New insights into the origin of visible light photocatalytic activity of nitrogen doped and oxygen deficient anatase TiO_2

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Introduction

- TiO_2 is a non-toxic, relatively inexpensive and very promising photocatalyst for environmental applications.
- The bandgap of TiO_2 is large (3.0-3.2 eV) — its photocatalytic efficiency under visible light is very low.
- Many attempts have been made to improve its performance in visible light region:
  - Transition metal doping
  - Surface modifications.
  - Non-metallic elements doping

Nitrogen doping in anatase TiO_2

Two mechansims were proposed to account for visible light activity of N-doped TiO_2:

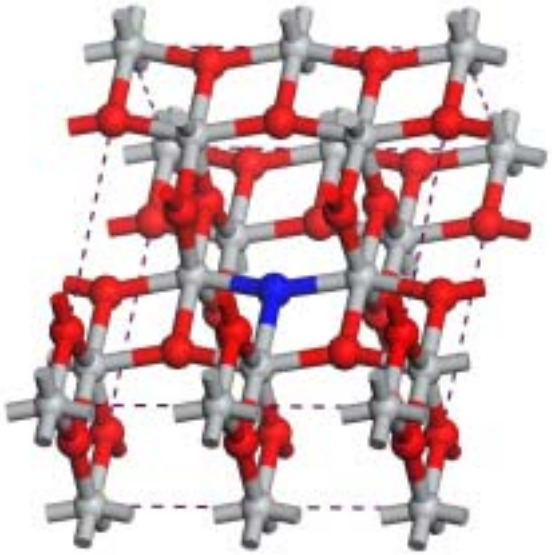
- **Oxygen vacancies introduced in TiO_2 when prepare samples. Nitrogen atoms just act as a blocker for electron and hole recombination.**
- **Nitrogen atoms doped into substitutional sites in TiO_2.**

The experimental preparation methods can introduce both doped nitrogen and oxygen vacancies → need theoretical approach.

Calculation methods

Modelling: $TiO_{2-x}N_x$ or TiO_{2-x}: replace or remove O in Supercell — 24, 48, and 96 atoms → x=0.125, 0.062, and 0.031

- **CASTEP**
  - **Spin-polarized GGA**
  - **Ultrasoft pseudopotential**
  - **Energy cutoff of Plane-wave: 500 eV**
  - **PBE XC functional**



Geometry optimization → electronic band structures → Optical absorption properties

The imaginary part of the dielectric constant:

$$\varepsilon_2(\hbar\omega) = \frac{2e^2\pi}{\Omega\varepsilon_0}\sum_{k,v,c}\left|\left\langle\psi_k^c\left|\hat{u}\cdot r\right|\psi_k^v\right\rangle\right|^2\delta\left(E_k^c - E_k^c - \hbar\omega\right)$$ (Scissors operator)

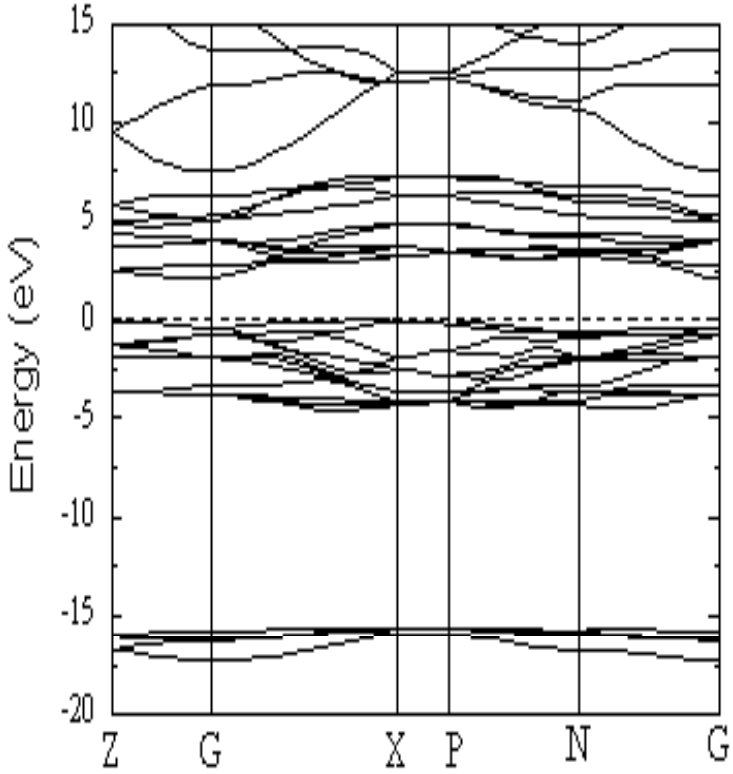
Stoichiometric TiO_2

❖ Optimized geometry:

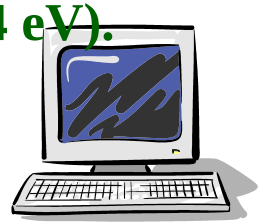
	This work	Experimental[a]
a (Å)	3.7845	3.782
c (Å)	9.7153	9.502
u[b]	0.2059	0.208

[a] J. K. Burdett, *JACS*, Vol. 109, 3639
[b] $u=d_{ap}/c$, d_{ap} is the apical Ti-O bond length.

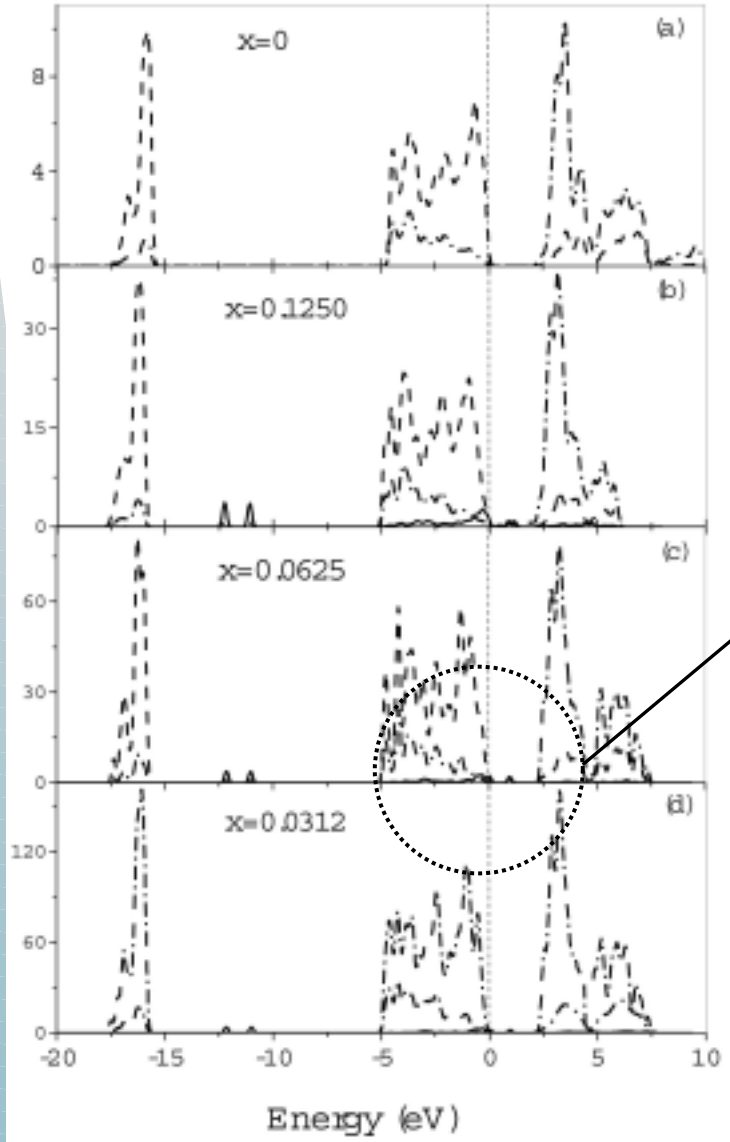
Mulliken analysis: Ti:+1.33 O:-0.66



Electronic band structure along high symmetry directions in stoichiometric TiO_2 crystal (indirect gap 2.14 eV).

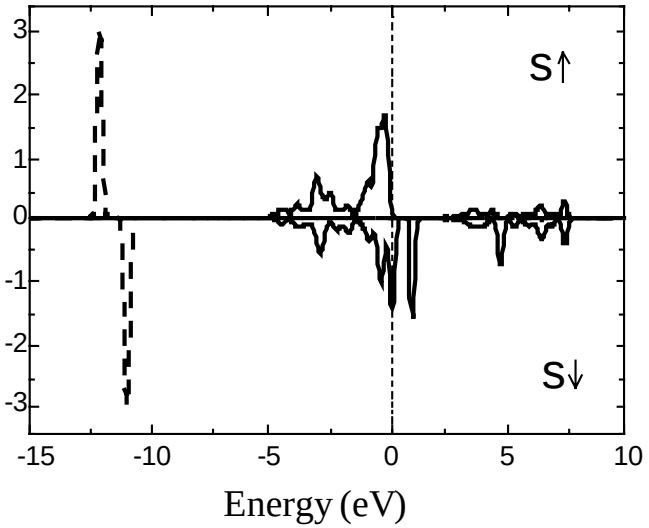


Nitrogen doped anatase TiO_2



Partial density of states plots calculated for different levels of the N doping in TiO_2 crystal.

Mulliken analysis: N -0.58 -->
N acts as a deep electron trap.



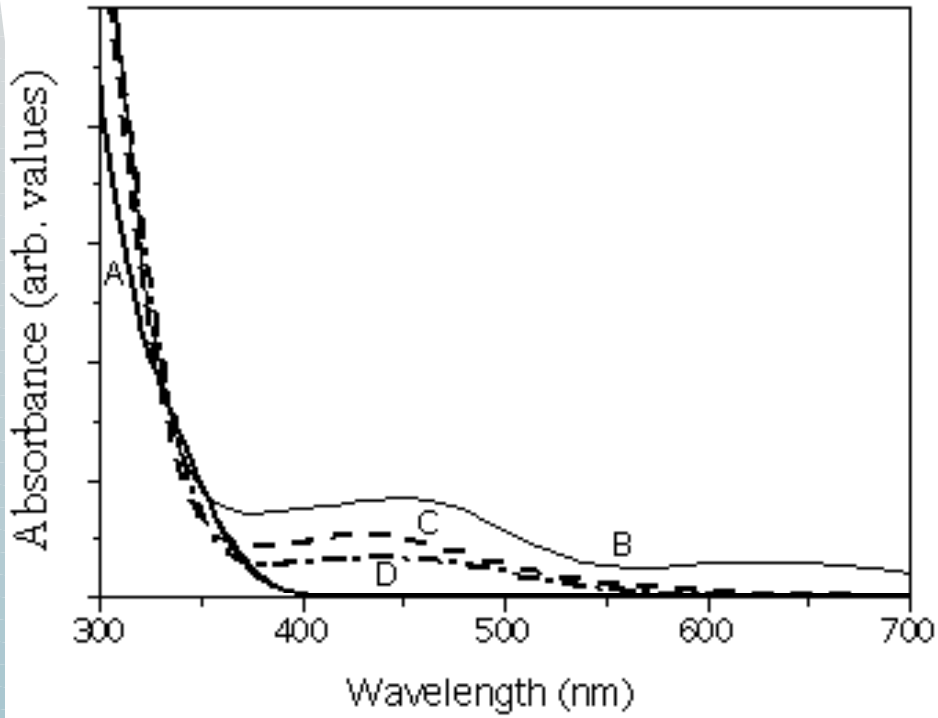
PDOS for spin-up (s↑) and spin-down (s↓) electrons in nitrogen atom (x=0.062).

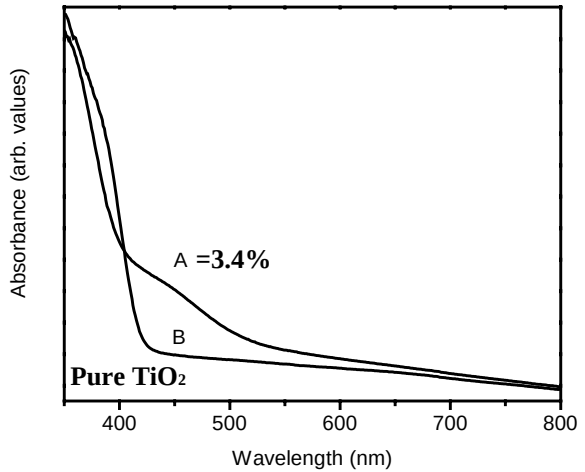
In high concentration (>20%), the N 2p states mix with the O 2p states → the transfer of photoexcited carriers to reactive sites at the catalyst surface within their lifetime.

High doping might cause some problems :

- **Form TiN;**
- **Introduce significant number of defects.**

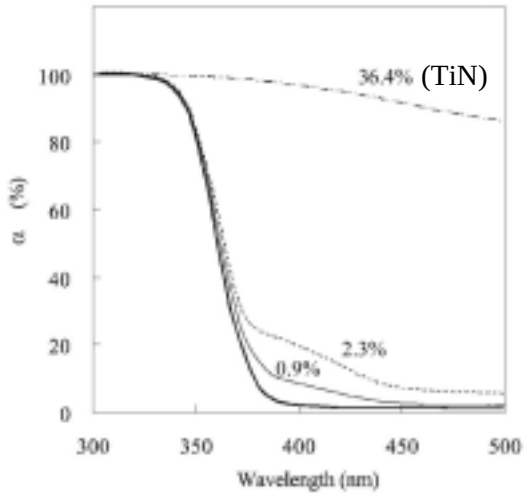
Optical absorption spectra of N-doped TiO_2 in visible light region





Made by Chemistry department of Cambridge

The optical absorption spectra calculated for various N concentrations in polycrystalline TiO_2. (A) undoped TiO_2, (B) 12.5% nitrogen doped, (C) 6.2% nitrogen doped, (D) 3.1% nitrogen doped.



M. Miyauchi, *PCCP*, Vol. 6, 865

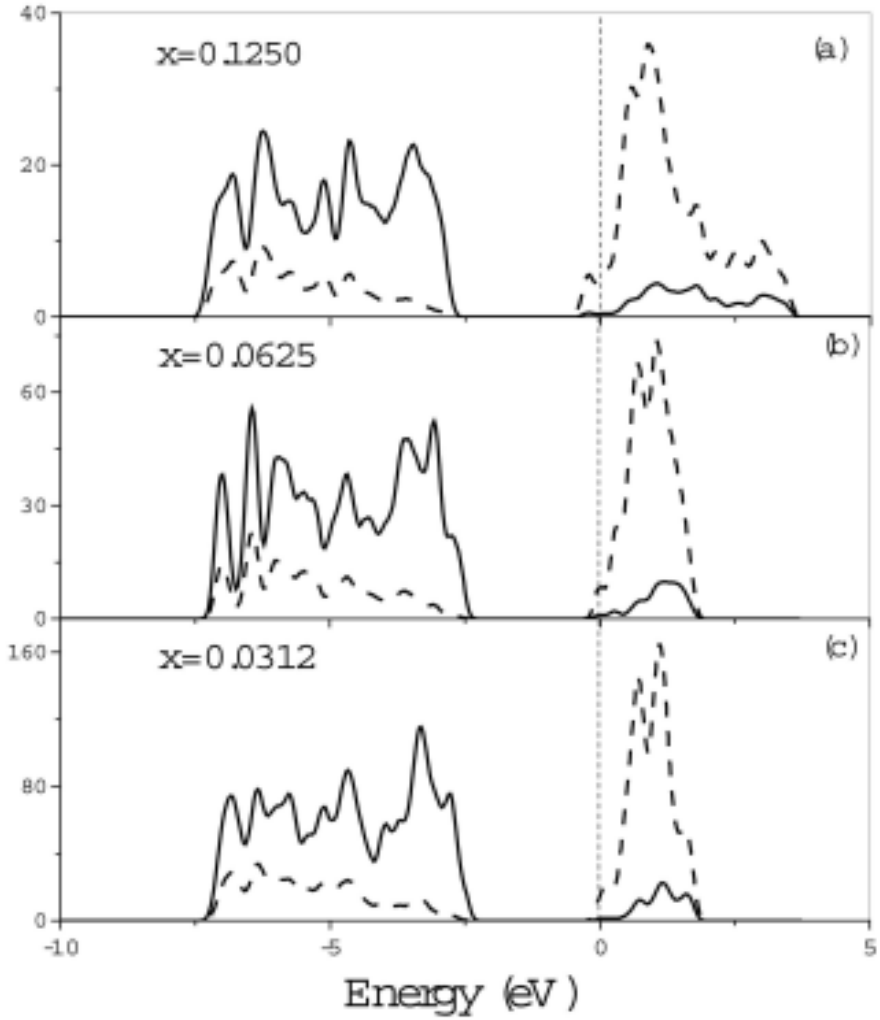
Oxygen deficient TiO_2

Mulliken analysis: excess electrons were redistributed by the nearest neighbour Ti atoms around the oxygen vacancy site.

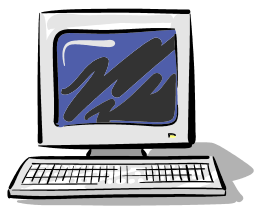
The donor states:

Calculated: 0.15 ~ 0.30 eV below the conduction band edge.

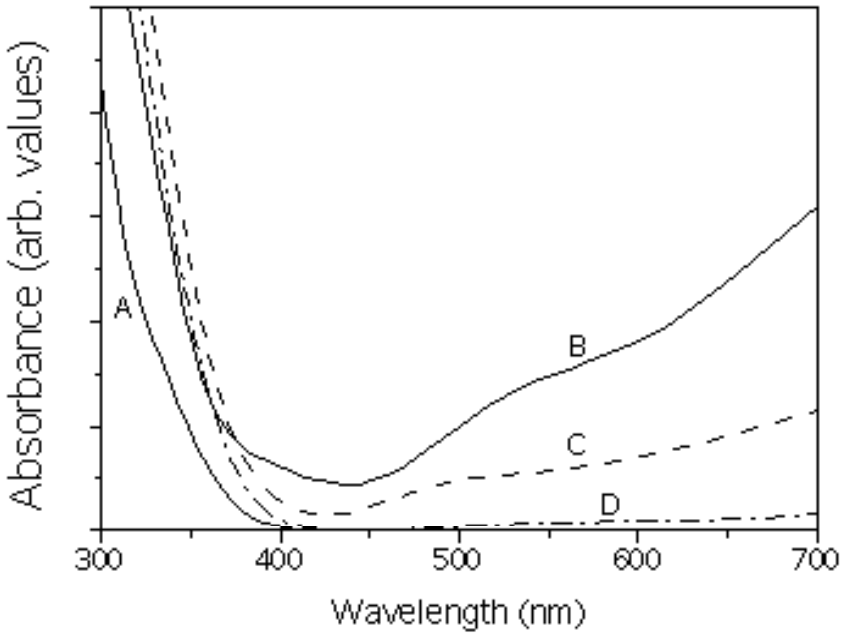
Experimental: 0.75 eV below.

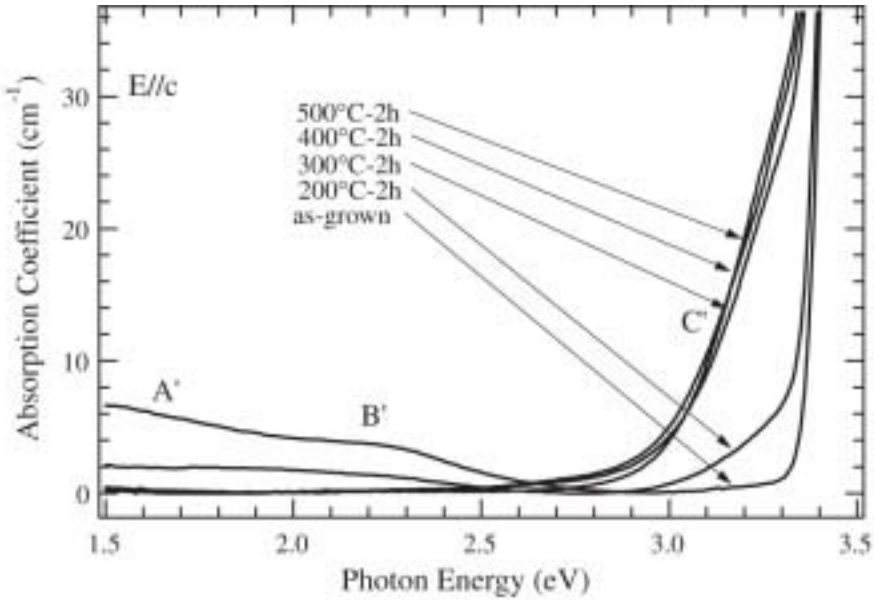


PDOS with the oxygen vacancies concentration in TiO_2 crystal.



Optical absorption spectra of oxygen deficient TiO_2 in visible light region





Optical absorption spectra of polycrystalline TiO_2 with different O vacancy contents. (A) updoped TiO_2, (B) 12.5 % oxygen vacancies, (C) 6.2 % oxygen vacancies (D) 3.1% oxygen vacancies.

TiO_2 crystals were heat treated by hydrogen gas.
T. Sekiya, *J. Phys. Soc. Jpn*, Vol. 73, 703

Conclusion

- The electronic band structures of nitrogen doped and oxygen deficient TiO_2 with different levels of doping /vacancies (e.g. 12.5%, 6.2% and 3.1%) were obtained;
- Subsitutionally doped nitrogen introduce localized N 2p acceptor states above the top of the valence bands, while oxygen vacancies result in the donor states below the bottom of conduction bands;
- The calculated optical absorption spectra of both cases are in good agreement with experimental data.
- The visible light absorption of the nitrogen doped and the oxygen deficient TiO_2 are very different; the former mainly absorbs the light from 400 to 500 nm, while the latter mainly absorbs the light above 500 nm.

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