$\lambda_{1/2}$ versus $f_{\text{anatase}}$

absorption edge wavelength
anatase: ca. 370 nm
rutile: ca. 410 nm

oxygen evolution & silver metal deposition

$R \gg A$  
$A \gg R$

inner-filter effect by rutile

dehyderogenation of methanol

CR-EL  
Aldrich(A<R)  
Wako(R)  
Merck+CR-EL  
Wako(A)+CR-EL  
P25 (1473 K)

decomposition of acetic acid

CR-EL(1473 K)  
P25 (1473 K)  
CR-EL  
Aldrich(A<R)  
Wako(R)  
Merck+CR-EL  
Wako(A)+CR-EL  
P25  
Merck  
Hombikat  
TIO-5  
TIO-2
anatase absorption in anatase-rutile mixture

photon flux reachable to anatase is reduced by rutile

 photon flux reachable to anatase
thin film of TiO$_2$ coated on glass plates

(without preheating) small CA before irradiation

order of the onset wavelength = that of absorption

wavelength dependence of superhydrophilicity

different behavior depending on the water contact angle:

> 10 degree
ordinary oxidation of surface contaminants

<= 10 degree
different mechanism, presumably including surface bound hydrogen peroxide or peroxy species

unit cell of crystal

- unit of repetition: connected to all directions
- Atoms (ions) are shown in a dot at their center
- Apexes are occupied by atoms (ions), which are shared by unit cells.

- x-y-z (a-b-c) is set as a right hand.
two-dimensional unit cells
two-dimensional unit cells
unit cell of rutile

xyz is as a right-handed
x: thumb
y: index finger
z: mid finger

An order of xyz is decided from same length.

Miller index: William Hallowes Miller
crystal structure of anatase (1)

red: O

green: Ti

0.9514 nm

0.3785 nm
Q How many TiO$_2$ s are included in a unit cell?

A $1 + 4(1/2) + 8(1/8) = 4$ $<$4TiO$_2$$>$

Octahedron in anatase is a little skewed.
Why do all the crystal structures of titania consist of octahedrons?

Ionic crystals (but not 100%) have a ratio of ionic radii of Ti$^{4+}$ and O$^{2-}$ is 0.536.

- Ti$^{4+}$: 0.075 nm
- O$^{2-}$: 0.14 nm
Q How can we determine the size of atoms, e.g., silicon in its crystal?

Q How can we determine the size of ions in ionic crystals?
coordination number $r_c/r_a$

- **linear** (2): 0.154
- **tetrahedral** (4): 0.225
- **cubic** (8): 0.414
- **triangle** (3): 0.732
- **octahedral** (6): 0.732
radius ratio and structure

• Radius ratio is calculated from the structure.
• distance between the center and a vertex.
Q Show x, y, and z directions.

unit cell of rutile

black: Ti
white: O

direction of axis

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sharing of octahedrons in anatase

Q How the central octahedron is connected to the other octahedrons?

A Connected to four octahedrons by "ridge" sharing
ridge sharing and point (apex) sharing

- absence of face sharing = impossible to make crystal structure
- "ridge sharing = 2 additional coordination by a central metal ion"
- "point (apex)" sharing = 1 additional coordination by a central metal ion
- titanium(IV) oxide = 6 oxygen atoms in an octahedron requires 18 coordination by titanium ions
- in anatase crystal
  - central titanium ion: 6
  - 4 ridge sharing: 8 (2 each)
  - requiring 4 point sharings
ridge sharing and point (apex) sharing

- absence of face sharing = impossible to make crystal structure
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- titanium(IV) oxide = 6 oxygen atoms in an octahedron requires 18 coordination by titanium ions
- in anatase crystal
  central titanium ion: 6
  4 ridge sharing: 8 (2 each)
  requiring 4 point sharings
brookite

- 8 TiO$_2$
- ridge sharing: 3
- point sharing: 6
crystal structure of brookite

(left) no atoms (ions) at the apexes!
(center) VICS and (right) Chime (three dimensional modeling softwares)
(left) displaying by VESTA
(lower) a model made of paper
data files for VESTA

- anatase  http://pcat.cat.hokudai.ac.jp/class/crystal/anatase.vesta
- anatase (101)  http://pcat.cat.hokudai.ac.jp/class/crystal/anatase2.vesta
- rutile  http://pcat.cat.hokudai.ac.jp/class/crystal/rutile.vesta
- brookite  http://pcat.cat.hokudai.ac.jp/class/crystal/brookite.vesta

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<nickname>
<comments on this lecture>
<question(s) if any>
sample mail

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subject: pc20170720-12345678

pc20170720-12345678
zzz@yyy.hokudai.ac.jp

大谷文章
某教授
光触媒の応用例について知り、その基本が化学であることを学びました。光と物質のかかわりについてさらに知りたいので本を調べてみます。
絶版になっている「光触媒標準研究法」はどこかで入手可能ですか。