-6_2,
Springer Science+Business Media, LLC 2012

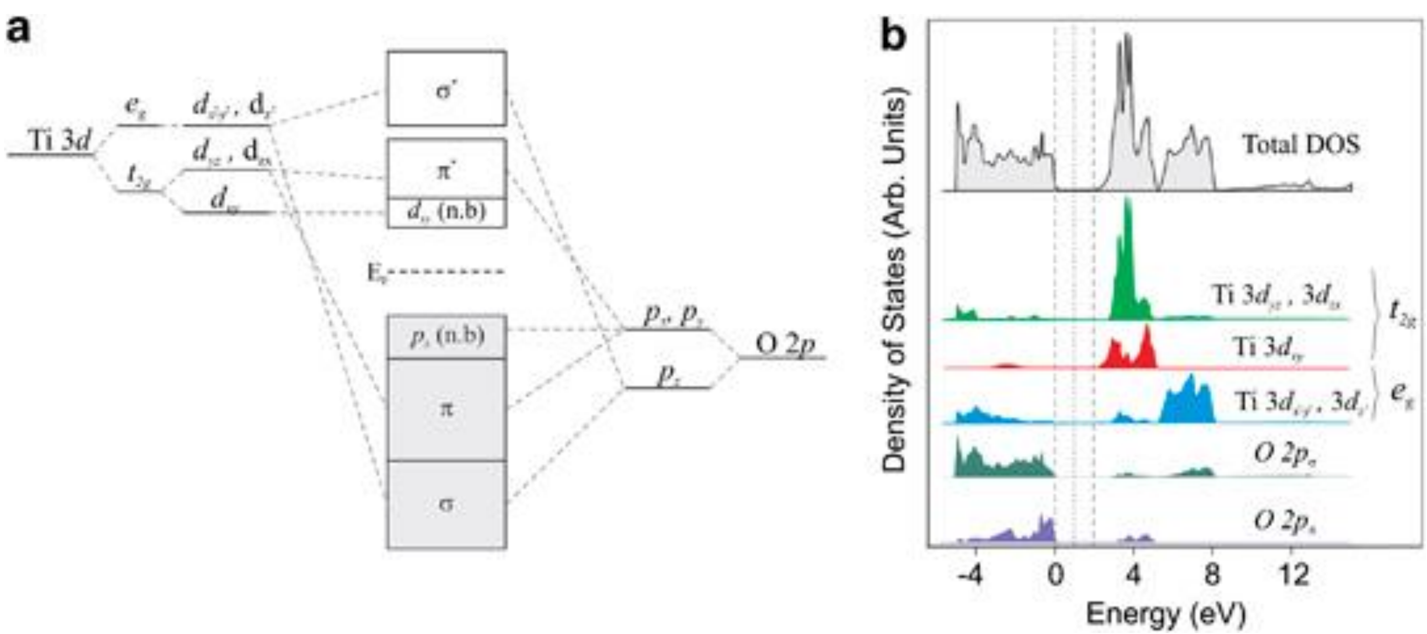
Electronic band structure and density-of-states (DOS) TiO_2



The black parts of the DOS indicate completely filled bands.

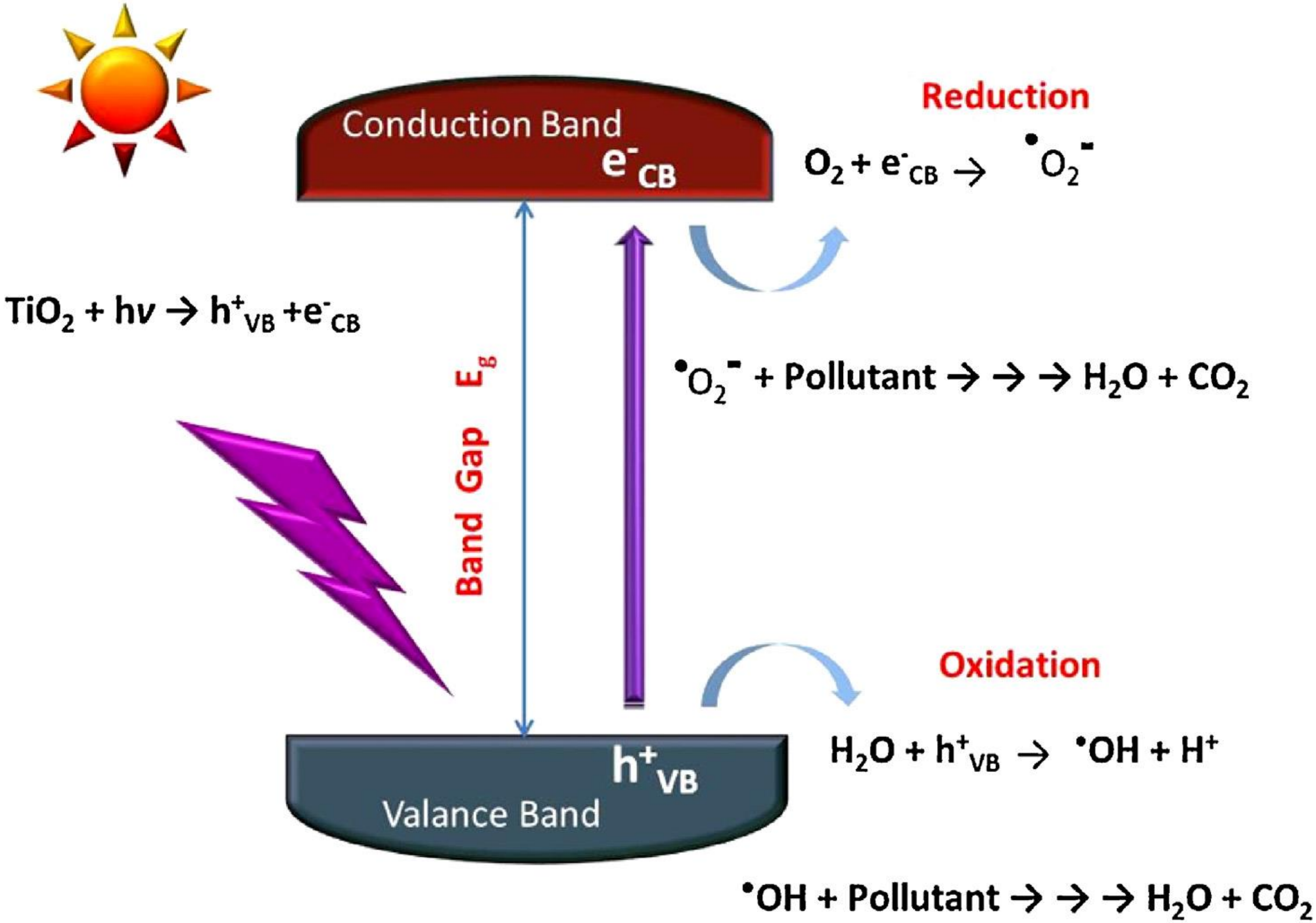
Adapted from Hoffmann, R.: Solids and Surfaces – A Chemist's View of Bonding in Extended Structures.
Wiley-VCH, Weinheim (1988)

Electronic band structure and density-of-states (DOS) TiO2.



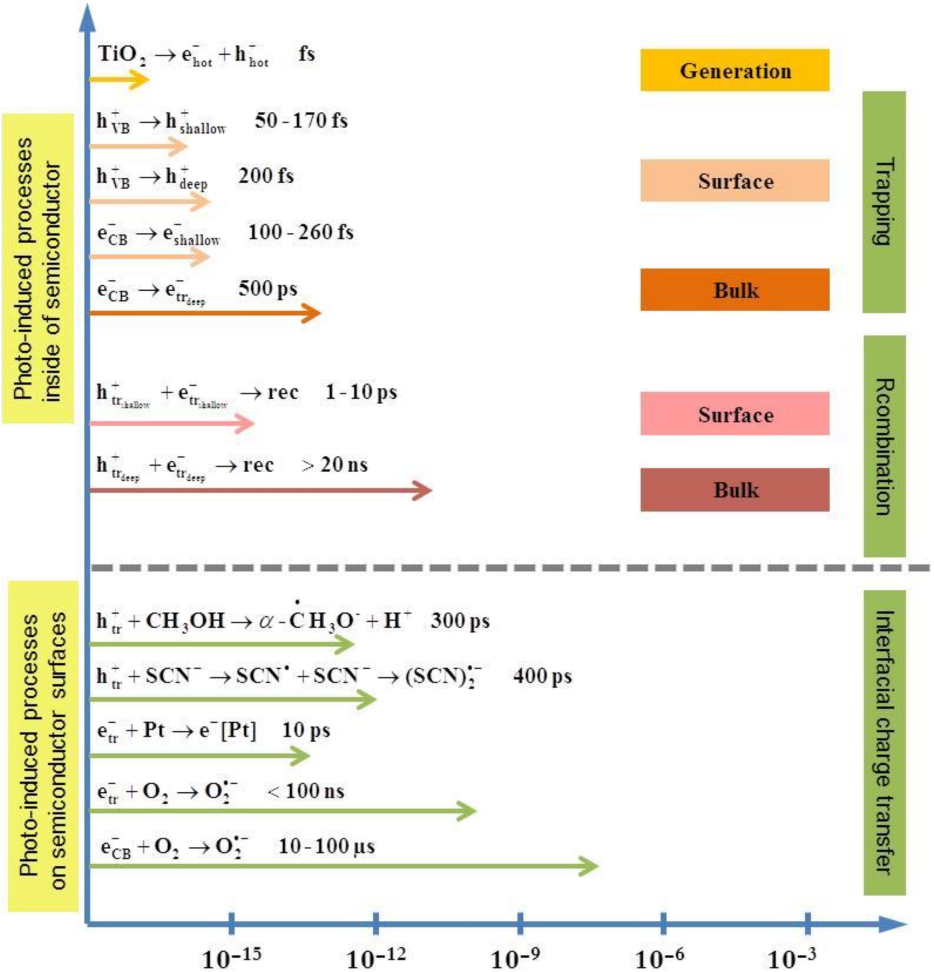
Molecular orbital energy-level diagram of anatase TiO_2 (adapted from Asahi *et al.*). (**b**) Calculated total density of states (top) and projected density of states for Ti 3*d* and O 2*p* orbitals (below), as labelled (adapted from Jiang *et al.*).

What is photocatalysis?



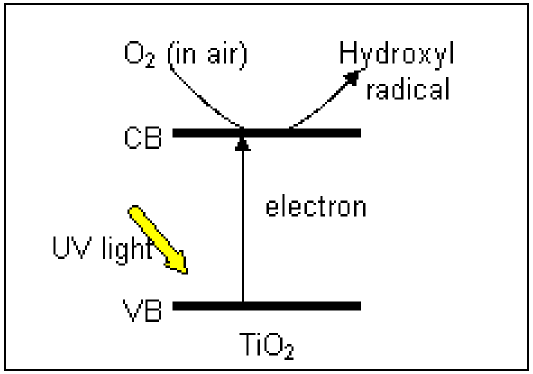
Swagata Banerjee, Dionysios, D. Dionysioub, Suresh C. Pillai *Applied Catalysis B: Environmental* 176 (2015) 396–428

Various steps involved in TiO_2 photocatalysis

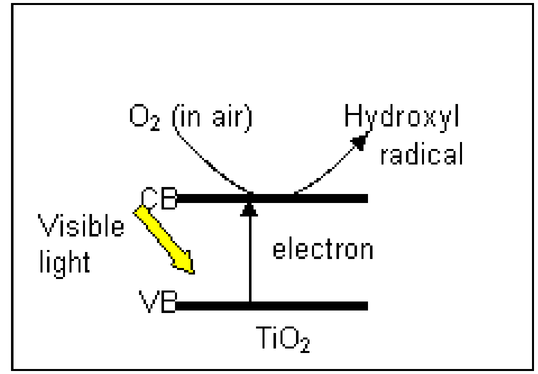


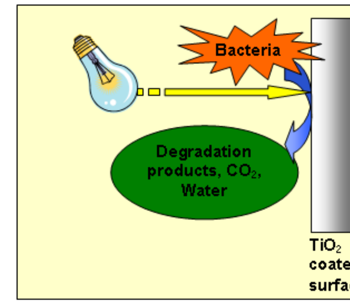
J. Schneider, M. Matsuoka, M. Takeuchi, J. Zhang, Y. Horiuchi, M. Anpo, D.W. Bahnemann, Chem. Rev., 114 (2014) 9919.

Visible light activity



Tuning of Band Gap





Conventional TiO_2

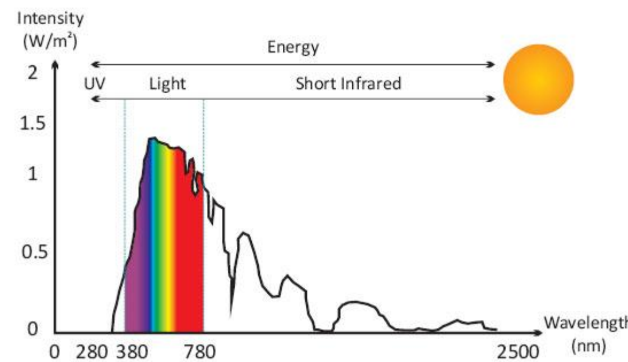
Visible light active TiO_2

Band gap 3.2 eV

$E=hc/\lambda$

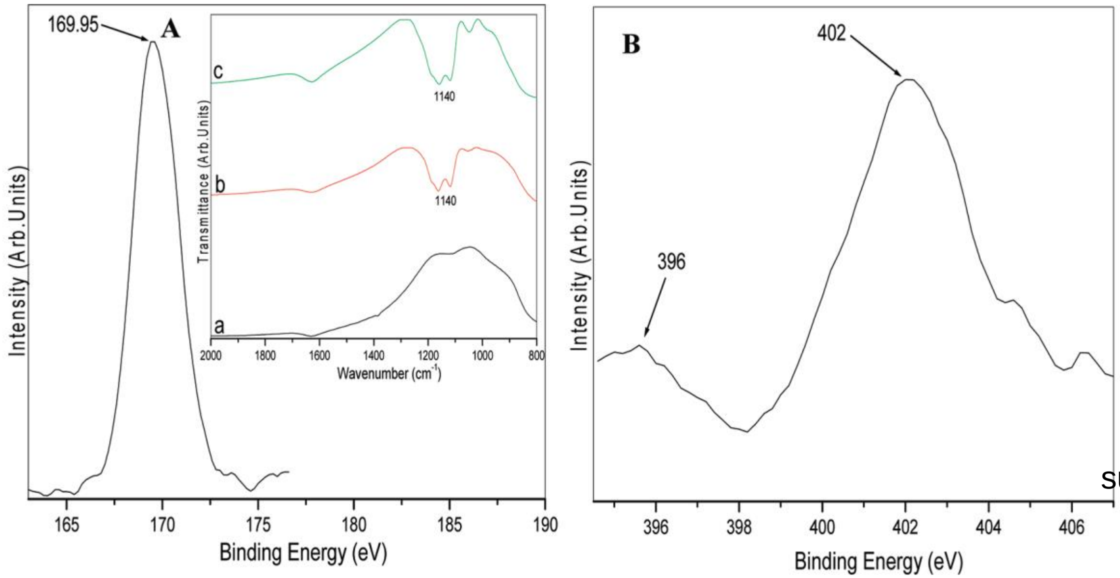
$\lambda=hc/E$

$\lambda=1240/3.2=387.5\text{nm}$



Irradiation with UV light is not practical in hospitals. Visible or room light irradiation is ideal

XPS Analysis of N,S doped photocatalyst



lattice nitrogen (N−Ti−N at 396 eV)

interstitial (Ti−N−O at 402 eV)

404.5 and 406.5 represent

surface-adsorbed nitrogen species such as NO_X and NH_X

S 2p peak at 169.95 eV - S^{6+} cation.

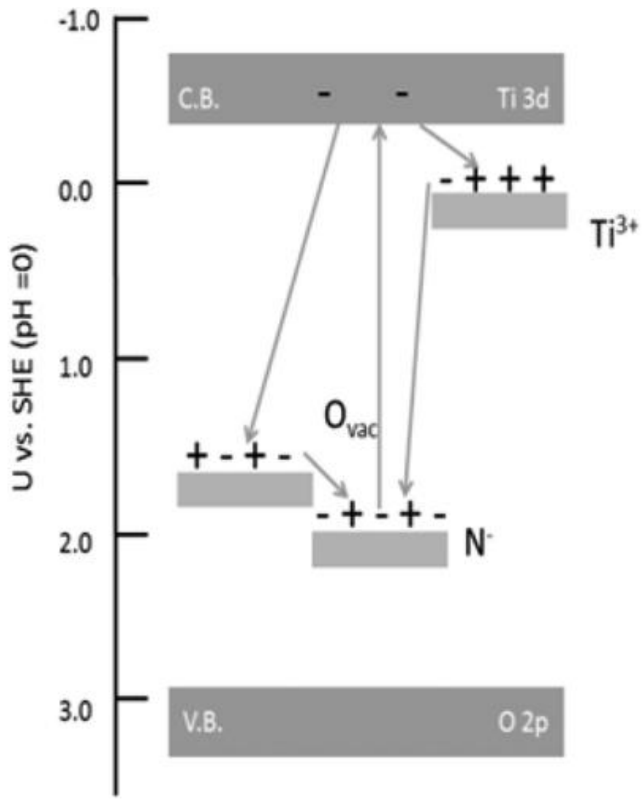
FTIR 1140 cm^{-1} - bidentate sulfate ions

No Ti−S bonds (162−163 eV)

Ionic radius of S^{2-} (1.7 Å) compared to that of O^{2-} (1.22 Å).

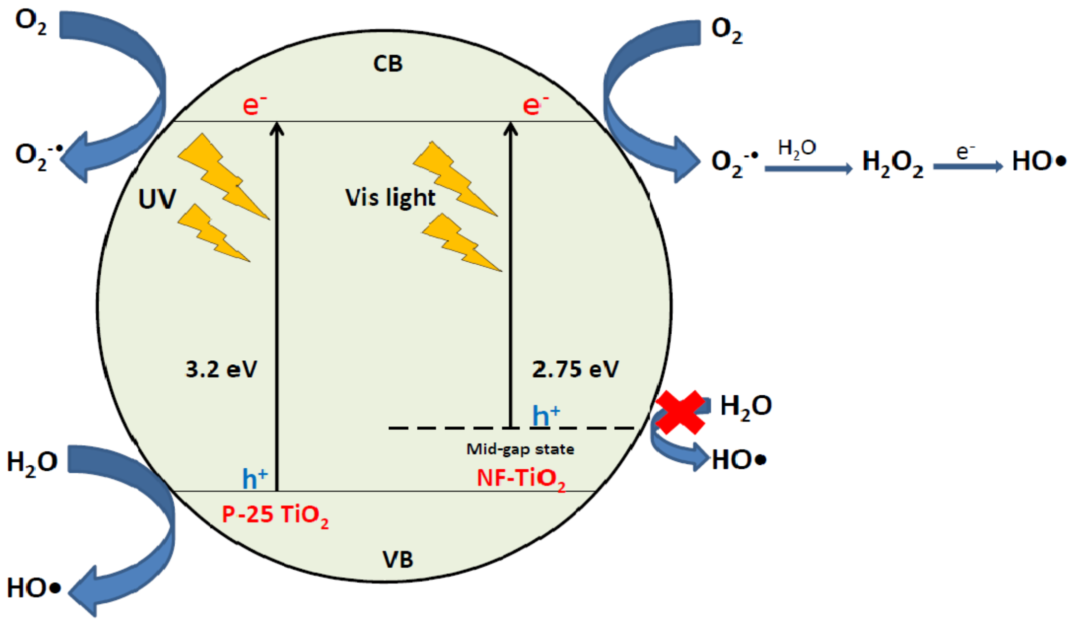
V. Etacheri, M. K. Seery, S. J. Hinder and S. C. Pillai*, *Inorganic Chemistry*, **2012**, 51, 7164−7173

Visible light excitation of N-F co-doped TiO_2 and refilling of empty N states

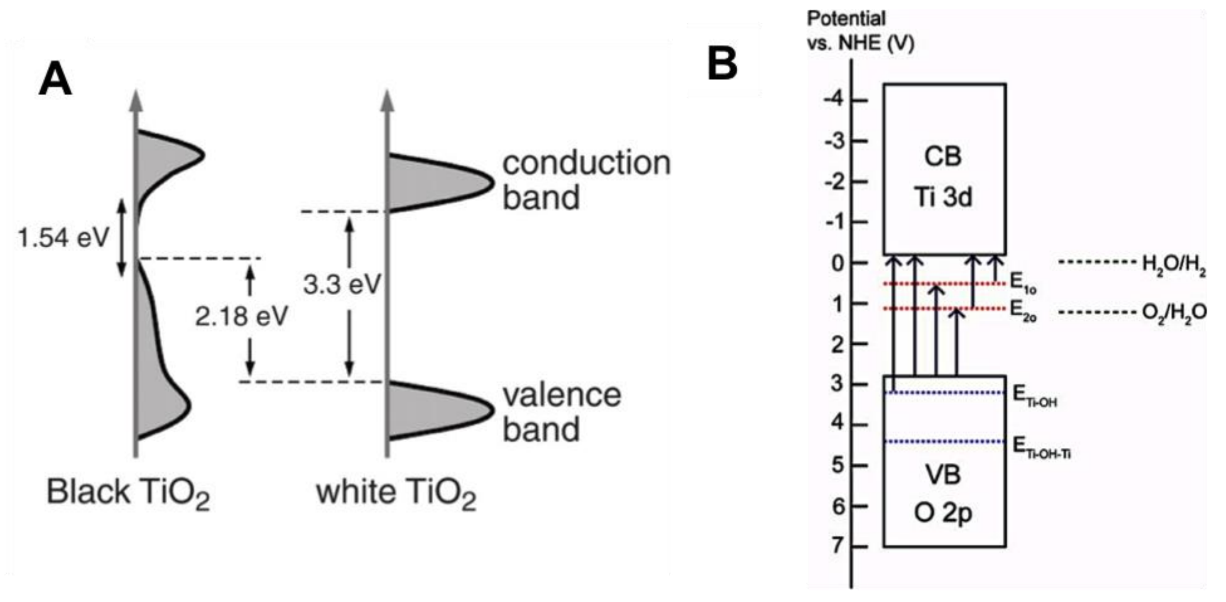


Hamilton *et al*. *J. Phys. Chem. C, Vol 118,* 2014 pp 12206–12215

Production of different ROS during the visible light active photocatalytic processes



Density of states of black TiO_2 and white TiO_2 nanocrystals



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Inorganic Chemistry

Article

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Inorganic Chemistry, **2012**, 51, 7164−7173

Nanostructured $Ti_{1-x}S_xO_{2-y}N_y$ Heterojunctions for Efficient Visible-Light-Induced Photocatalysis

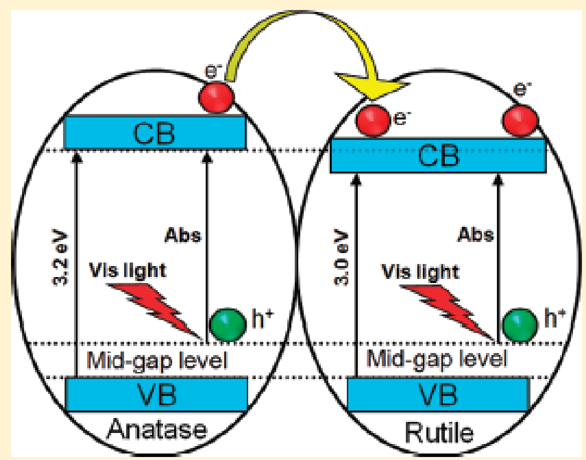
Vinodkumar Etacheri,[†,‡] Michael K. Seery,[‡] Steven J. Hinder,[§] and Suresh C. Pillai*[,†]

[†]Centre for Research in Engineering Surface Technology (CREST), FOCAS Institute, and [‡]School of Chemical and Pharmaceutical Sciences, Dublin Institute of Technology, Kevin Street, Dublin 8, Ireland

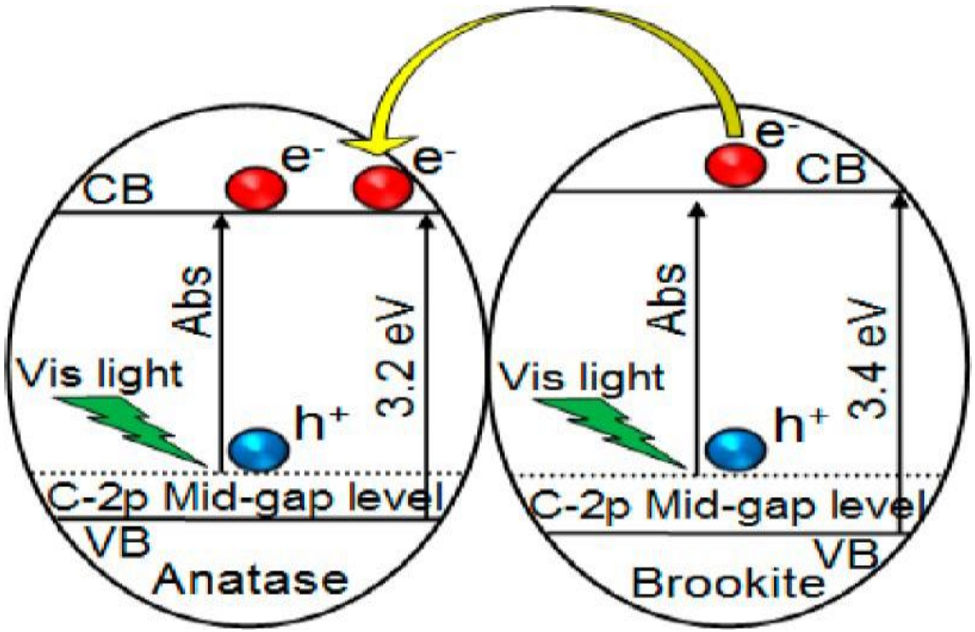
[§]The Surface Analysis Laboratory, Faculty of Engineering and Physical Sciences, University of Surrey, Guildford, Surrey, GU2 7XH, United Kingdom

Supporting Information

ABSTRACT: Highly visible-light-active S,N-codoped anatase−rutile heterojunctions are reported for the first time. The formation of heterojunctions at a relatively low temperature and visible-light activity are achieved through thiourea modification of the peroxo−titania complex. FT-IR spectroscopic studies indicated the formation of a Ti^{4+}−thiourea complex upon reaction between peroxo−titania complex and thiourea. Decomposition of the Ti^{4+}−thiourea complex and formation of visible-light-active S,N-codoped TiO_2 heterojunctions are confirmed using X-ray diffraction, Raman spectroscopy, transmission electron microscopy, and UV/vis spectroscopic studies. Existence of sulfur as sulfate ions (S^{6+}) and nitrogen as lattice (N−Ti−N) and interstitial (Ti−N−O) species in heterojunctions are identified using X-ray photoelectron spectroscopy (XPS) and FT-IR spectroscopic techniques. UV−vis and valence band XPS studies of these S,N-codoped

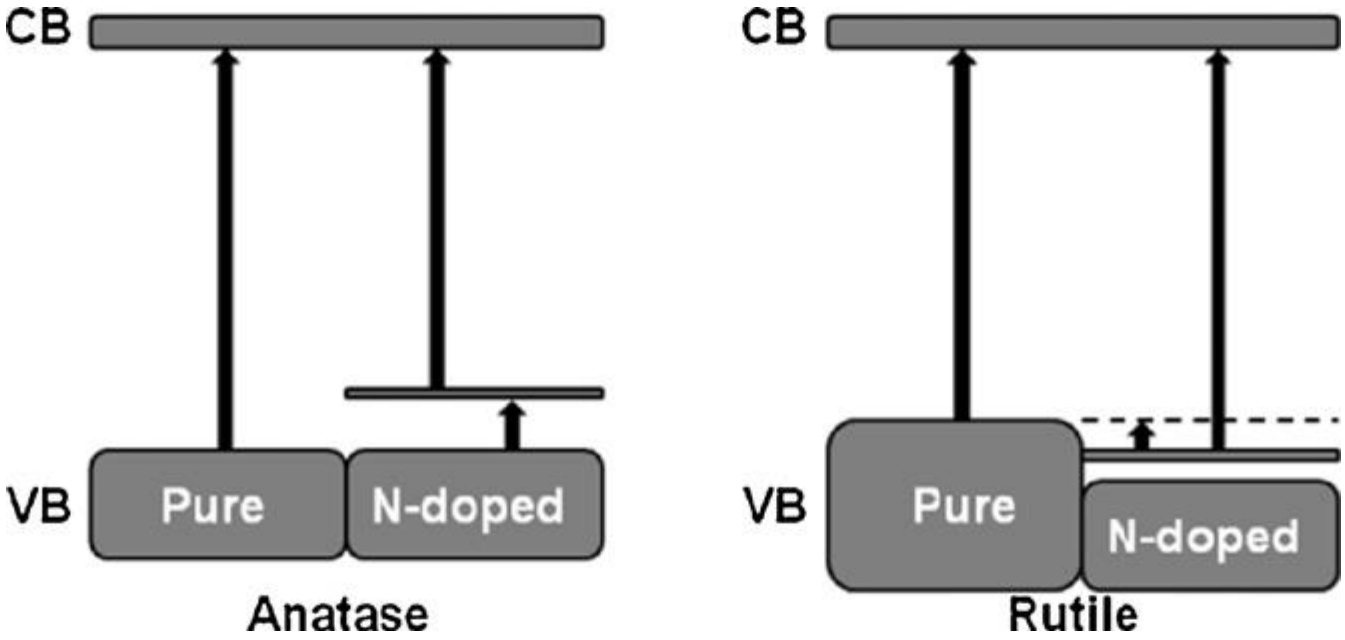


Anatase-Brookite Heterojunctions



V. Etacheri, M. K. Seery, S. J. Hinder, and S. C. Pillai*, *ACS Appl. Mater. Interfaces*, 2013

Why N- doped Rutile doesn't show any visible light activity?



N.T. Nolan D. W. Synnott, M. K. Seery, S. J. Hinder, A. V. Wassenhovend, S. C. Pillai* *Journal of Hazardous Materials* , **2012**, *211– 212,* 88– 94

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FULL PAPER

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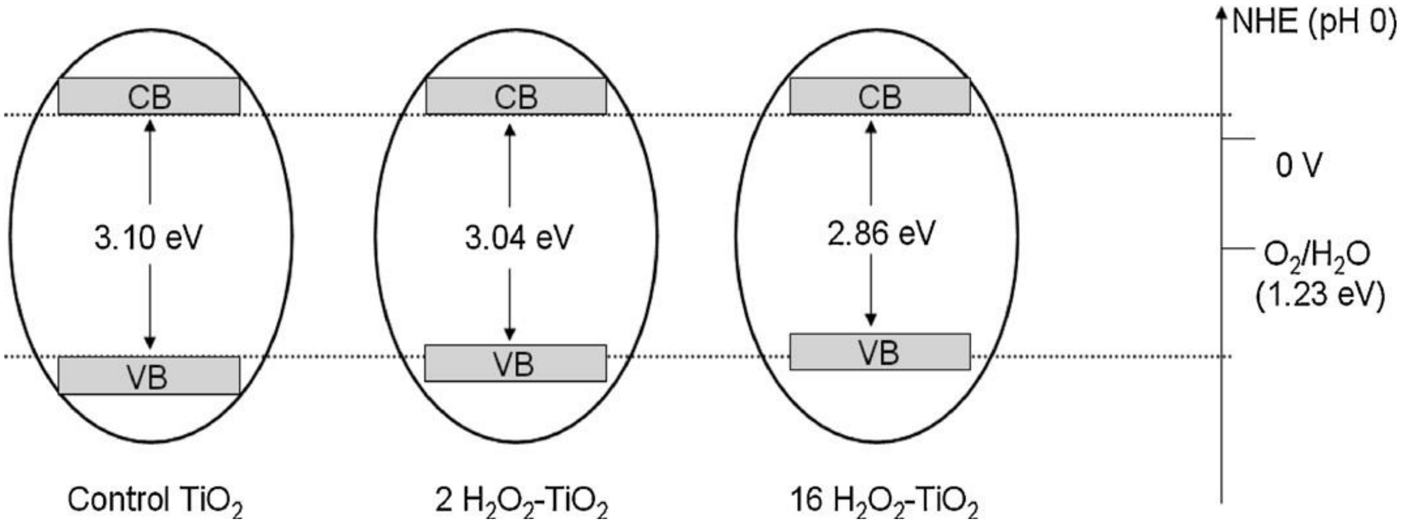
Oxygen Rich Titania: A Dopant Free, High Temperature Stable, and Visible-Light Active Anatase Photocatalyst

*Vinodkumar Etacheri, Michael K. Seery, Steven J. Hinder, and Suresh C. Pillai**

The simultaneous existence of visible light photocatalytic activity and high temperature anatase phase stability up to 900 °C in undoped TiO_2 is reported for the first time. These properties are achieved by the in-situ generation of oxygen through the thermal decomposition of peroxo-titania complex (formed by the precursor modification with H_2O_2). Titania containing the highest amount of oxygen (16 H_2O_2-TiO_2) retains 100% anatase phase even at 900 °C, where as the control sample exists as 100% rutile at this temperature. The same composition exhibits a six-fold and two-fold increase in visible light photocatalytic activities in comparison to the control sample and the standard photocatalyst Degussa P-25 respectively. Among the various parameters affecting the photocatalytic action, such as band gap narrowing,

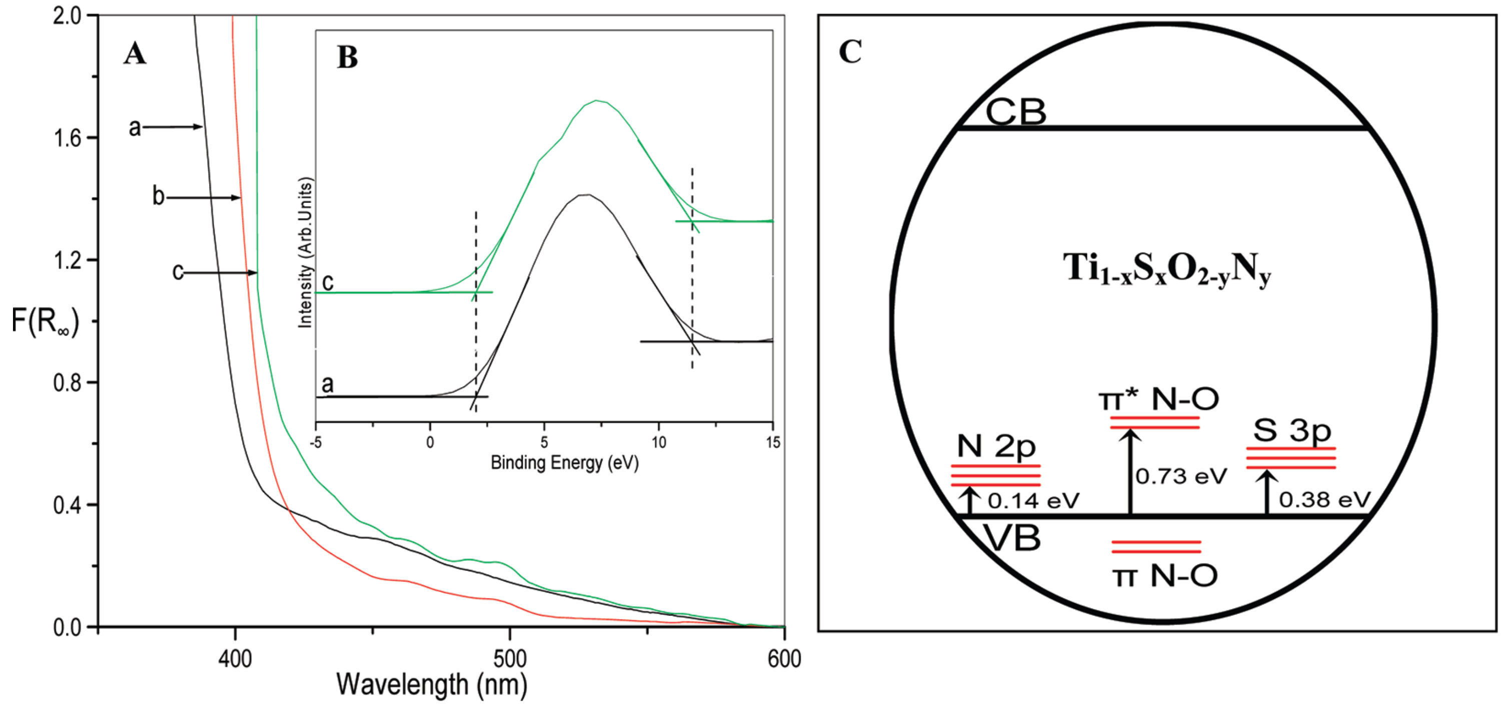
dioxide in comparison to other semiconductor nanoparticles arise from the high redox potential, chemical stability, inexpensiveness, and non-toxicity. Among the three polymorphs of titania, anatase phase is reported as the most photocatalytically active because of its higher charge-carrier mobility and an increased density of surface hydroxyls.[12–14] On the other hand, rutile phase is found to be less active and photocatalytic activity of brookite phase is seldom investigated.[15] Photocatalytic activity of titania depends on various factors such as phase purity, surface area,

Band-gap narrowing by introducing oxygen excess defects



V. Etacheri, M. K. Seery, S. J. Hinder, S. C. Pillai, *Adv. Funct. Mater*. **2011**, 21, 3744–3752

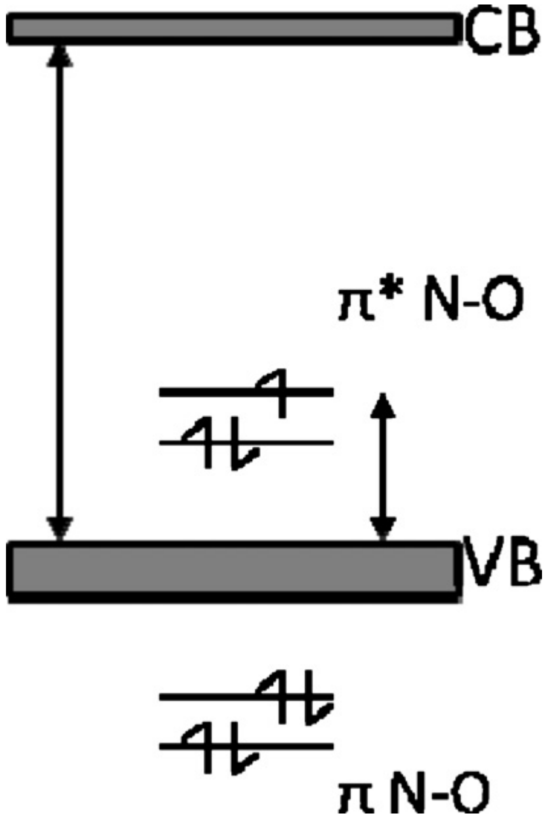
Is the band gap narrowing happening in all cases?



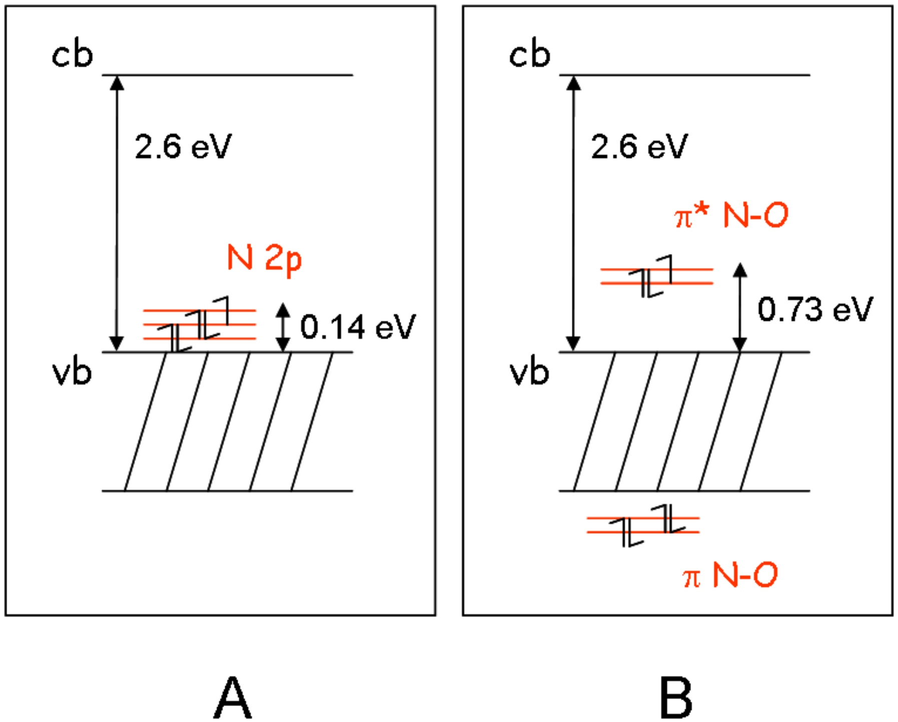
Isolated impurity states in the band gap

V. Etacheri, M. K. Seery, S. J. Hinder and S. C. Pillai*, *Inorganic Chemistry,* **2012**, 51, 7164−7173

Isolated impurity state in interstitial nitrogen doped TiO_2

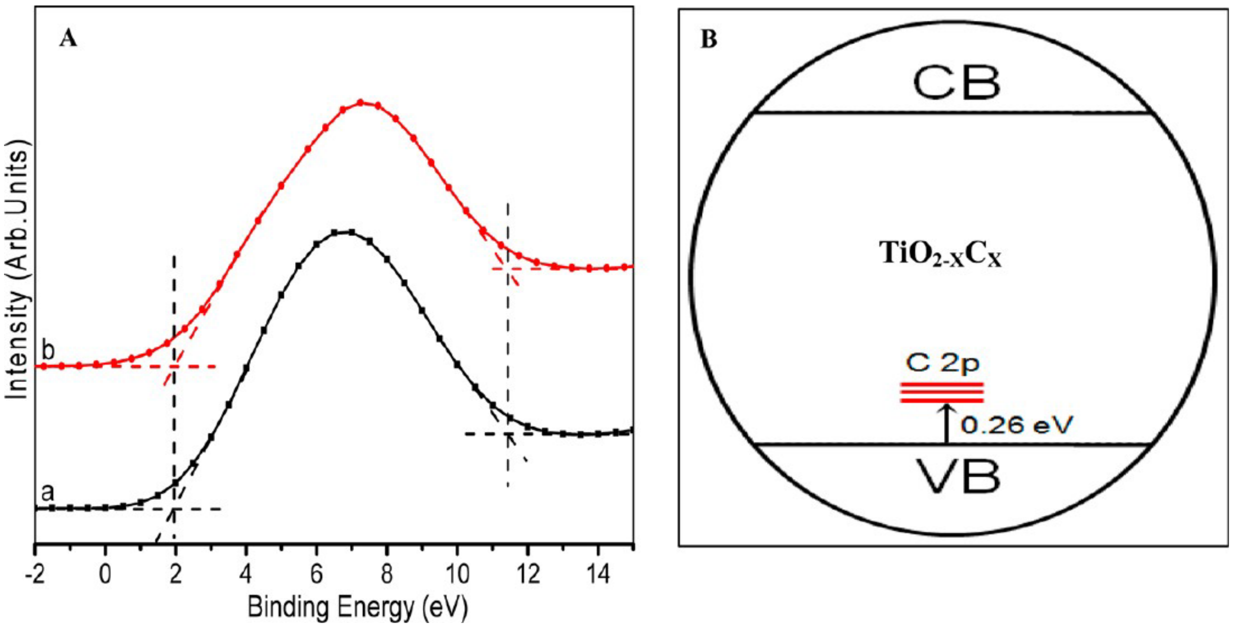


N.T. Nolan D. W. Synnott, M. K. Seery, S. J. Hinder, A. V. Wassenhovend, S. C. Pillai* *Journal of Hazardous Materials* **2012**, *211– 212*, 88– 94



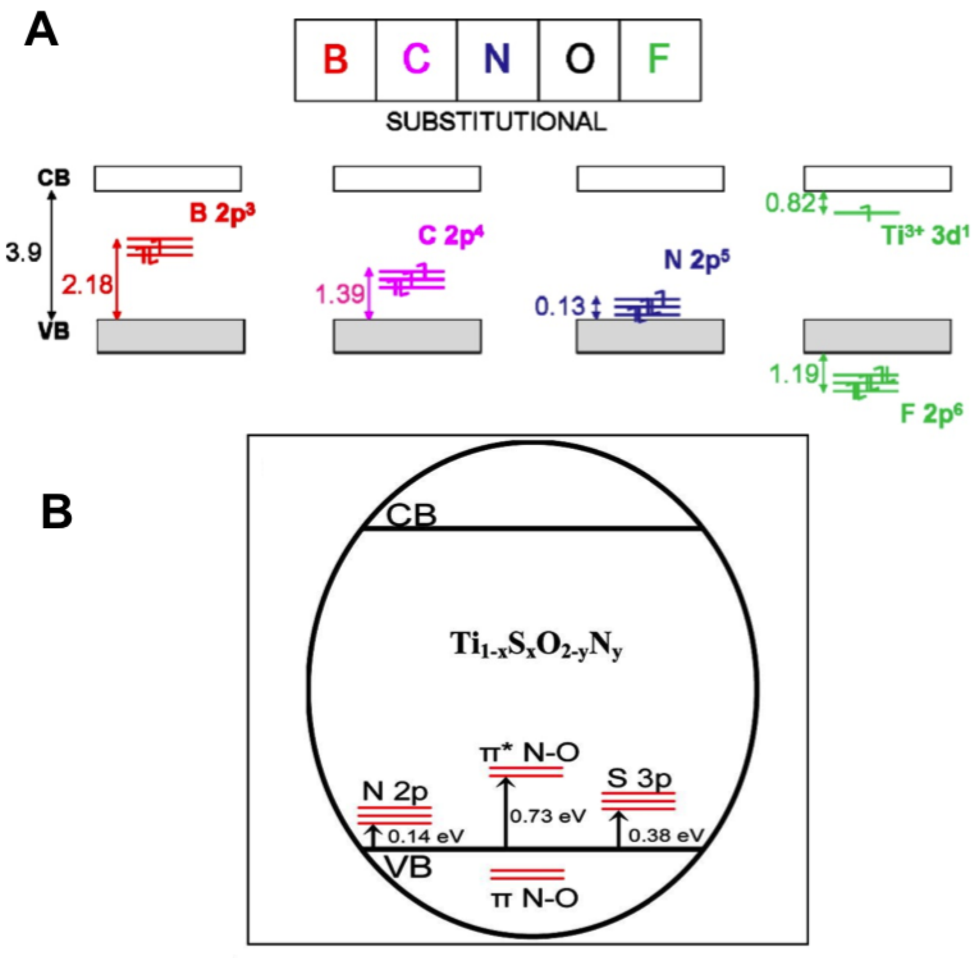
C.D. Valentin, G. Pacchioni, A. Selloni, S. Livraghi, E. Giamello, J. Phys. Chem. B, 109 (2005) 11414.

Isolated impurity states in the band gap



V. Etacheri, M. K. Seery, S. J. Hinder, and S. C. Pillai*, *ACS Appl. Mater. Interfaces*, 2013

Localized impurity energy states



substitutionally doped TiO_2

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New Insights into the Mechanism of Visible Light Photocatalysis

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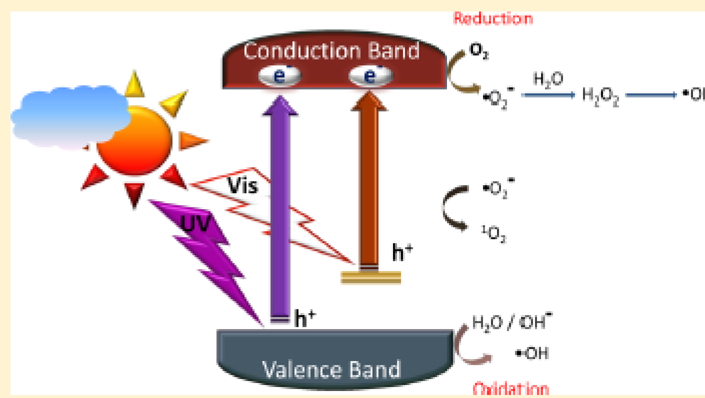
[#] Nanotechnology and Integrated Bio-Engineering Centre, School of Engineering, Faculty of Computing and Engineering, University of Ulster, Newtownabbey, Northern Ireland BT37 0QB, United Kingdom

[¶] Environmental Engineering and Science Program, School of Energy, Environmental, Biological, and Medical Engineering, University of Cincinnati, Cincinnati, Ohio 45221-0012, United States

ABSTRACT: In recent years, the area of developing visible-light-active photocatalysts based on titanium dioxide has been enormously investigated due to its wide range of applications in energy and environment related fields. Various strategies have been designed to efficiently utilize the solar radiation and to enhance the efficiency of photocatalytic processes. Building on the fundamental strategies to improve the visible light activity of TiO_2-based photocatalysts, this Perspective aims to give an insight into many contemporary developments in the field of visible-light-active photocatalysis. Various examples of advanced TiO_2 composites have been discussed in relation to their visible light induced photoconversion efficiency, dynamics of electron–hole separation, and decomposition of organic and inorganic



- **Applications of visible light active photocatalysts:**

Hygiene coatings

Simultaneous production of visible light activity and high temperature anatase stability

Fluorine

Chem. Mater., 19 (18), 2007, 4474-4481.

Nitrogen

J. Phys. Chem. C, 111(4), 2007, 1605–1611.;

Sulphur

J. Phys. Chem. C, 112 (20), 2008, 44–7652.

Nitrogen and Sulphur (co-doping)

J. Phys. Chem. C, 113,(8), 2009, 3246-3253;

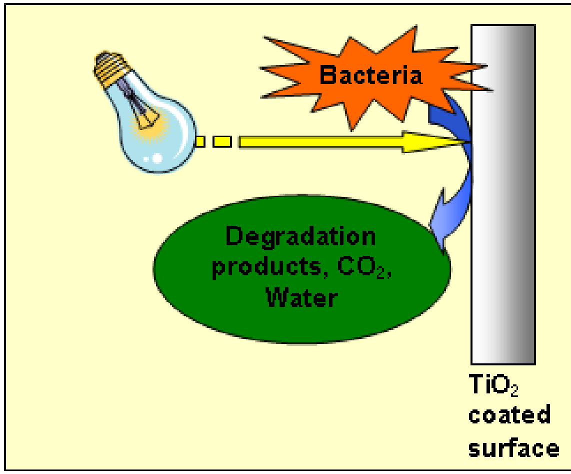
Inorganic Chemistry, 2012.

Nitrogen doped heterojunctions

Chem. Mater., 22, 2010, 3843–3853

Oxygen

Adv. Funct. Mater. 21, 2011, 3744–3752



Improved High-Temperature Stability and Sun-Light-Driven Photocatalytic Activity of Sulfur-Doped Anatase TiO_2

Periyat *et al*, *J. Phys. Chem.* C, *112* (20), **2008**, 44–7652.

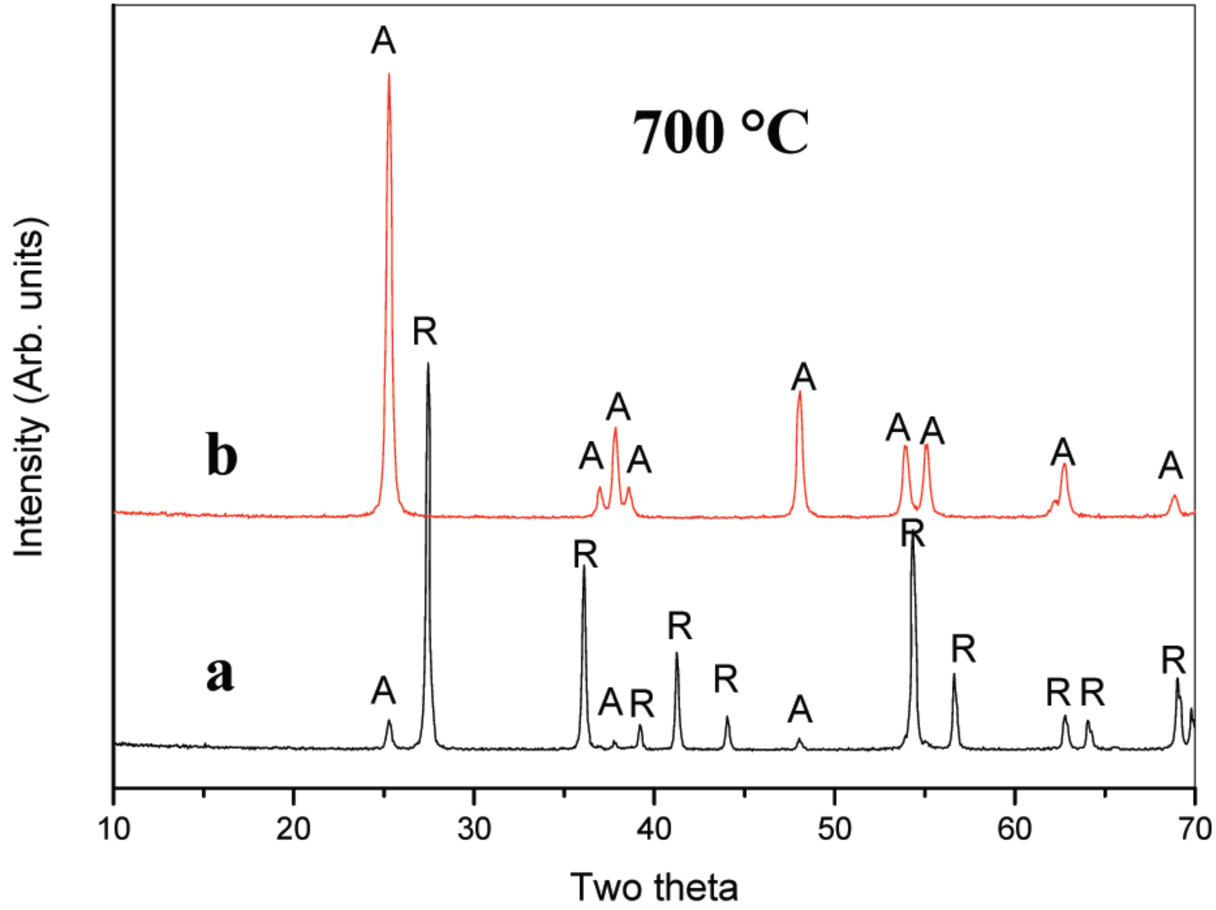
Experiment

$$Ti(OPr)_4 + H_2SO_4 + H_2O \rightarrow TiOSO_4 + 4(CH_3{-}CH(OH){-}CH_3)$$

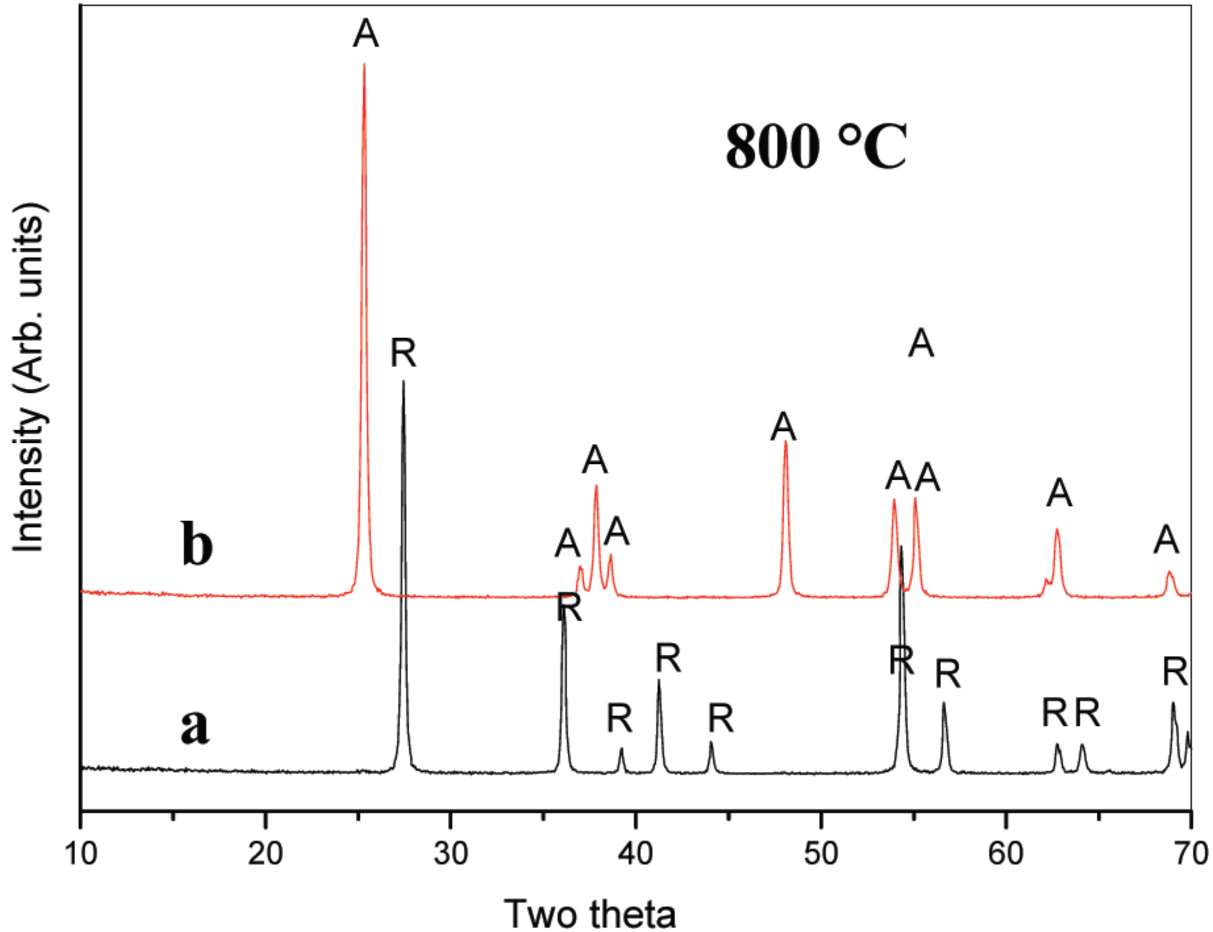
$$2TiOSO_4 \rightarrow 2Ti_{1-x}S_xO_2 + (2-x)SO_2 + O_2$$

- **It was then dried at 350 °C for 6 h.**
- **The dried powder was calcined at various temperatures (600, 700, 800, 850, and 900 °C) at a heating rate of 5 °C per minute and held at these temperatures for 2 h**

Effect of S- doping- XRD

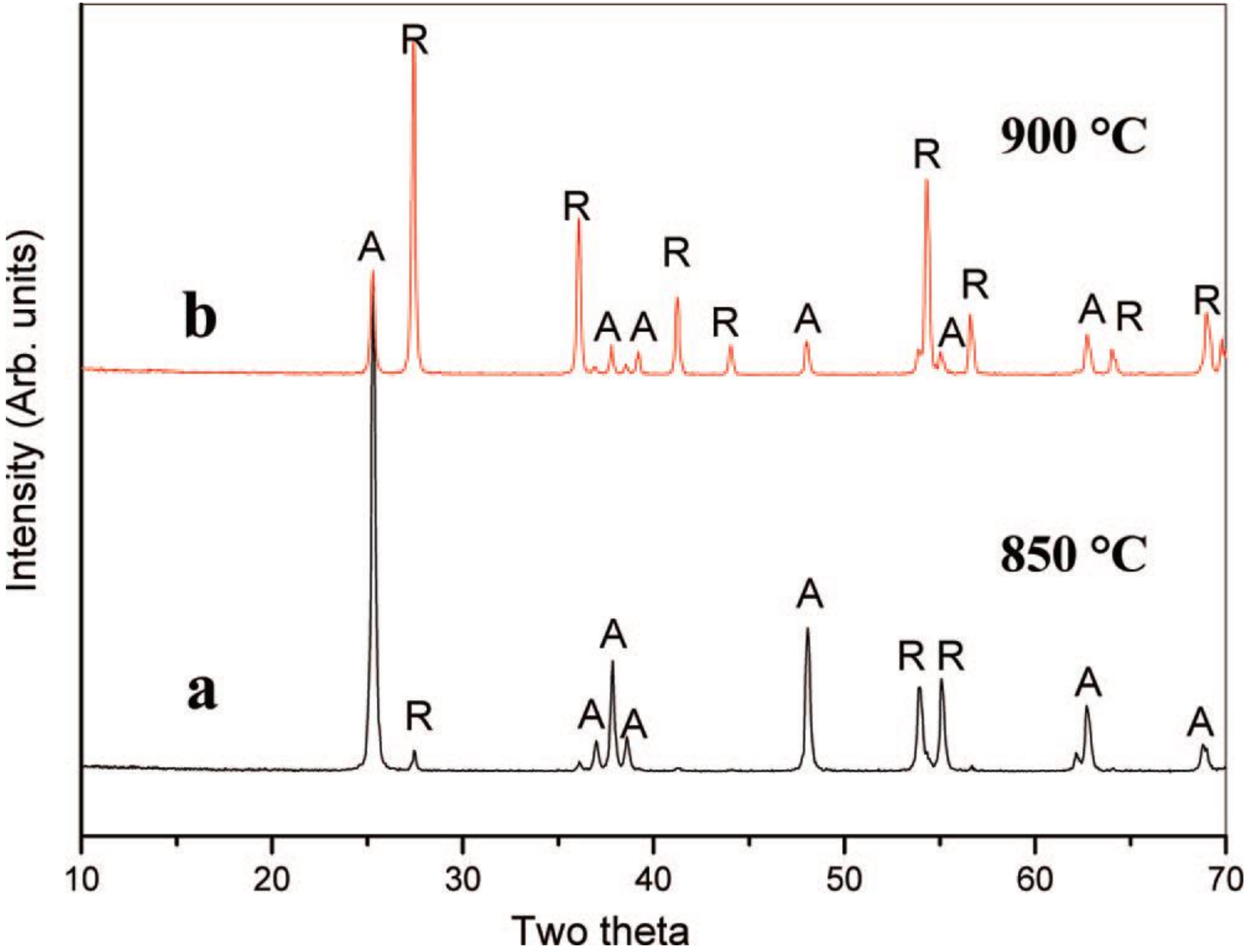


800 C

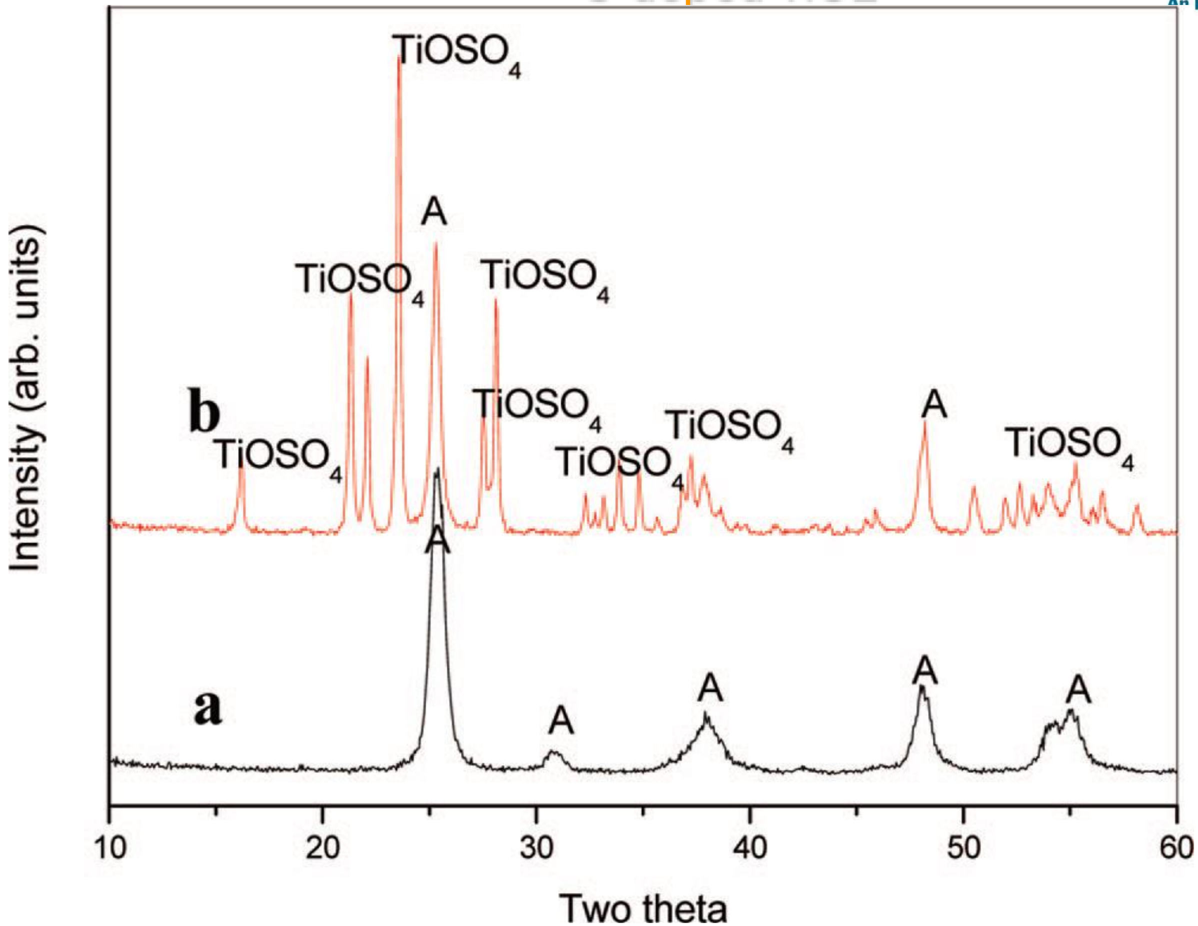


800 °C
A
R
A
A
A
A
A
A
A
A
A
b
a
R
R
R
R
R
R
R
R
R
Intensity (Arb. units)
10
20
30
40
50
60
70
Two theta

Effect of S- doping

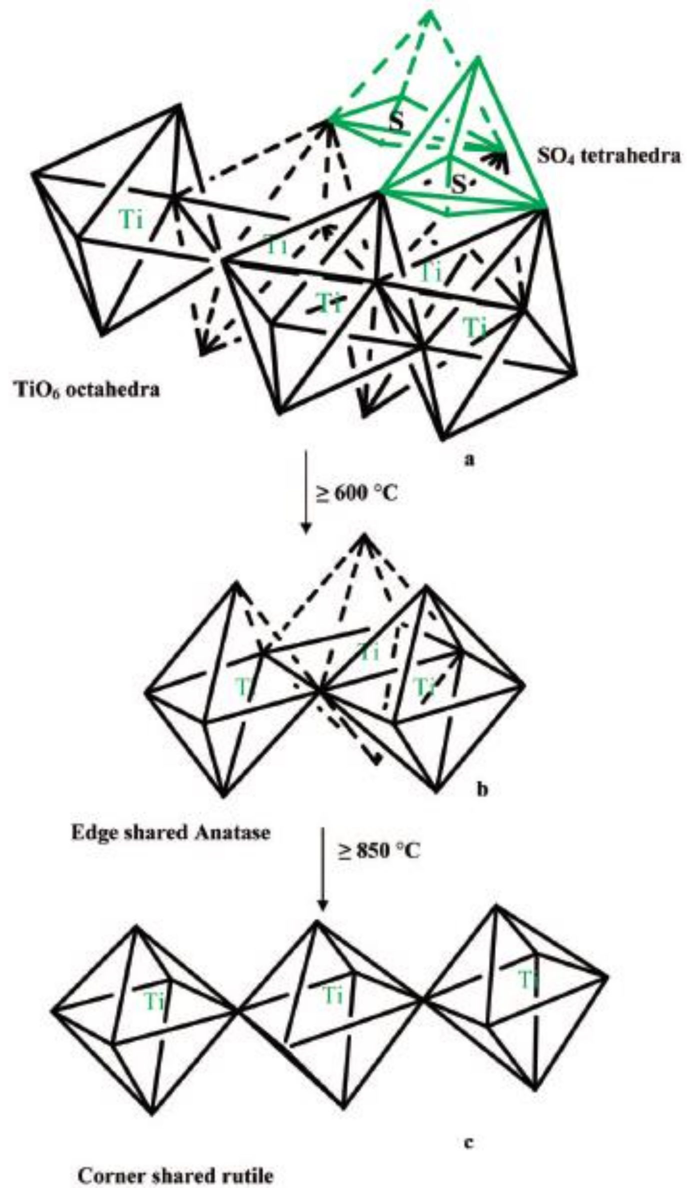


XRD of the samples calcined at 600 °C; (a) control, (b) S-doped TiO2



$$2TiOSO_4 \rightarrow 2Ti_{1-x}S_xO_2 + (2-x)SO_2 + O_2$$

How a delayed phase transition happened?



100% Anatase at 900 C

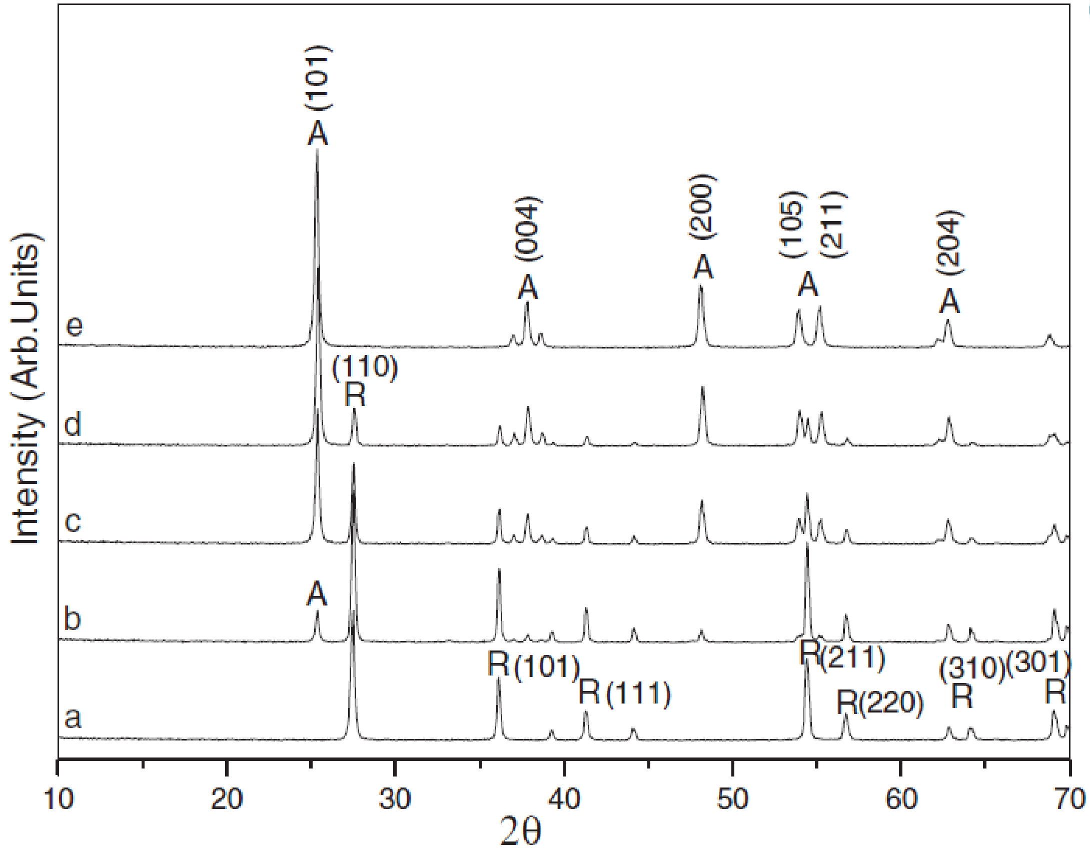


Figure 2. XRD patterns of TiO2 calcined at 900 °C: a) control TiC b) $2H_2O_2$-TiO_2. (c) $4H_2O_2$-TiO_2 (d) $8H_2O_2$-TiO2 (e) $16H_2O_2$-TiO_2 (A anatase: R = rutile)

V. Etacheri, M. K. Seery, S. J. Hinder, S. C. Pillai, *Adv. Funct. Mater*. **2011**, 21, 3744–3752