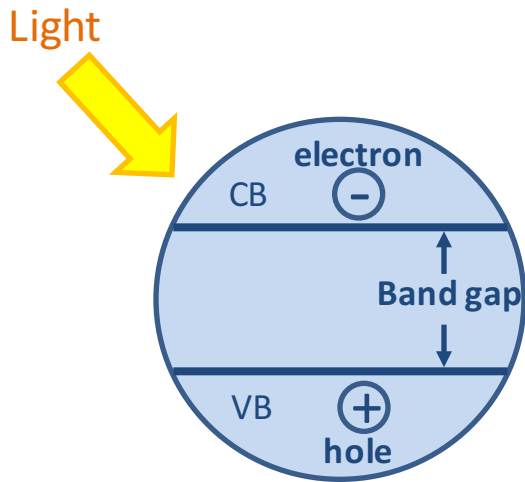


Photocatalysis on TiO₂ Surfaces

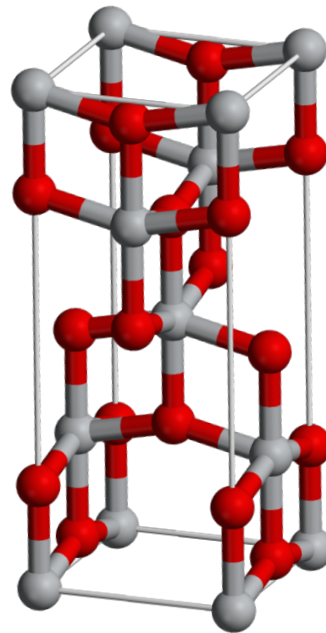
Kira Wyckoff
June 6, 2016

Introduction

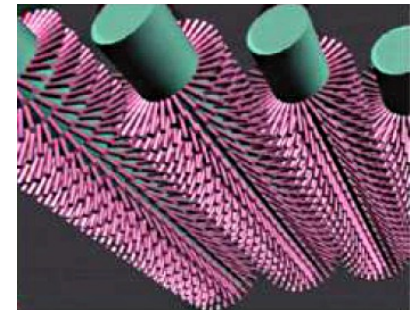
Electronic Excitation



TiO₂ Properties

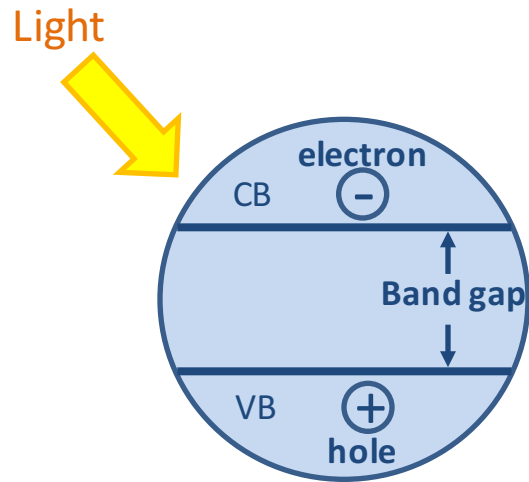


Photocatalytic Applications



Introduction

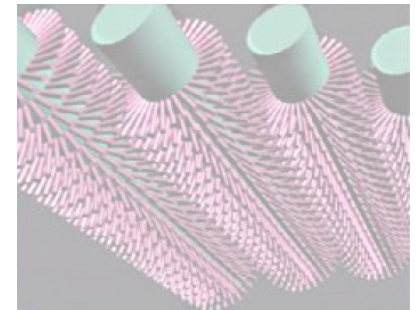
Electronic Excitation



TiO₂ Properties



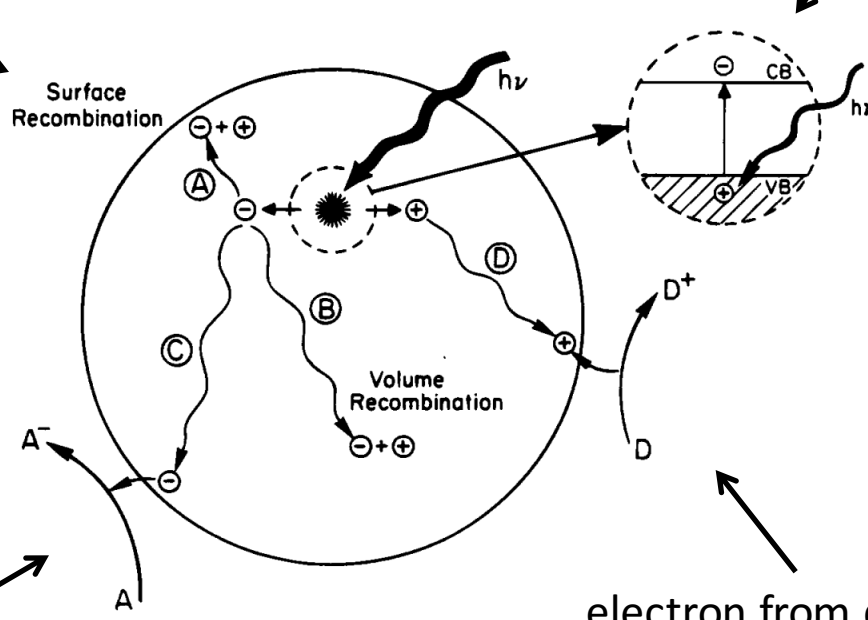
Photocatalytic Applications



Generation of electron-hole pairs in semiconductor particles

Hole and electron can recombine on Surface or in volume

Excitation of electron from VB to CB by light with energy equal to band gap



donate electrons to reduce an electron acceptor

electron from donor can combine with hole to oxidize donor

Quantum Yield has ideal value of 1 for the photocatalytic process

- Idealization
- **Recombination does occur**
- Concentration of electrons (n_s) and holes (p_s) at the surface is not equal
- Charge carrier traps used to promote trapping of electrons and holes at surface
- For TiO_2 , $n_s > p_s$ because electron transfer to O_2 is slow

Quantum Yield or Efficiency

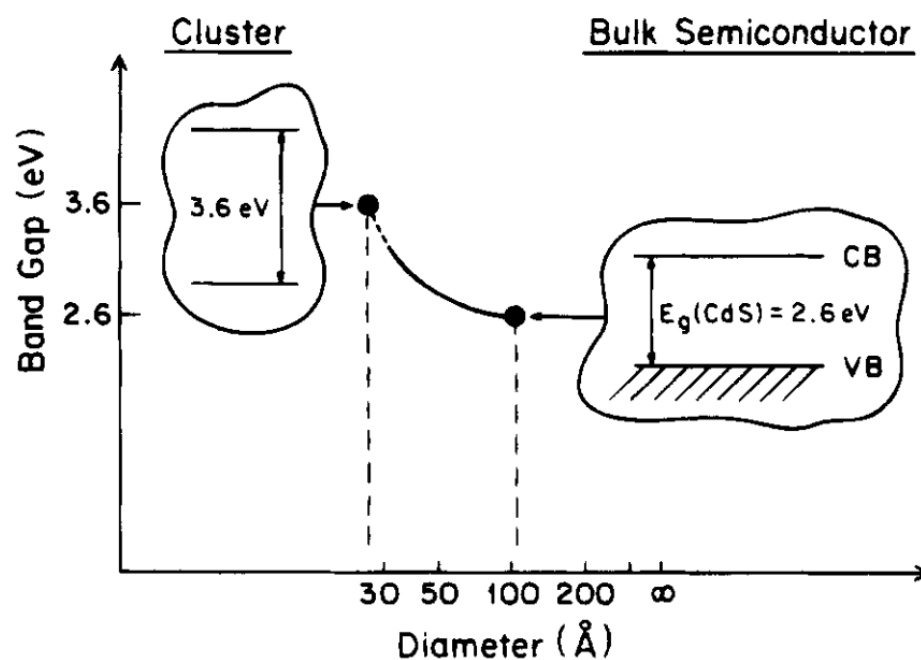
Charge transfer rate

$$\Phi \propto \frac{k_{CT}}{k_{CT} + k_R}$$

Electron-hole recombination rate

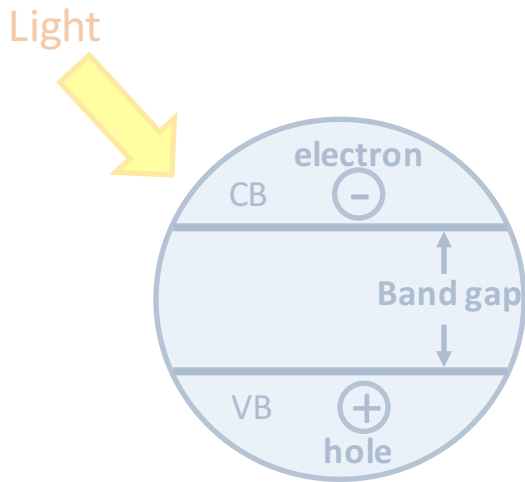
Increase in Band Gap for Decreasing Particle Size

- Quantum size effects occur for semiconductor particles on order of 10-100 Å
- Arise when size of particle is comparable to de Broglie wavelength
- Confinement produces quantization of discrete electronic states
- **Increases effective band gap**

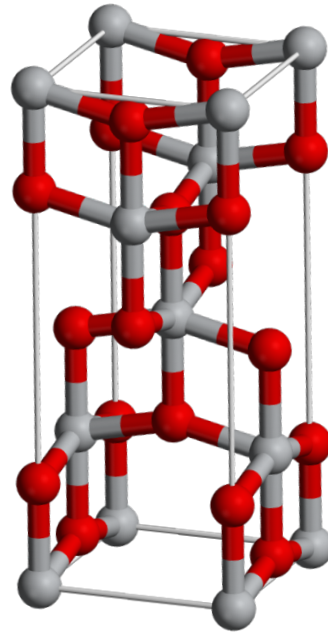


Outline

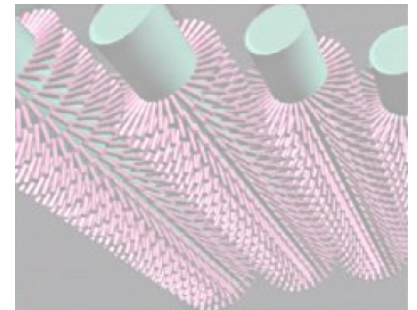
Electronic
Excitation



TiO₂
Properties

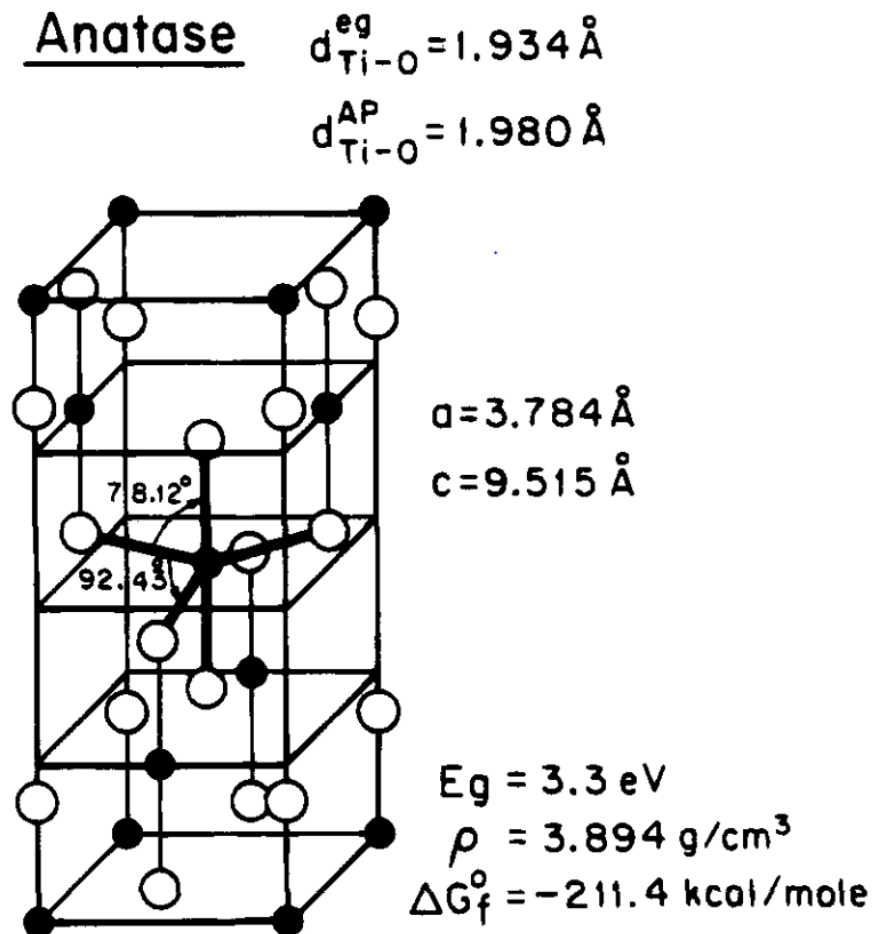


Photocatalytic
Applications

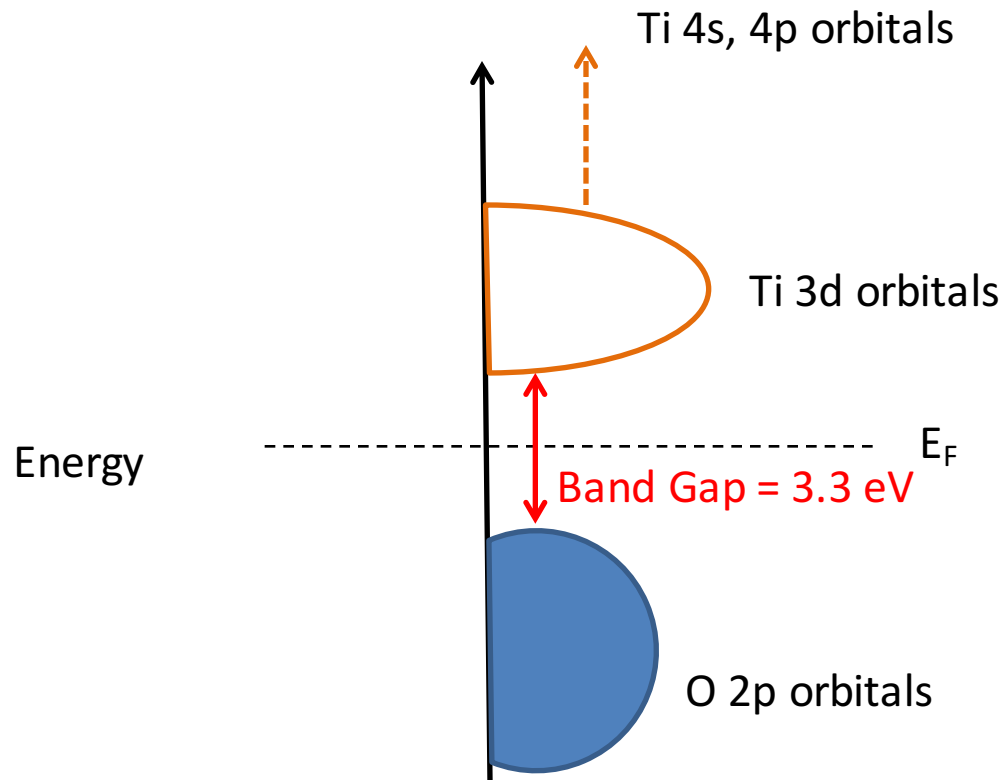


TiO₂ Anatase shows higher photocatalytic activity

- Chains of TiO₆ octahedra
- Each Ti⁴⁺ is surrounded by six O²⁻ ions
- Octahedron distorted to lower symmetry than orthorhombic
- Each octahedron in contact with eight neighbors
- **Lattice structure causes different electronic band structure**

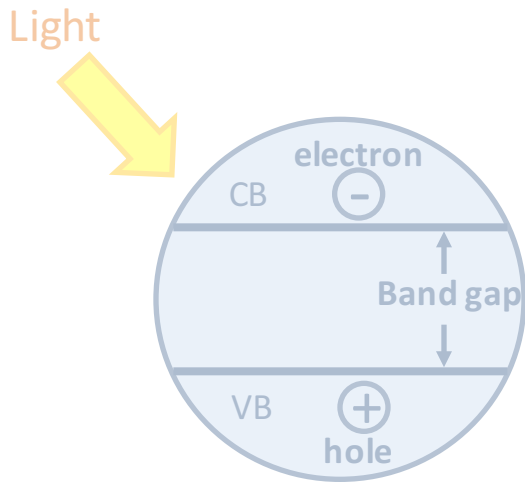


DOS shows large band gap



Outline

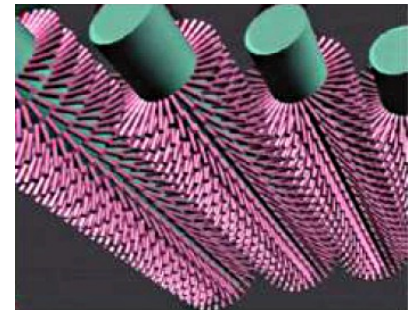
Electronic Excitation



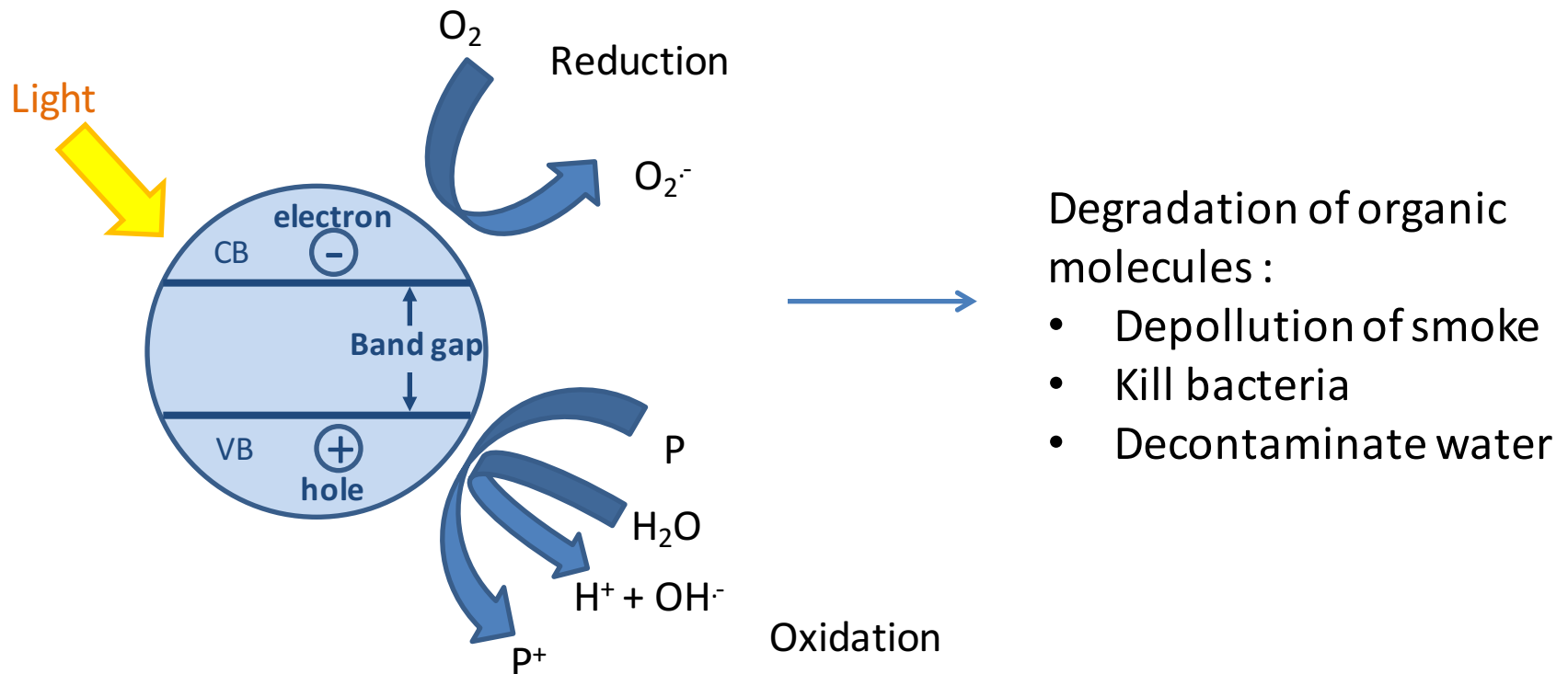
TiO₂ Properties



Photocatalytic Applications



Application: environmental cleanup

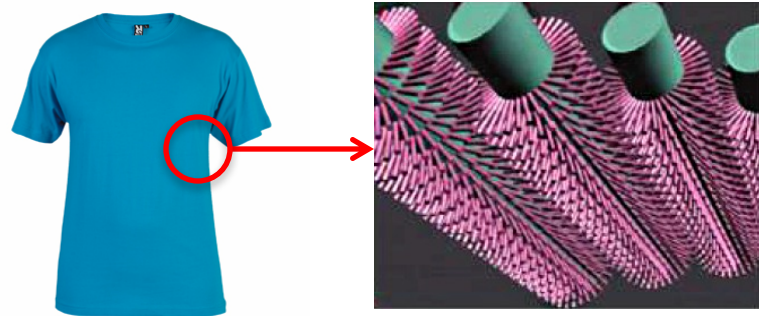


Many different novel commercial applications

Self cleaning windows

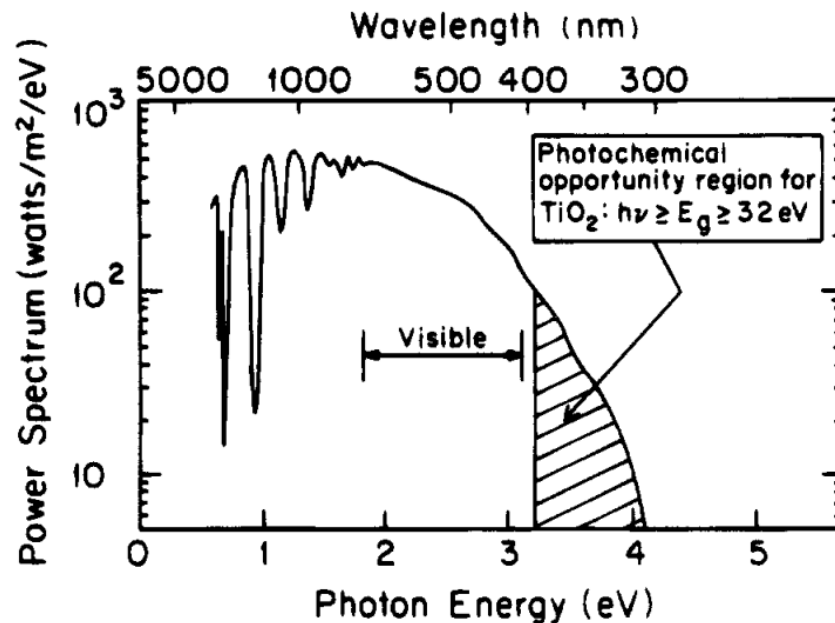


Clothing

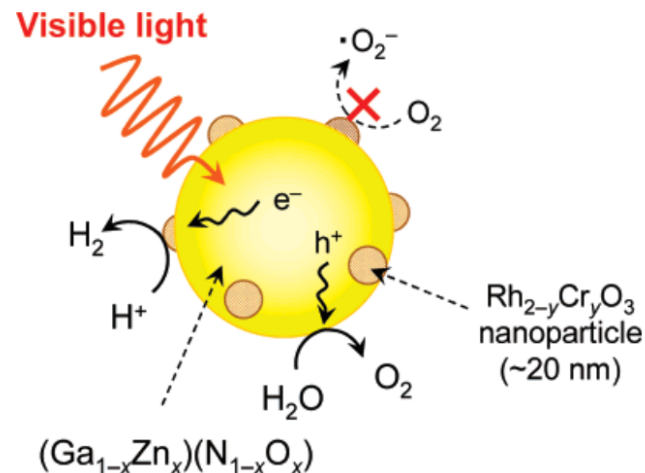


Research towards a catalyst sensitive to visible light

- TiO_2 does not absorb light in the visible region



- GaN and ZnO
- Rh-Cr mixed oxide co-catalyst
- Can absorb in visible light
- Water splitting to form hydrogen and water using solar energy



Questions?

Extra

Anatase [TiO₂]

Structure Tetragonal

Space Group : *I* 4₁/*a m d* (No. 141)

a=3.7845 Å, *c*=9.5143 Å

a=*b*=*c*=90.00

Z=4

Atomic Positional Parameters

Ti 4a 0.0000 0.0000 0.0000

O 8e 0.0000 0.0000 0.2081

Extra

