ยินดีต้อนรับสู่การสัมมนาเชิงปฏิบัติการในหัวข้อเรื่อง

การเตรียมไททาเนียมไดออกไซด์เพื่อใช้เป็นตัวเร่งปฏิกิริยาโดยใช้แสง

โดย

รศ. ดร. อภิสิฏฐ์ ศงสะเสน

วันศุกร์ที่ 26 ตุลาคม พ.ศ.2550

เวลา 9.30-11.00 น.

ณ ห้อง 519 ชั้น 5 อาคารกฤษณา-ชุติมา ภาควิชาเคมี

คณะวิทยาศาสตร์ มหาวิทยาลัยเกษตรศาสตร์

WORK SHOP

PERCH-CIC

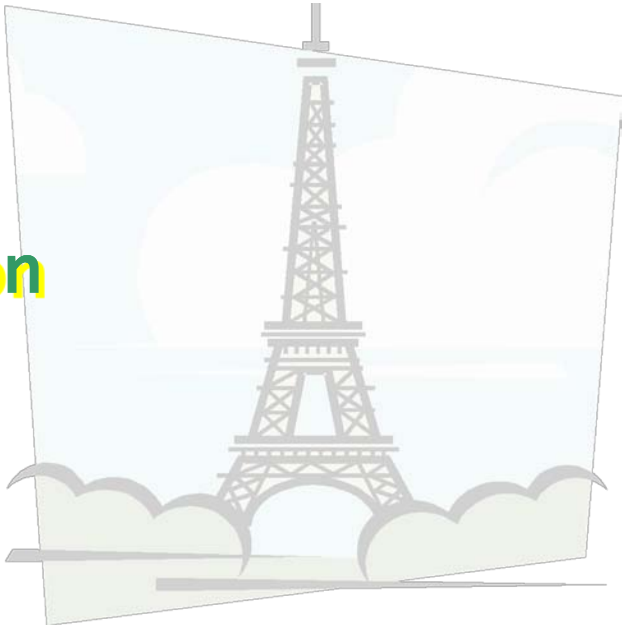
TiO_2

Introduction

Preparation

Characterization

Applications



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Introduction

History of TiO_2

The element Ti was dicovered in 1791 by William Gregor. He isolated an impure oxide from ilmenite ($FeTiO_3$) by treatment with HCl and H_2SO_4. Martin H. Klaproth prepared TiO_2 (1795).

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Introduction

History of TiO_2

Usage of TiO_2

1. Paint opaque (white pigment),
   - very white
   - very high refractive index.

(Hence, with its high refractive index, relatively low levels of titania pigment are required to achieve a white opaque coating. One of the major advantages of the material for exposed applications is its resistance to discoloration under UV light.)

2. **Photocatalyst**
3. Stripping organic compound
4. Cosmetic product

etc.

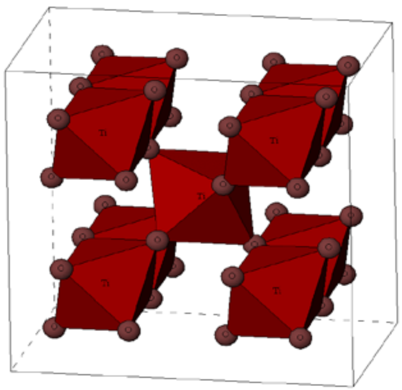
Introduction

Physical/chemical properties

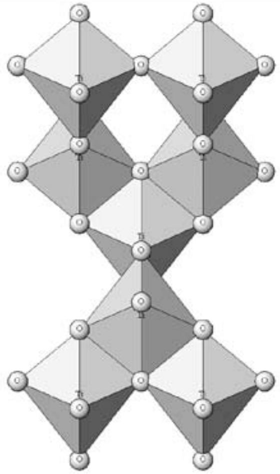
Molecular formula	TiO_2
Molecular weight	79.87 g/mol
Appearance	White solid
Density	4.23 g/cm^3
Melting point	1870 ^{0}C
Boiling point	2972 ^{0}C
Solubility	Insoluble
CAS number	13463-67-7

Introduction

Structural properties



Rutile



Anatase

Properties	Rutile	Anatase
System	Tetragonal	Tetragonal
a(Å), b(Å), c(Å)	a=b≠c	a=b≠c
α(deg),β(deg),γ(deg)	$\alpha=\beta=\gamma=90^0$	$\alpha=\beta=\gamma=90^0$
unit cell volume(Å)^3	62.42	136.5
D_x(g/cm^3)	4.25	3.89

Table1 Structural properties of TiO_2

Introduction

Phase transformation of TiO_2

$$n\lambda = 2d\sin\theta$$

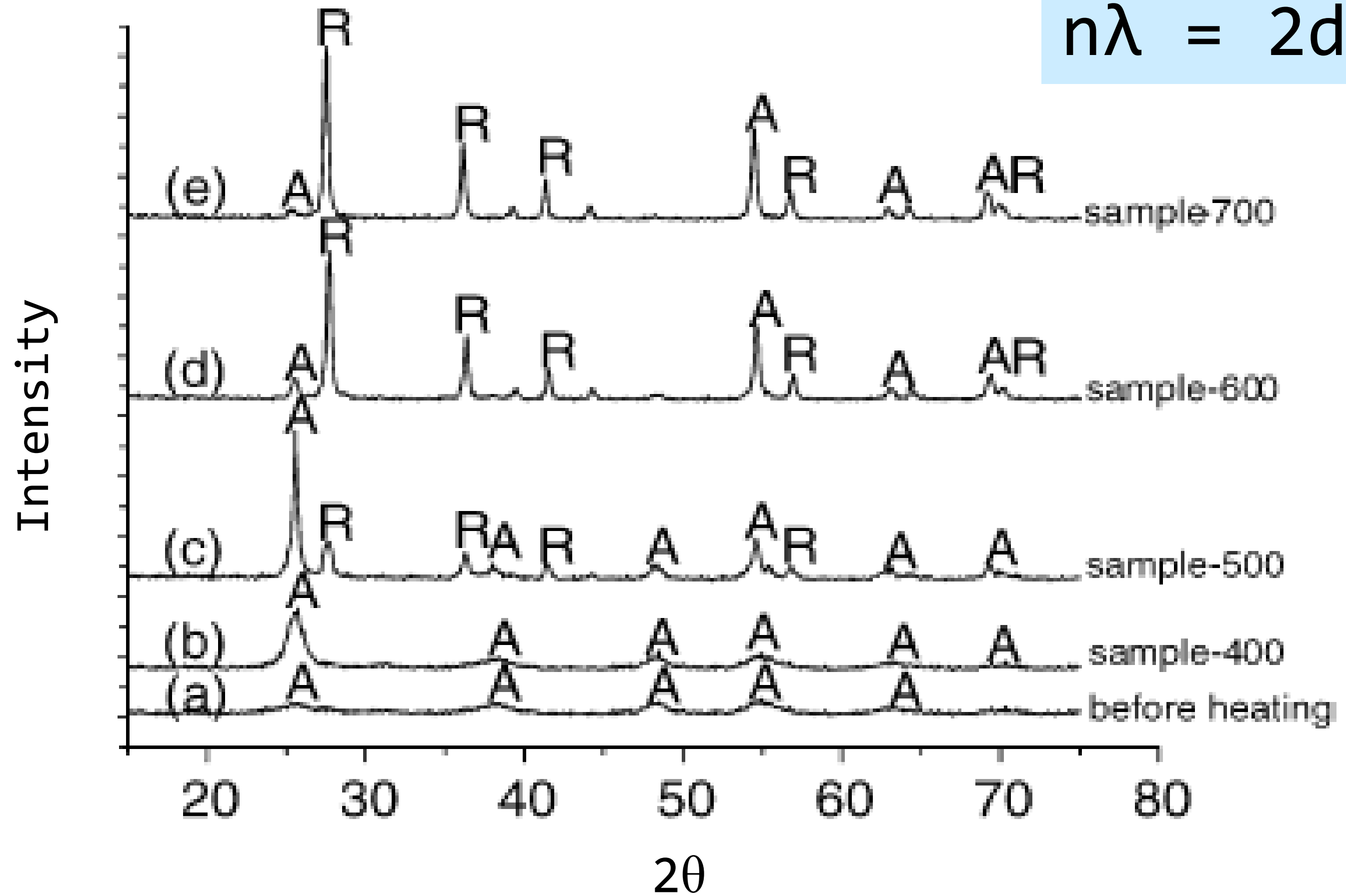


Fig.1 XPD pattern of phase transformation of TiO_2

Introduction

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Crystallite size

Sherrer's equation

$$s = \frac{k\lambda}{\beta\cos\theta}$$

s = crystallite size(nm)

k = constant(0.9)

λ = wavelength of radiation (Cu K_α = 1.54 Å)

β = the full width at half maximum (FWHM)(radian)

θ = the Bragg's angle (degree)

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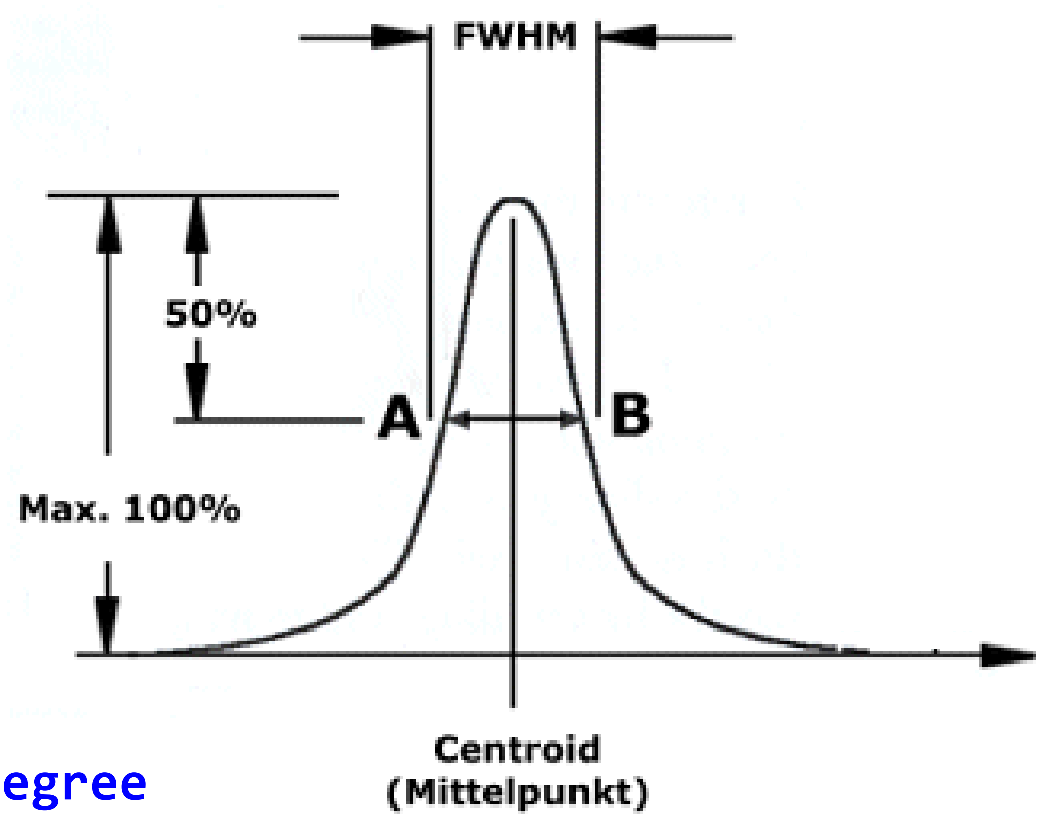
Introduction

Crystallite size



$2\pi r$ = 360degree

Introduction

The effect of temperature on crystallite size

Calcination temperature (T_c) (°C)	Diffraction angle (2θ)	FWHM (radian)	Crystal size (nm)
Before annealing (A)	25.55	0.037520	4.10
400 (A)	25.64	0.011010	13.96
500 (A)	25.65	0.008740	17.60
500 (R)	27.51	0.008323	18.78
600 (A)	25.46	0.007426	20.68
600 (R)	27.51	0.005941	26.31
700 (A)	25.56	0.005812	26.44
700 (R)	27.44	0.004455	35.07

Table2 Results of XPD measurement of TiO_2 samples

FWHM = Full width at half maximum

Introduction

Commercial TiO_2

- Degussa corp. Germany
  - Degussa P-25
  - Composition 75 % for anatase and 25 % for rutile
  - Nonporous with cubic particles
  - Particle size ~ 25 nm.
  - Surface area 35-65 m^2/g

Produced by high temperature flame hydrolysis of $TiCl_4$ or titanium tetra isopropoxide($T>1200^oC$) in the presence of O_2 and H_2.

Preparation

How to synthesize TiO_2?

- Sol-gel method
- Reverse micellar sol-gel method
- Precipitation
- Hydrothermal method
- Thermal decomposition method

etc.

Preparation

1.Sol-gel method

sol: a colloid that has a continuous liquid phase in which a solid is suspended in a liquid.

gel: a colloidal system in which a porous network of interconnected nanoparticles spans the volume of a liquid medium.

Sol-gel process: the time for gel formation and a wet-chemical technique for the fabrication of materials starting from a chemical solution containing colloidal precursors (*sol*).

Preparation

4 steps of sol-gel method

1) Formation of gel:

Typical precursors are metal alkoxides and metal chlorides which undergo two reactions

1. hydrolysis
2. polycondensation

that both are nucleophillic substitution reaction to form a colloid.

M-OR	+	HOH	$\longrightarrow$	M-OH	+ ROH	hydrolysis
M-OH	+	RO-M	$\longrightarrow$	M-O-M	+ ROH	} condensation
M-OH	+	HO-M	$\longrightarrow$	M-O-M	+ HOH	

Preparation

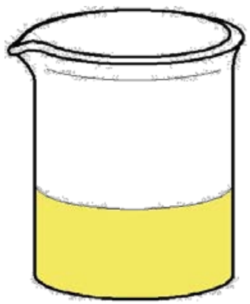
4 steps of sol-gel method

2) **Aging of gel:** the time for gel formation and remove solvent from gel, however, liquid phase still in porous in matrix.

3) **Removal of solvent:** serves to remove the liquid phase from the gel thus forming a porous material.

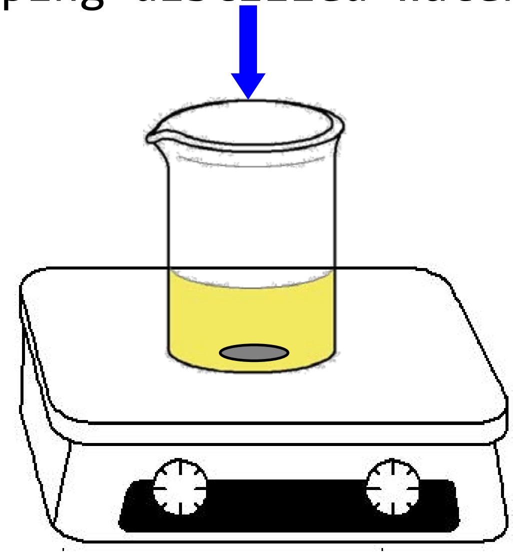
4) **Heat treatment/Calcination:** is the process of subjecting a substance to the action of heat, but without fusion, for the purpose of causing some change in its physical or chemical constitution. The objectives are usually; (1) to drive off water, present as absorbed moisture, (2) to drive off CO_2 or other volatile constituents, (3) to oxidize a part or the whole of substance.

Preparation



$$\frac{\text{Titanium alkoxide}}{\text{Distilled water}} = \frac{1}{2}$$

Dropping distilled water



Stirred for 30 min

Titanium alkoxide
:**Titanium(IV)bis(ethylacetoacetato)diisoproproxide**

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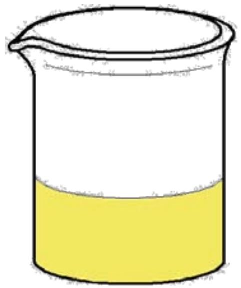
Preparation



Dried at 120 ^{0}C, 2 hr.

TiO_2 amorphous phase

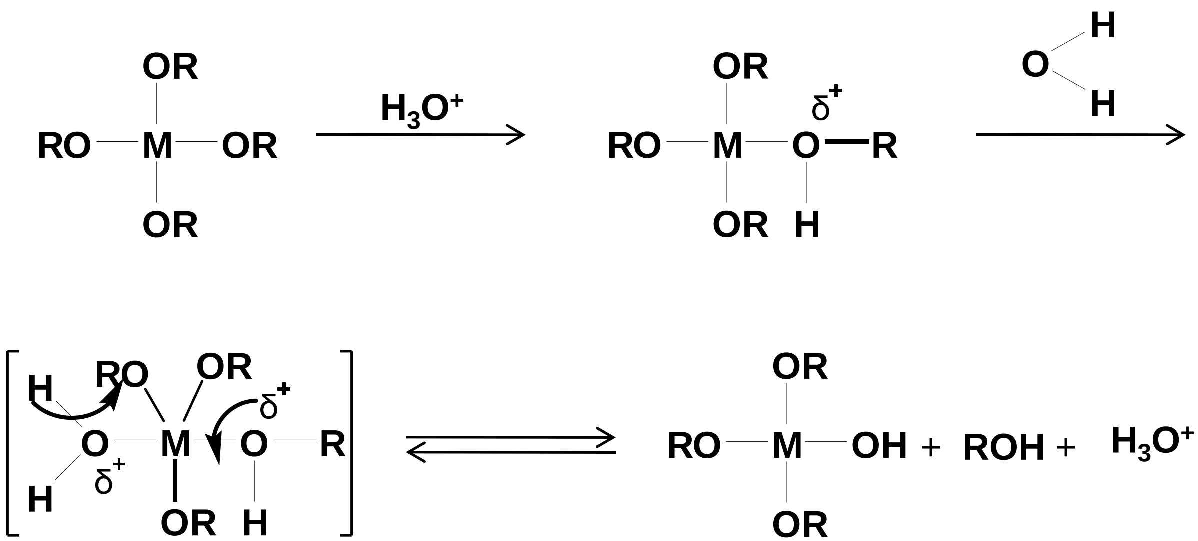
Calcined at various temperatures

Characterization

Preparation

The effect of pH on sol-gel process

- Mechanisms
  - Acidic condition



transition state showing pentacoordition

Fig.2 Mechanism in case of acidic condition

Preparation

The effect of pH on sol-gel process

- Mechanisms
  - Basic condition

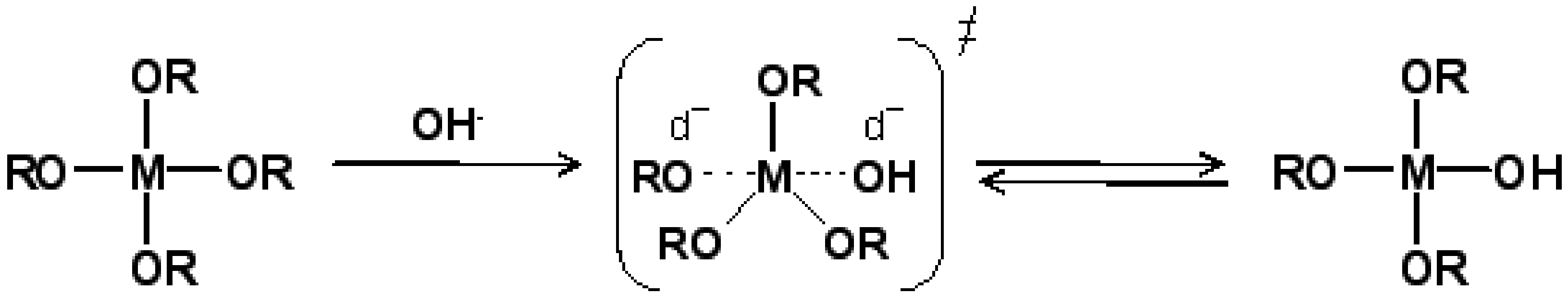


Fig.3 Mechanism in case of basic condition

Preparation

The effect of pH on sol-gel process

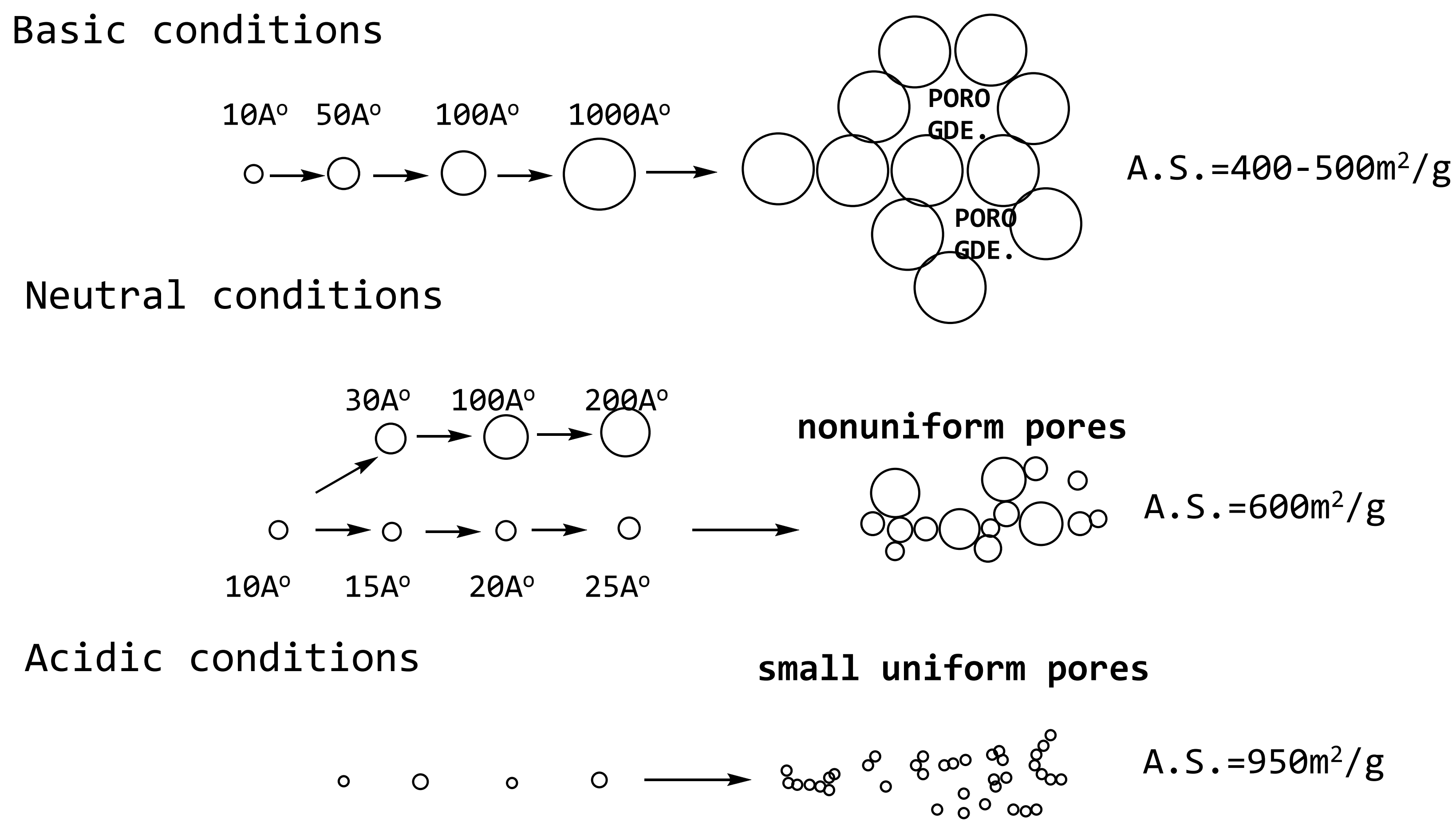


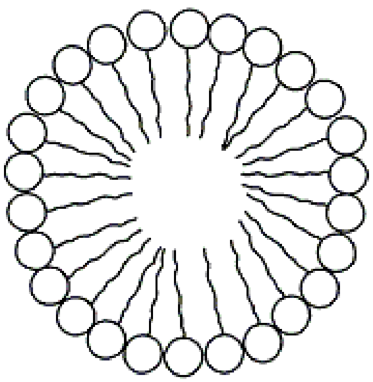
Fig.4 The formation of a gel from a colloidal solution

Preparation

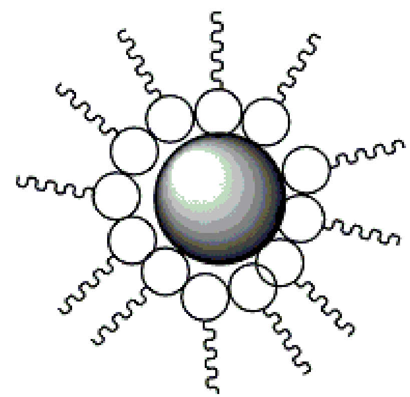
2.Reverse micellar sol-gel method

Surfactants

- Chemical surfactant such as Tween 80, CTAB
- Biosurfactant such as Rhamnolipid, Sophorolipid



Micelle



Reverse micelle

Fig.5 Structural types of micelle

Preparation

3.Precipitation method

Titanium tetraisopropoxide
$Ti(OC_3H_7)_4$

1. Span-Tween 80/water
2. Toluene
3. Stirring

TiO_2-precipitate

Titanium sulfate solution
$Ti(SO_4)_2$

NH_4HCO_3

$Ti(OH)_4$ gel

Centrifuge and wash

Dried at 80 ^0C

TiO_2-amorphous

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Preparation

4.Hydrothermal method

Hydrothermal synthesis; includes the various techniques of crystallizing substances from high-temperature aqueous solution at high vapor pressure.

The crystal growth is performed in an apparatus consisting of a steel pressure vessel called ”**autoclave**”

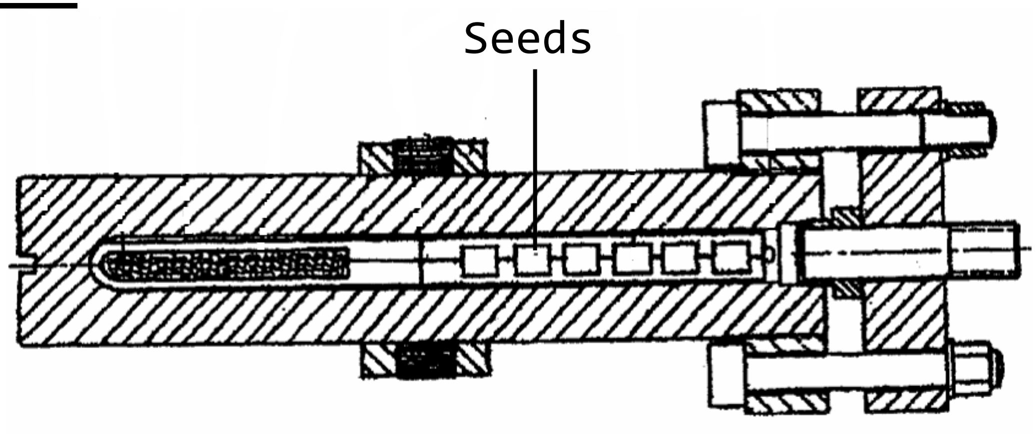
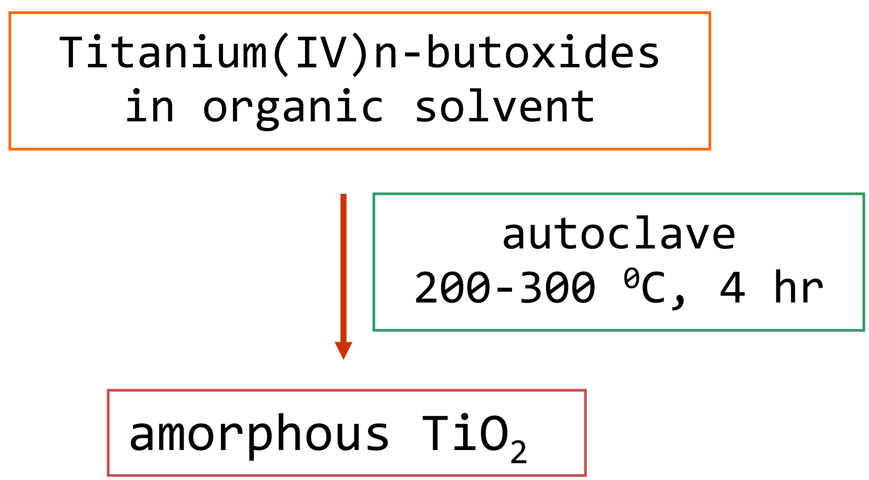


Fig.6 anatomy of the autoclave

Preparation

5.Thermal decomposition method

Thermal decomposition; is a chemical reaction whereby a chemical substance breaks up into at least two chemical substances when heated. It is an endothermic reaction as heat is required to break chemical bonds in the compound undergoing decomposition.



Advantages of the sol-gel process

- well-defined pore size distribution
- Purity & homogeneity
- Controlled porosity
- Ability to form large surface area materials at low temperature

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Characterization

Apparatuses

- Thermal Gravimetric Analysis (TGA)
- X-ray Powder Diffraction (XRD)
- UV-Vis Spectrophotometry
- Raman Spectrometry
- Scanning Electron Microscopy (SEM)
- Transmission Electron Microscopy (TEM)
- X-ray Photoelectron Spectroscopy

etc.

Applications

Photocatalysis

Photodegradation: is degradation of a photodegradable molecule caused by the absorption of photons, particularly those wavelengths found in sunlight, such as infrared radiation, visible light and ultraviolet light.

Choices of photocatalysts

TiO_2	3.2 eV
ZnO	3.2 eV
ZnS	3.6 eV
WO_3	2.8 eV
$SrTiO_3$	3.2 eV

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Applications

The advantages of TiO_2

- The strong oxidizing power of its holes (more powerful oxidation ability than ozone)
- High photostability
- Redox selectivity
- Commercial availability
- Ease for preparing in laboratory
- Non-toxic compound for environment and human

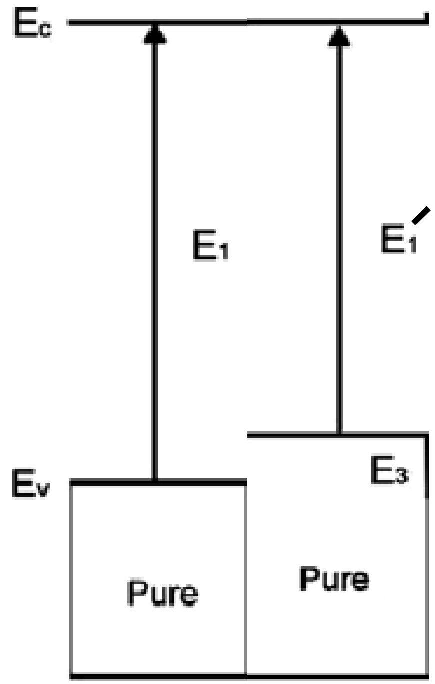
Applications

Electronic structure

TiO_2

Anatase

E_1 = 3.20 eV



Rutile

E_1' = 3.0 eV

Fig.7 Schematic electronic structure for pure anatase and rutile TiO_2

Applications

Photocatalytic reactions

Generation of electron and hole

$TiO_2 + h\nu \longrightarrow TiO_2(e^-_{cb} + h^+_{vb})$

Recombination

$TiO_2(c^-_{cb} + h^+_{vb}) \longrightarrow TiO_2 + heat$

Formation of hydroxyl radical

$h^+_{vb} + OH^- \longrightarrow \cdot OH$

$h^+_{vb} + H_2O \longrightarrow \cdot OH + H^+$

$e^-_{cb} + O_2 \longrightarrow \cdot O_2^-$

presence of water is required

vb-valance band

cb-conduction band

h^+_{vb} -hole

Applications

Photocatalytic model

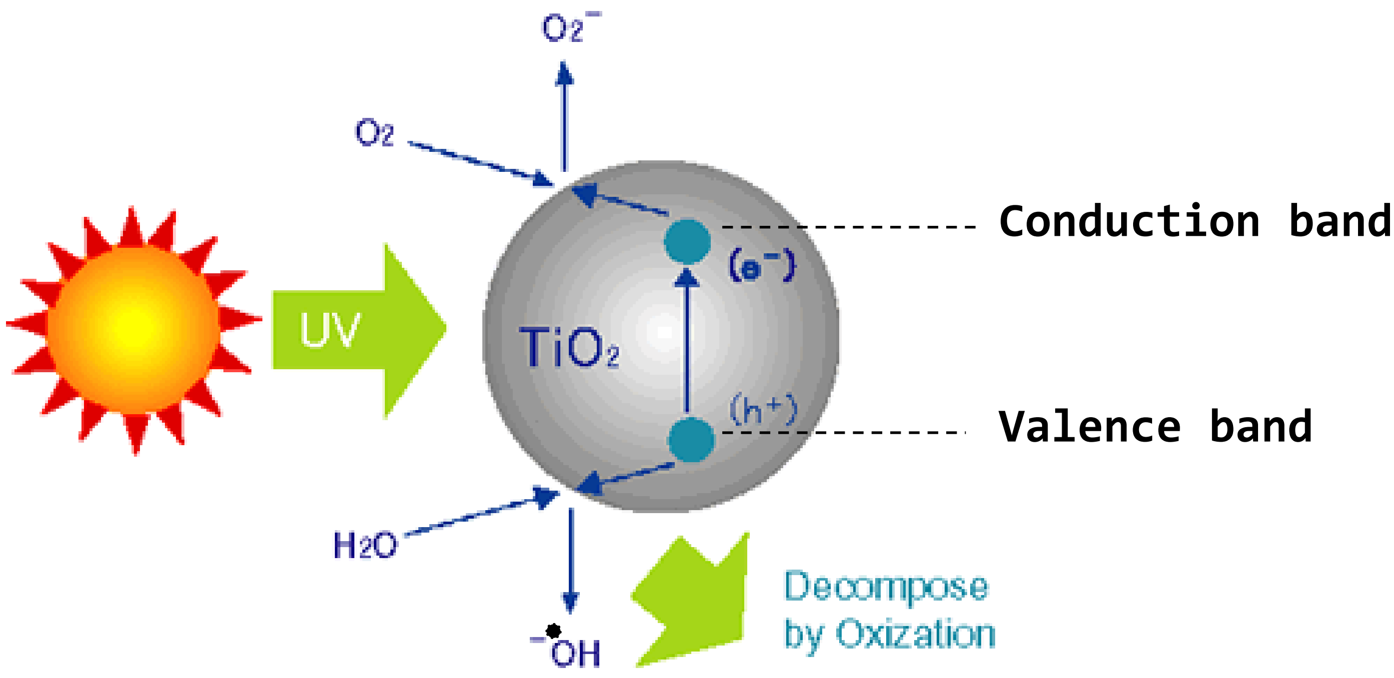


Fig.8 Mechanism of photodegradation

Applications

Electronic structure

P25 TiO_2 (75% for anatase, 25% for rutile)

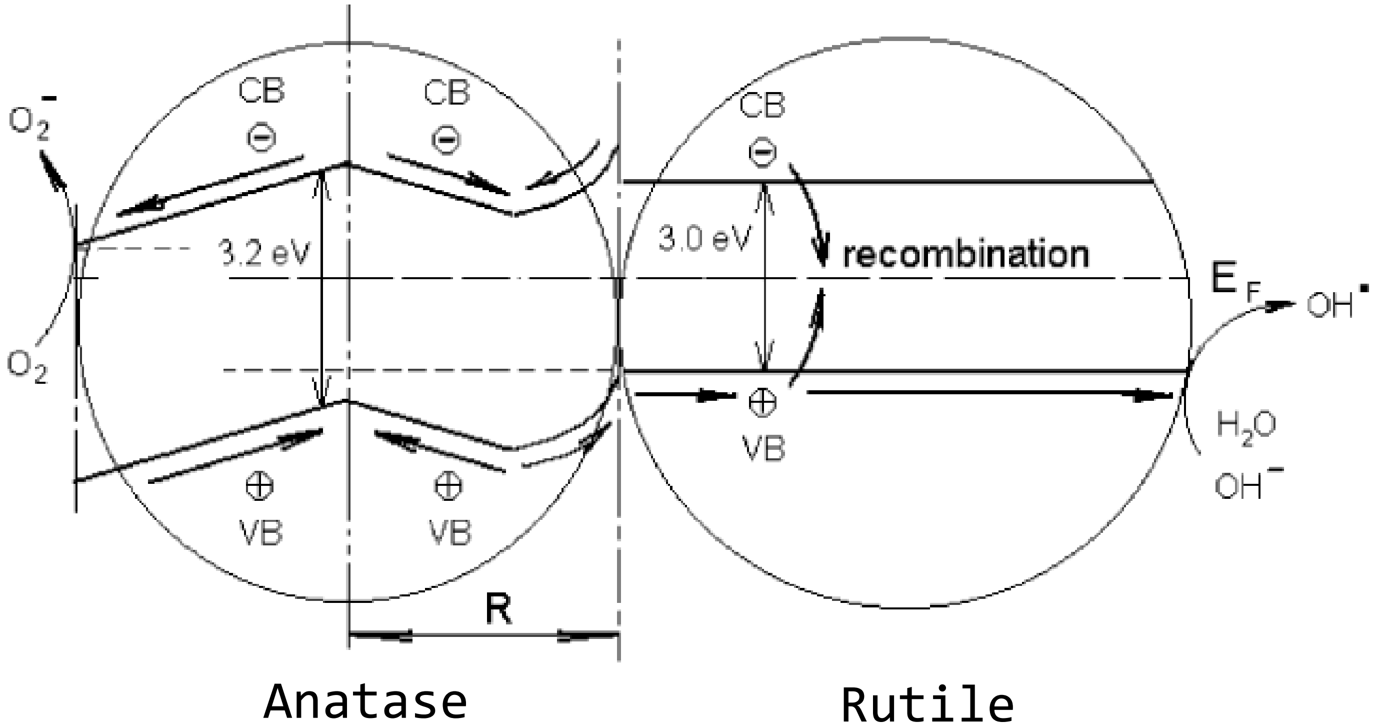


Fig.9 Schematic electronic structure for pure anatase and rutile TiO_2

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Applications

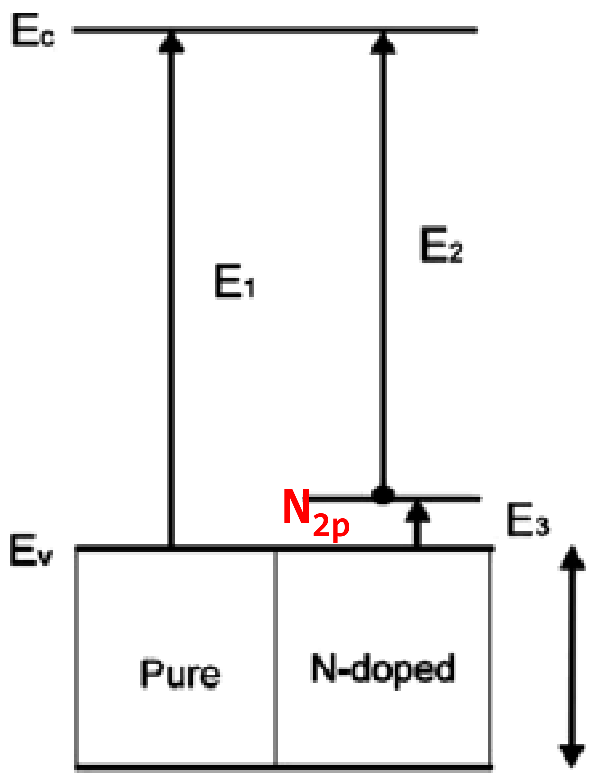
Modification of TiO_2

- Aim to decrease band gap energy of TiO_2 in the range of visible light because of nowadays only 5% of ultraviolet light passing through the earth.
  - Anion dopants such as S, N, C or B
  - Metal dopants such as Li(I), Zn(II), Pt, Co(III), Cr(III) or Mn(II)

Applications

Electronic structure

Anatase TiO_2



$E_1 = 3.2$ eV

$E_2 \approx 2.7$ eV

Fig.10 Schematic electronic structure for pure and N-doped anatase TiO_2

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Applications

Photodegradation of methylene blue(MB)

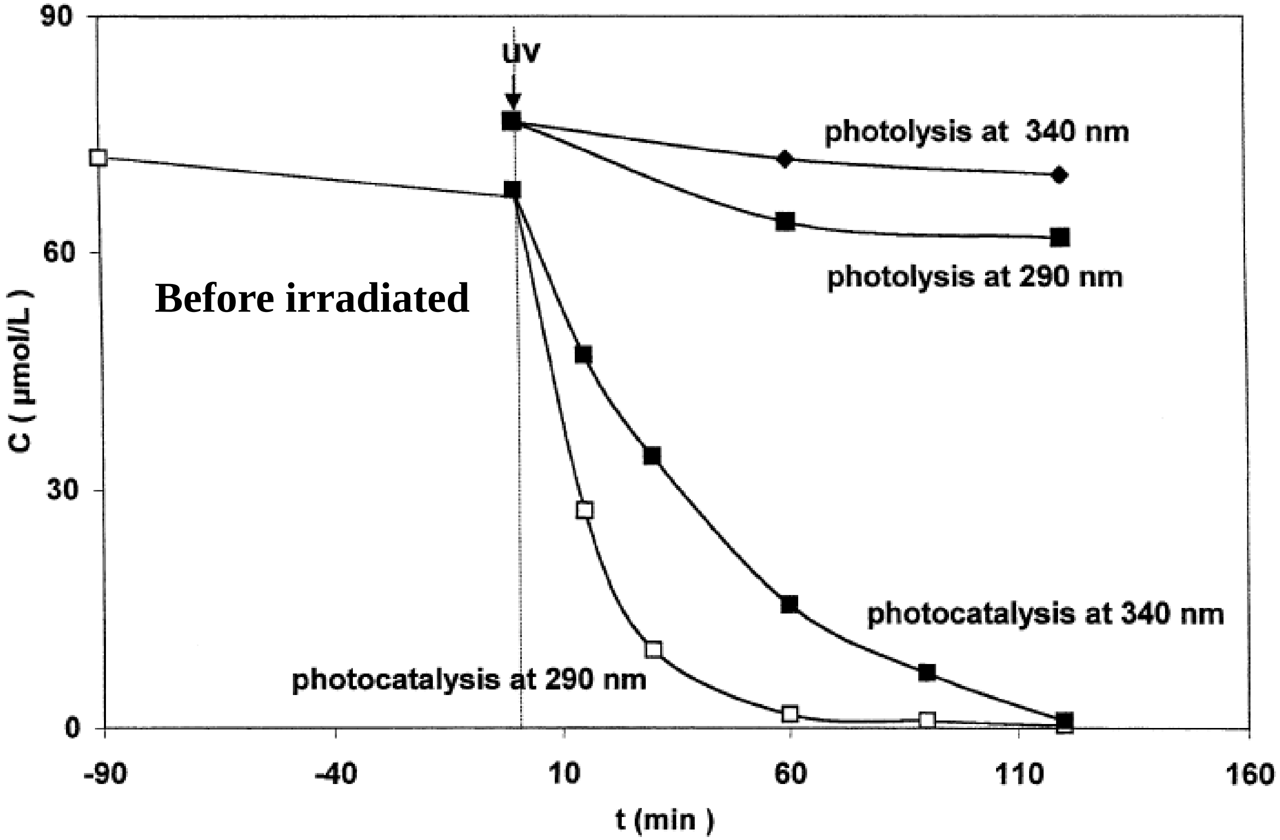

Fig.11 Disappearance of methylene blue by photocatalysis under UV-irradiation at λ = 290 nm. and 340 nm.

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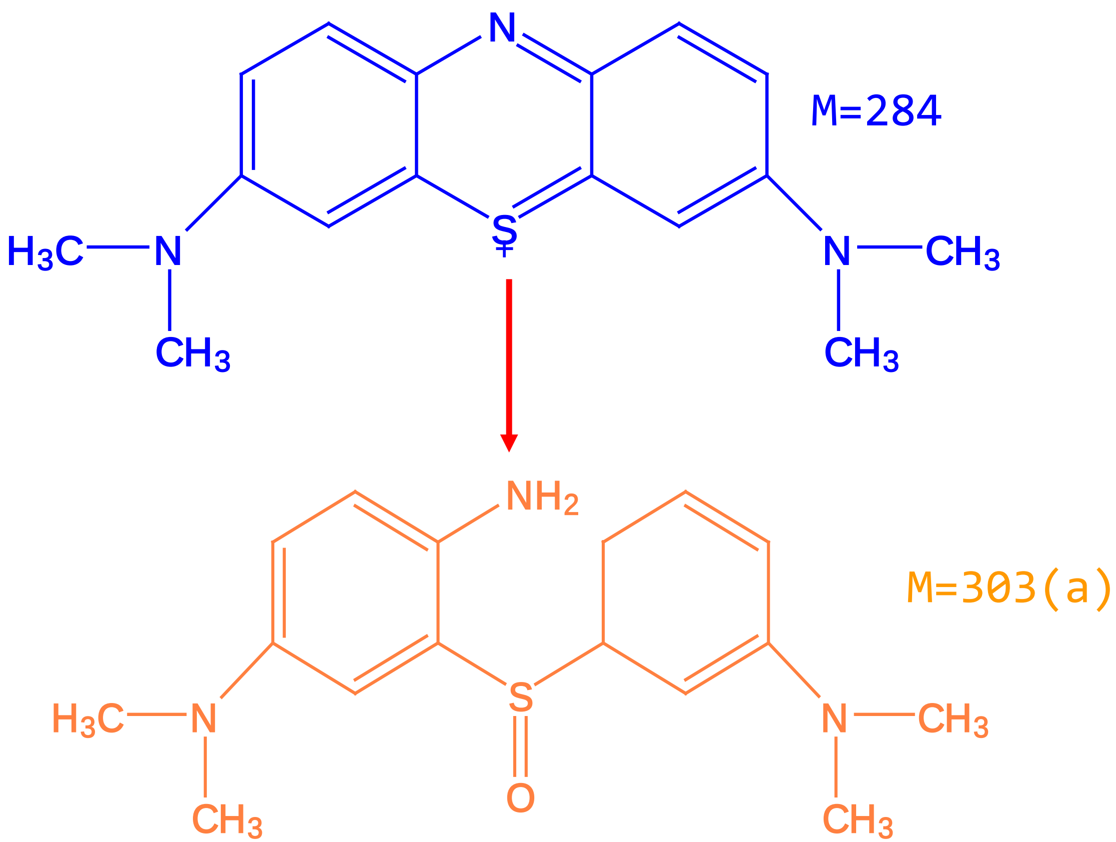
Applications

Photodegradation of methylene blue(MB)



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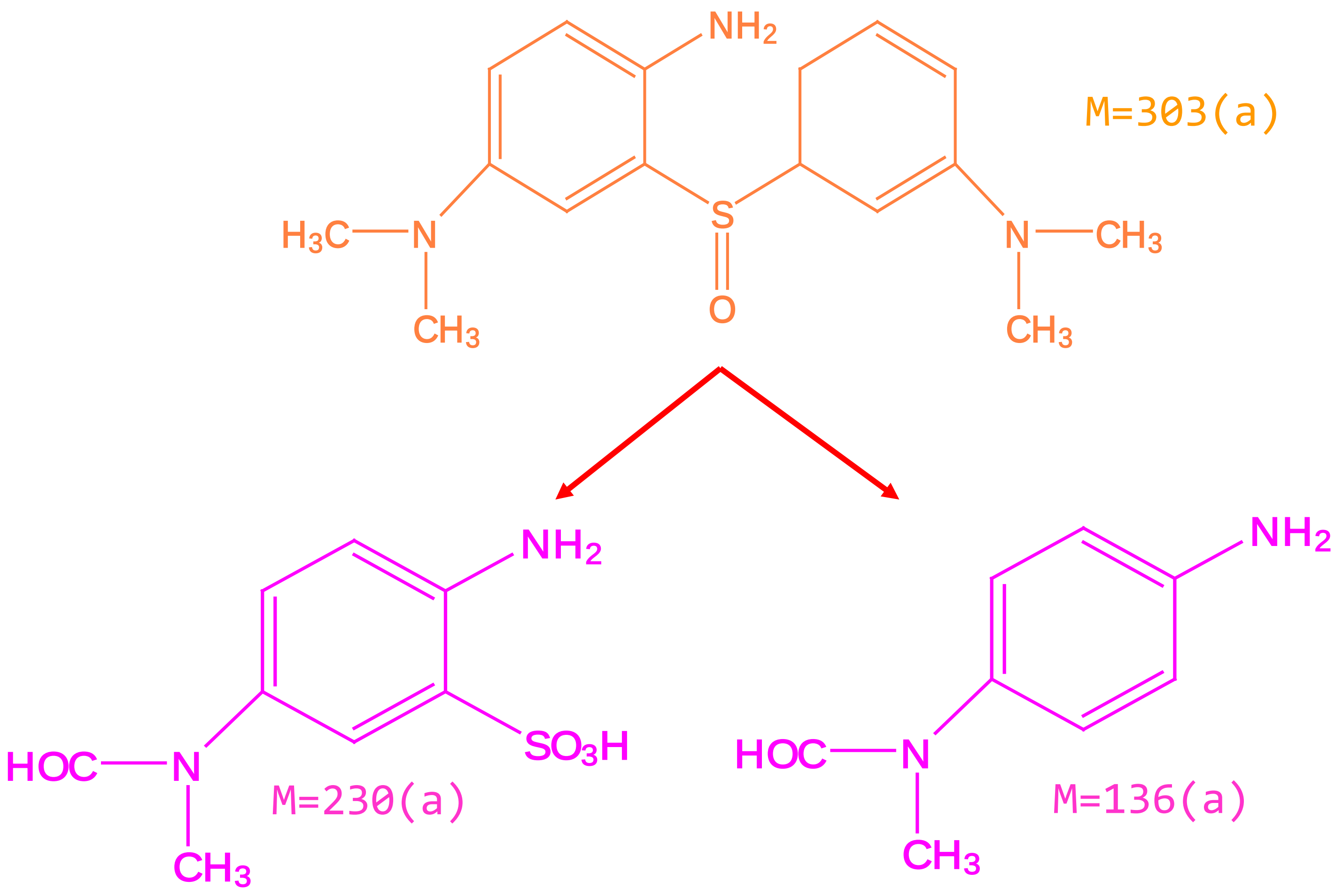
Applications

Photodegradation of methylene blue(MB)



Applications

Photodegradation of methylene blue(MB)

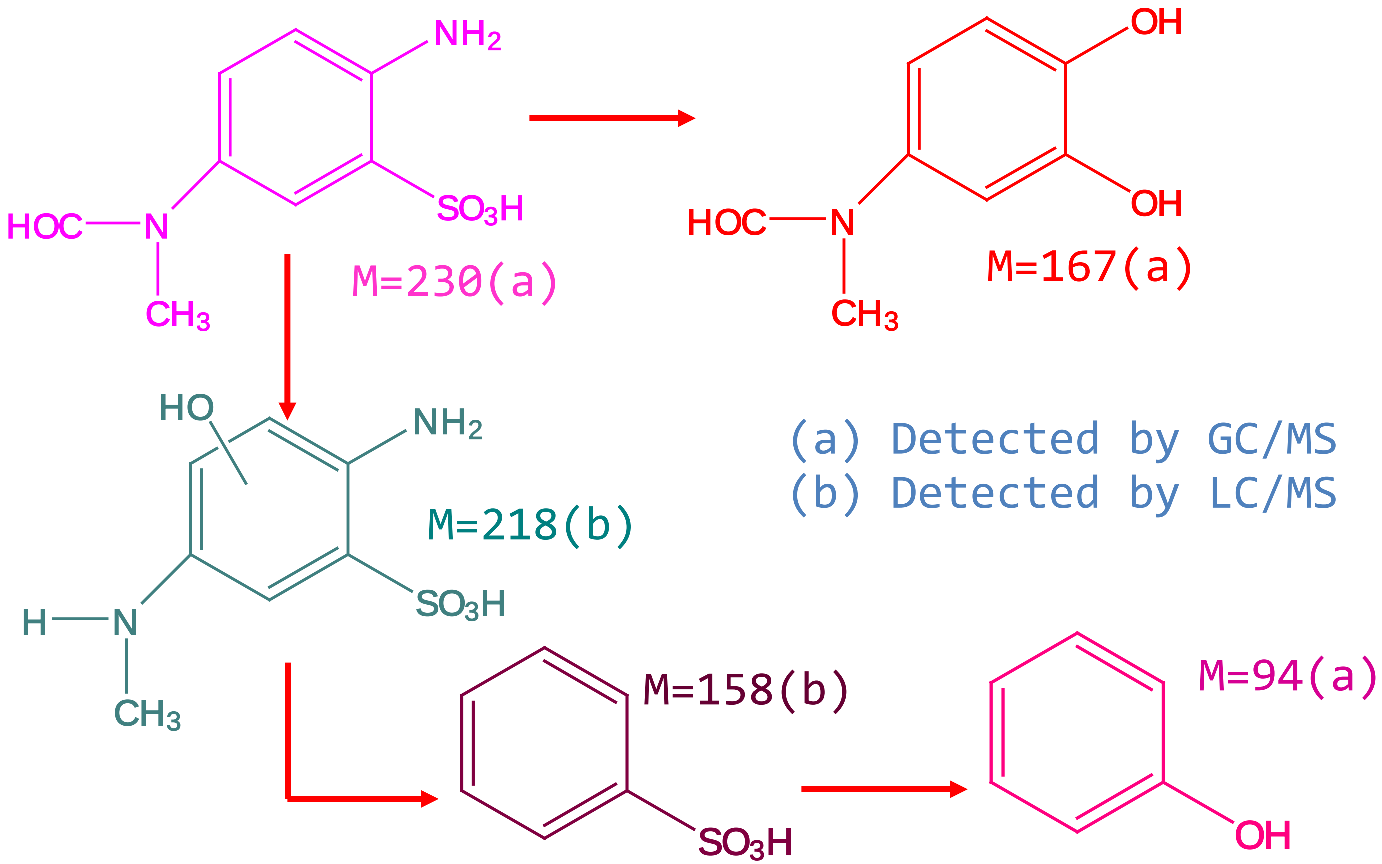


Fig.12 The possible reaction mechanism of MB oxidation by using illuminated TiO_2

Applications

Photodegradation of phenol

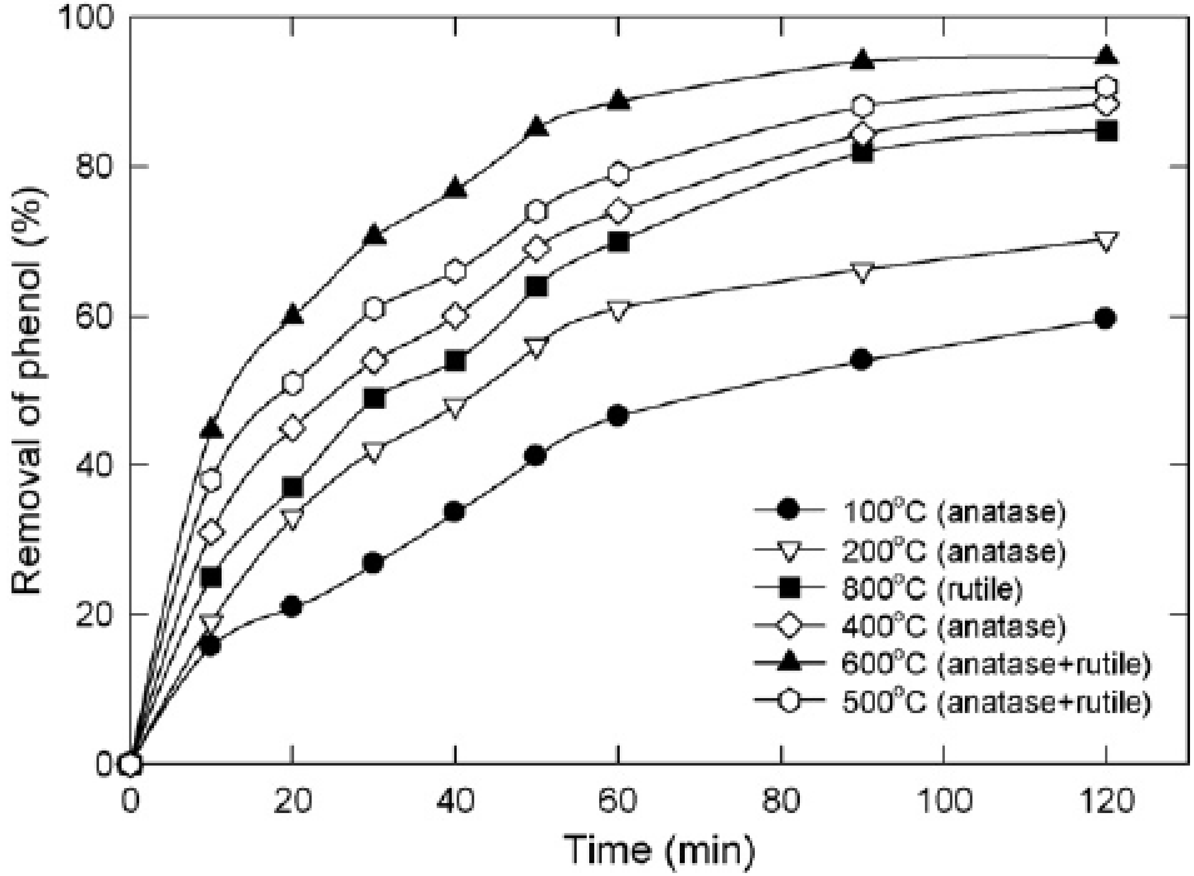


Fig.13 Photodegradation of phenol by using Pr-doped TiO_2

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Applications

Photodegradation of phenol

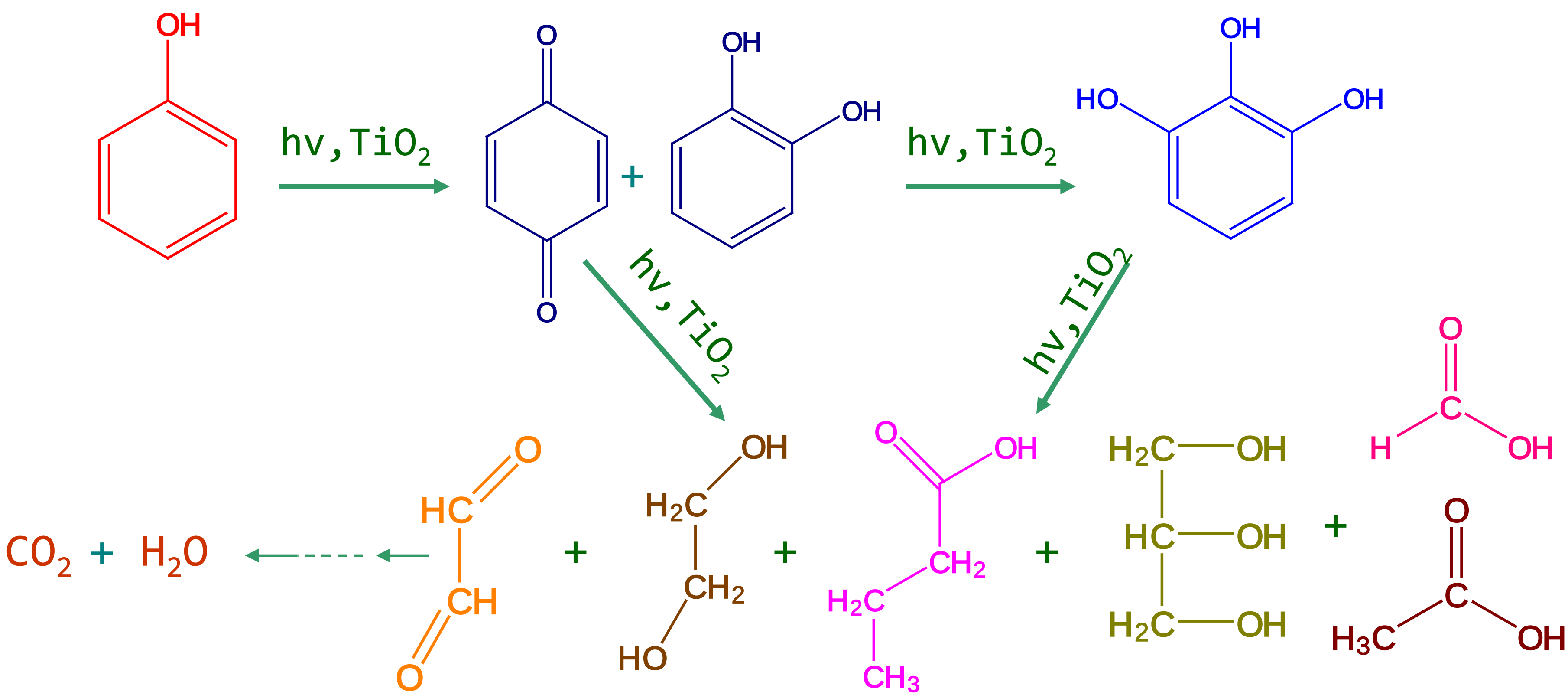

Fig.14 The possible reaction mechanism of phenol oxidation by using illuminated TiO_2

Conclusions

- TiO_2 can be synthesized by using sol-gel method and other techniques.
- TiO_2 can be applied for serving as the effective photocatalyst to terminate toxic.
- we can modify TiO_2 via doping techniques to narrow band gap energy of TiO_2.

THANK YOU