

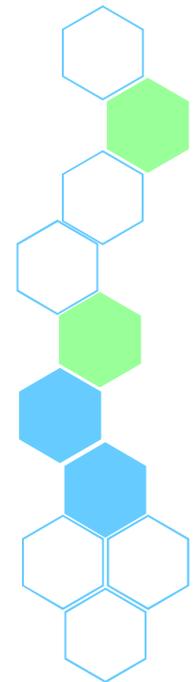
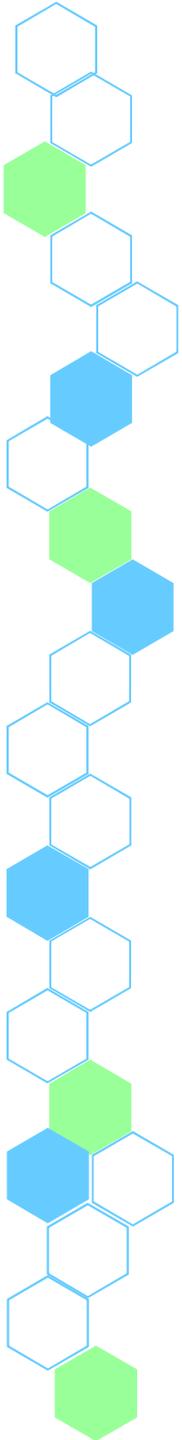
Titanium Dioxide Nanomaterials

TOC

- i. Introduction*
- ii. Synthetic Methods*
- iii. Properties*
- iv. Modifications*
- v. Applications*
- vi. Summary*

2011. 07.26 (Tue)

Kouji Yasuda (M1)





i. Introduction



Where TiO_2 is Used?



pigment



paint



ALL WHITE TOOTH PASTE

A Whitening toothpaste containing peroxide to help keep your teeth their whitest

ROCKY MOUNTAIN SUNSCREEN

High Exposure **SUNSCREEN**
with **TITANIUM DIOXIDE**

SPF **50+**

UVA • UVB
FRAGRANCE FREE
ALOE • MOISTURIZING
VERY WATER RESISTANT

6 Fl. Oz. (177 ml)

Metanium

Nappy
Rash
Ointment

Soothes & treats
your baby's
nappy rash



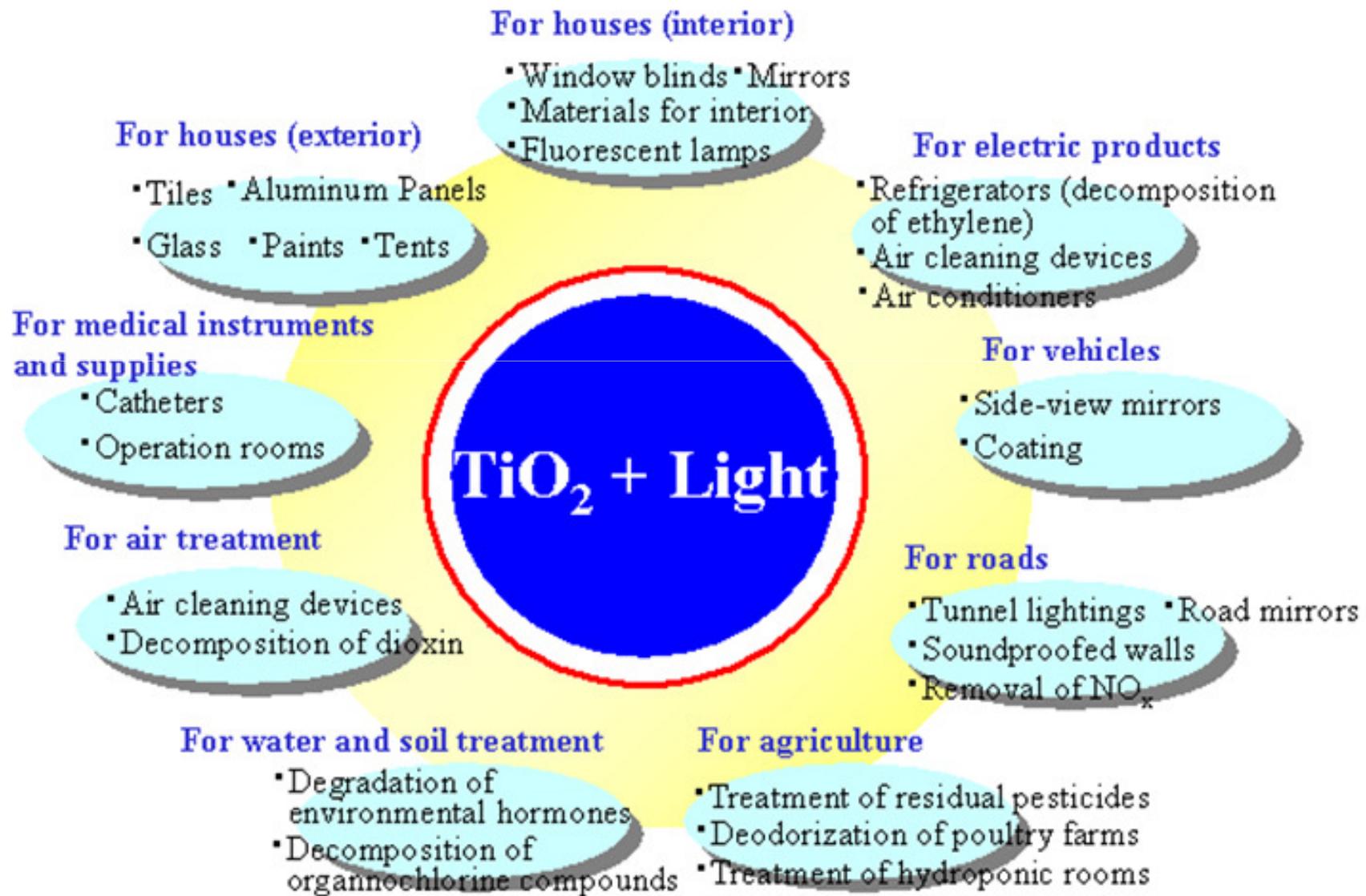
toothpaste

sunscreen

ointment

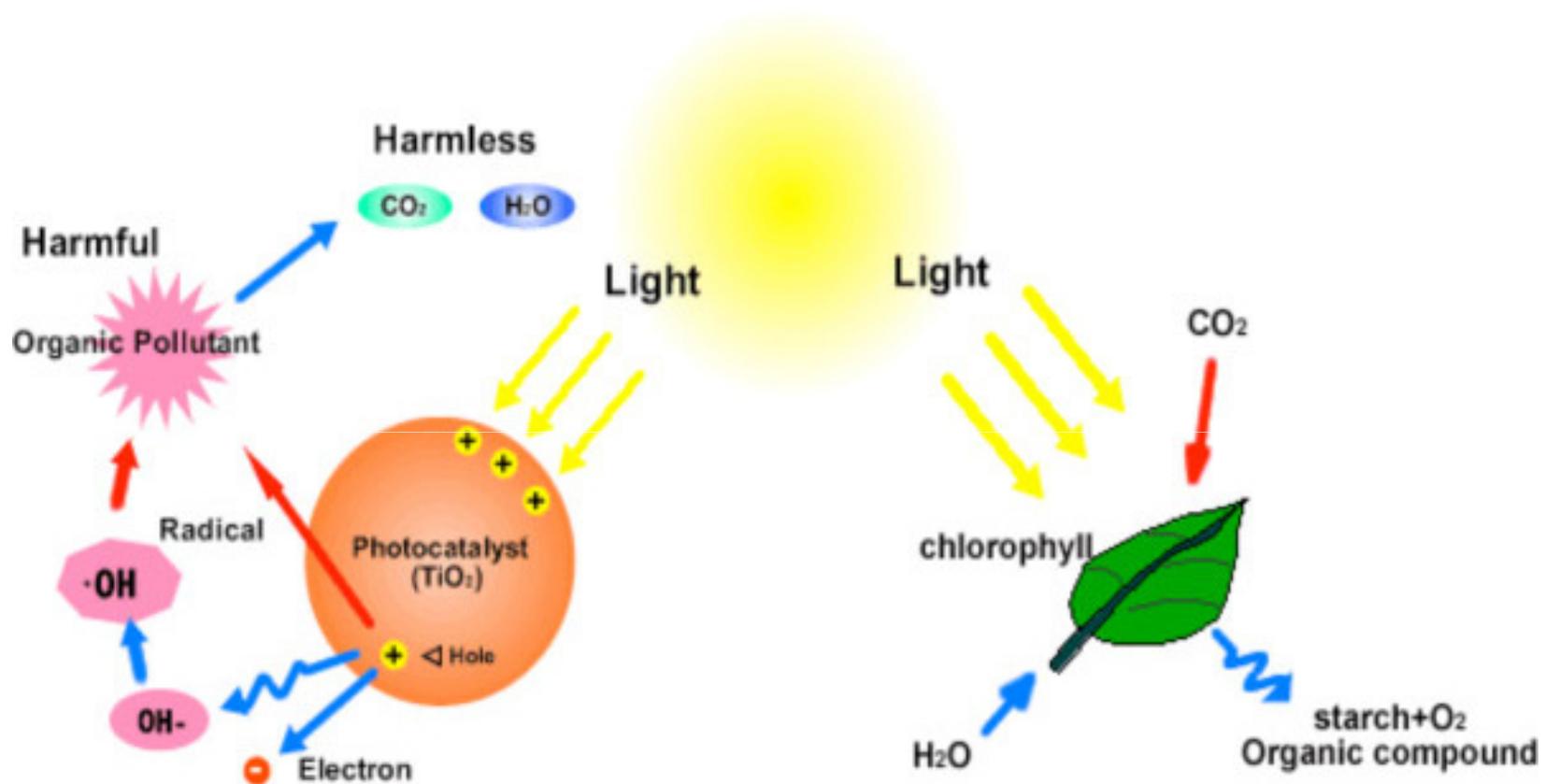


TiO₂ as Photo Catalysis





TiO₂ as Photo Catalysis



- 1, TiO_2 absorbs Ultraviolet radiation from sunlight.
- 2, Generated negative-electron (e^-) and positive-hole (h^+) pair.
- 3, Water-splitting reaction occurred.
- 4, Organic pollutant is split up to harmless products.

Why TiO₂ Nanomaterials Are Attracted now?

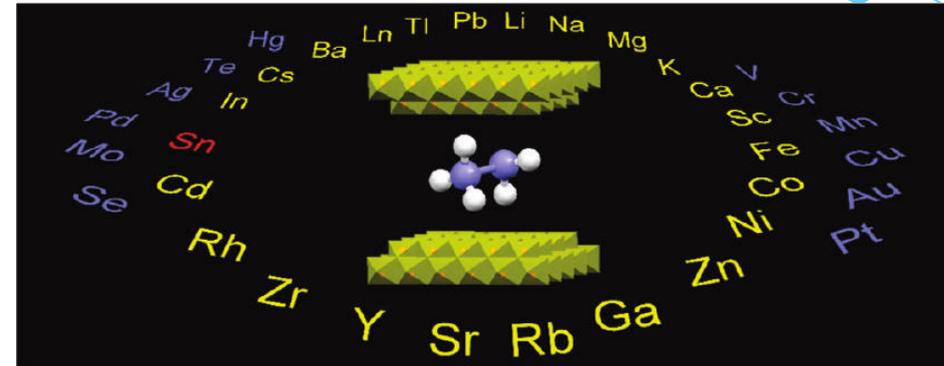


- Among the unique properties of nanomaterials, the movement of electrons and holes in semiconductor nanomaterials is primarily governed by the **well-known quantum confinement**, and the transport properties related to phonons and photons are largely affected by the **size** and **geometry** of the materials.
- It has possibility to help solving many serious environmental and pollution problems.
- It also bears tremendous hope in helping ease the energy crisis through effective utilization of solar energy based on **photovoltaic** and **photocatalytic** water-splitting devices.
- As another functionality of TiO₂ nanomaterials, it has many elements **adsorbent** capacity.

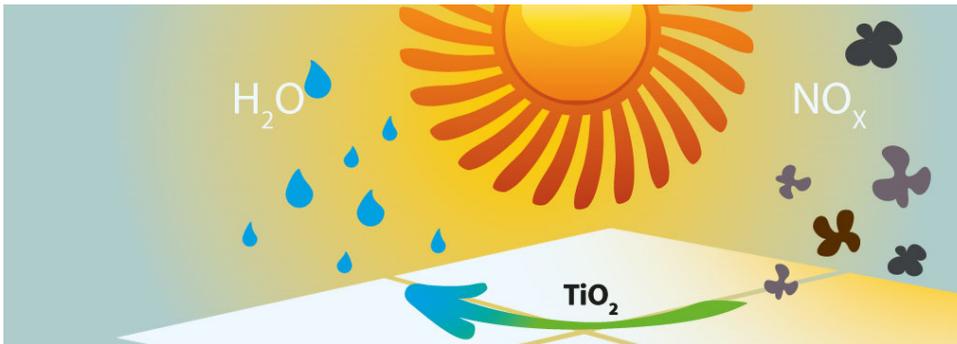
Applications of TiO_2 Nanomaterials



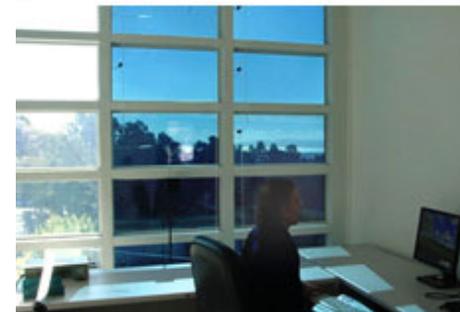
photovoltaics



adsorbents



photocatalysis



electrochromics

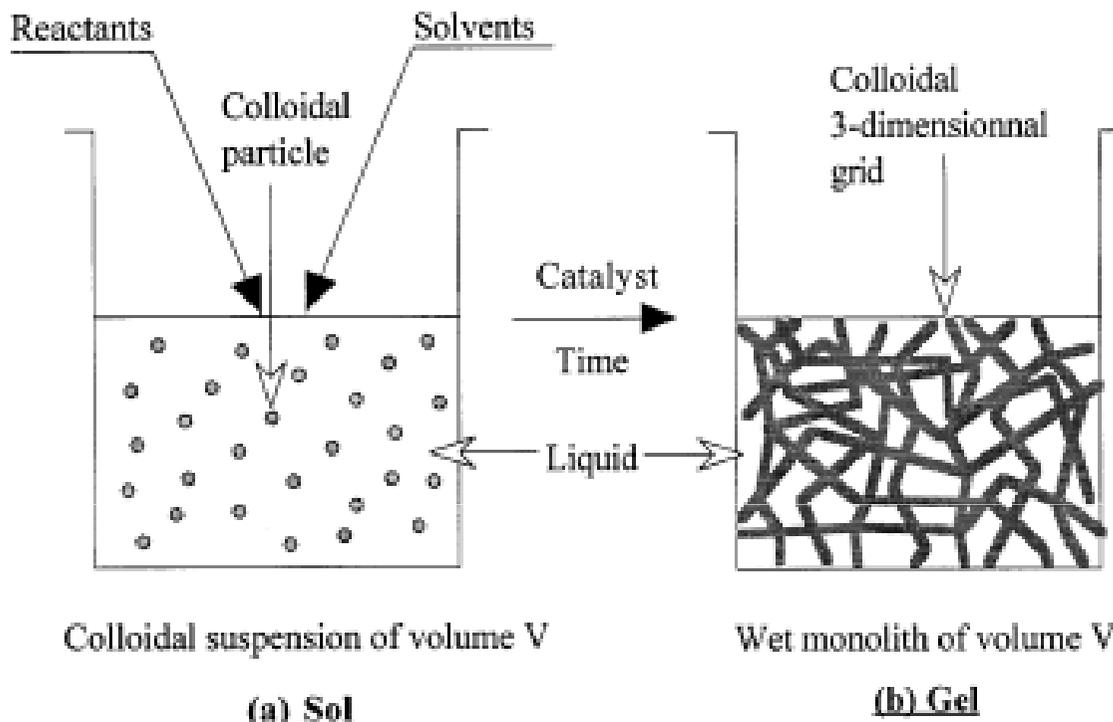


ii. Synthetic Methods

- i. Sol-Gel Method*
- ii. Micelle and Inverse Micelle Method*
- iii. Sol Method*
- iv. Hydrothermal Method*
- v. Solvothermal Method*



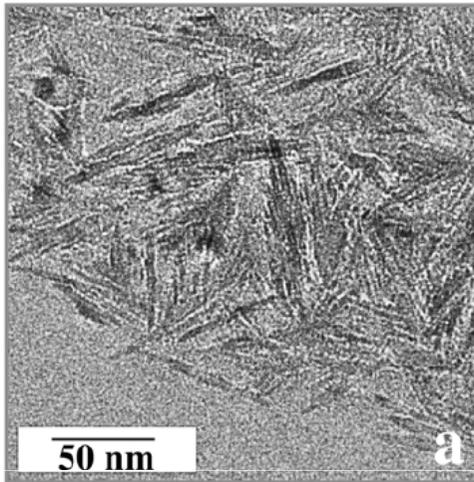
Sol-Gel Method 1



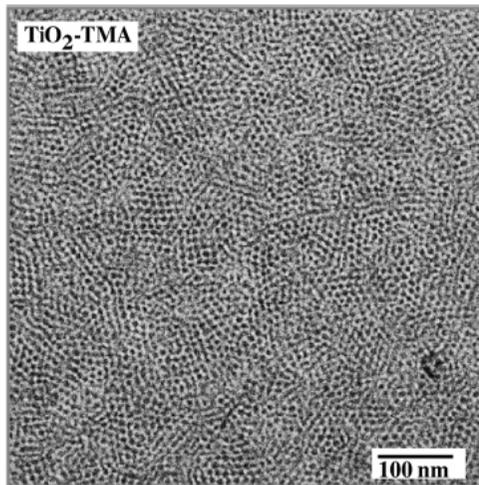
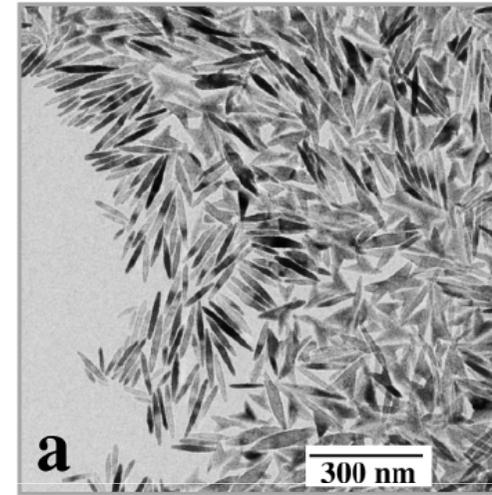
- This process normally proceeds via an acid-catalyzed hydrolysis step of titanium(IV) alkoxide followed by condensation.
- The development of Ti-O-Ti chains is favored with **low content of water, low hydrolysis rates, and excess titanium alkoxide** in the reaction mixture.
- 3-dimensional polymeric skeletons with close packing result from the development of Ti-O-Ti chains.



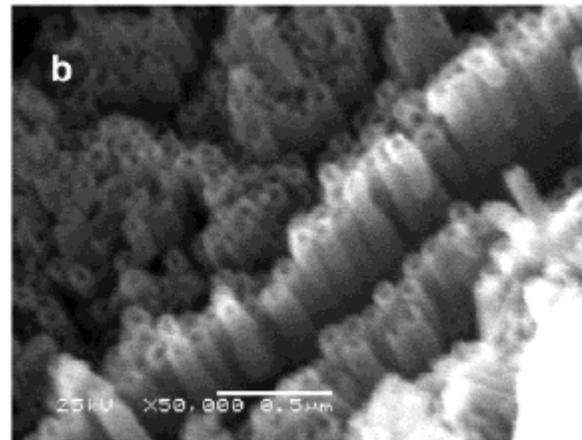
Sol-Gel Method 2



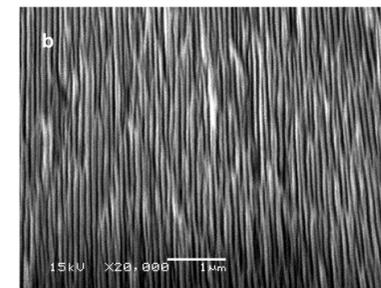
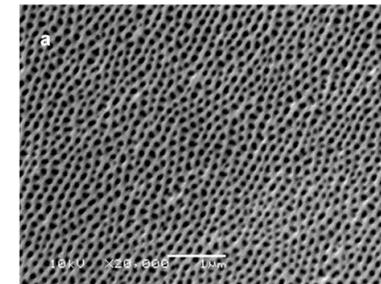
Autocrafting at 200 °C
2500 pKa, 5 h



Ti(OⁿBu)₄ as the titanium source in butanol.



TiO₂ nanotube synthesized by using anodic aluminum oxide templates (AAO)



AAO

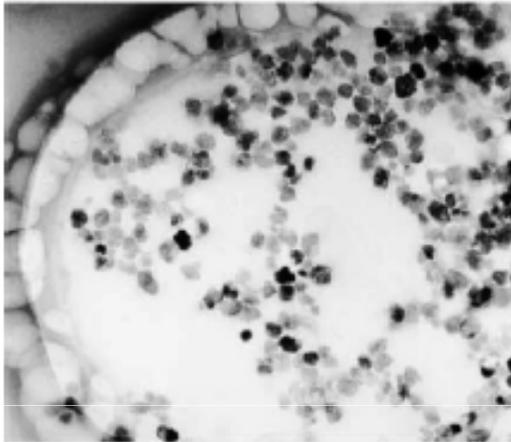
A.; Moritz, T. *et al.*, *Eur. J. Inorg. Chem.* **1999**, 235.

Zeng, H. C. *et al.*, *Chem. Mater.* **2002**, 14, 1391 ¹⁰

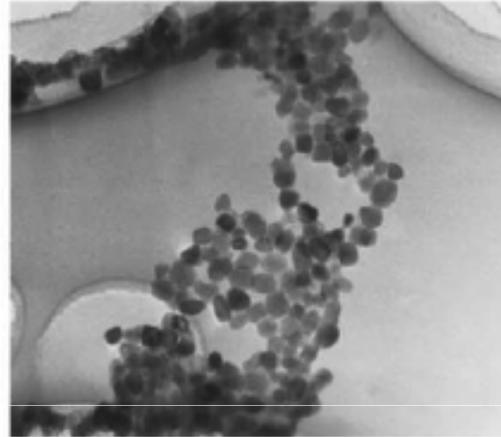


Sol-Gel Method 3

a) pH 9.6



b) pH 10.5



c) pH 11.5



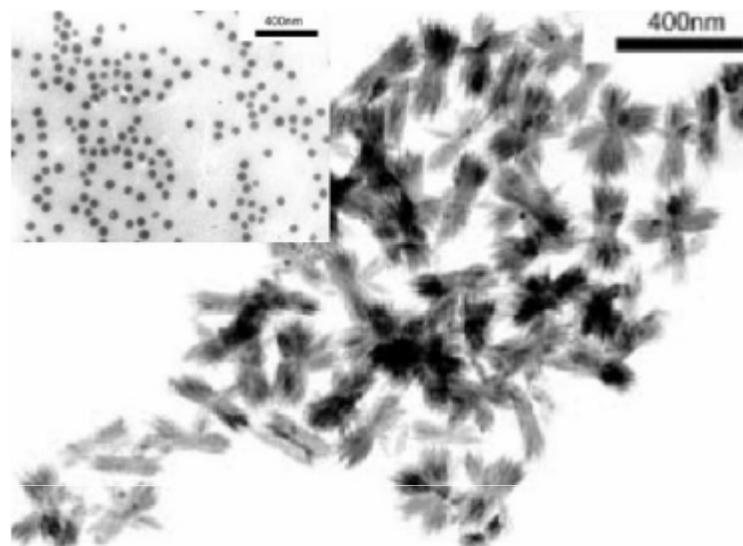
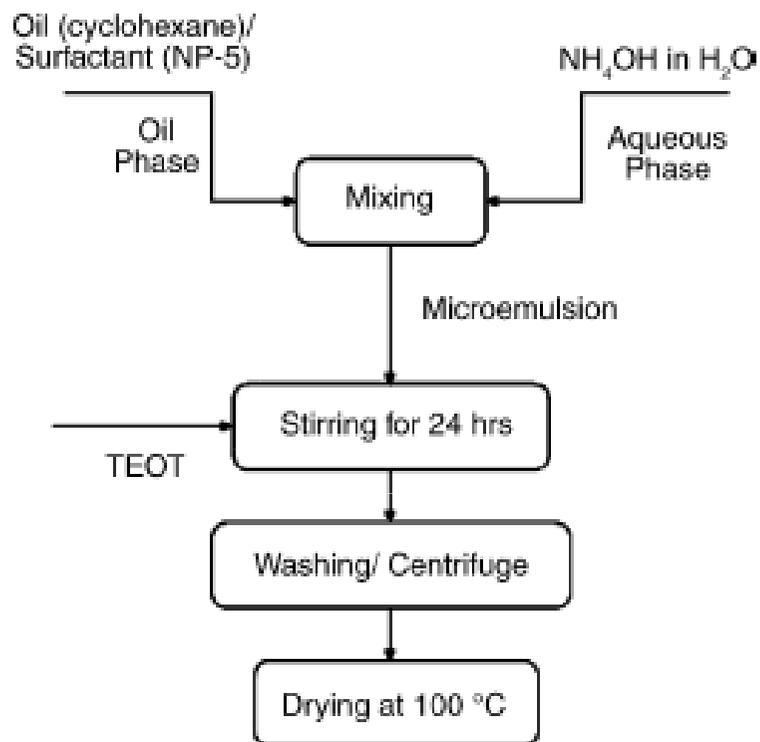
200 nm

TEM images of TiO₂ nanoparticles prepared by hydrolysis of Ti(OR)₄ in the presence of tetramethylammonium hydroxide. Muramatsu, A. *et al.*, *J. Colloid Interface Sci.* **2003**, 259, 53

- Amines are used as the shape controllers of the TiO₂ nanomaterials act as surfactants.
- Amines include triethanolamine (TEOA), diethylethlenetriamine, ethylenediamine, trimethylenediamine and triethylenetetramine.
- The morphology of the TiO₂ nanoparticles changes from cuboidal to ellipsoidal at pH above 11.
- The shape control is attributed to the tuning of the growth rate of the different crystal planes of TiO₂ nanoparticles by the specific adsorption of shape controllers to these planes under different pH conditions.



Micelle and Inverse Micelle Method



TEM images of the shuttle-like and round-shaped TiO₂ nanoparticles.

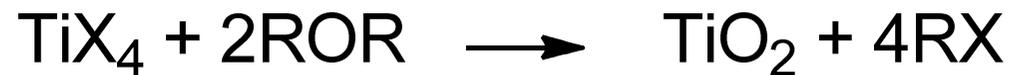
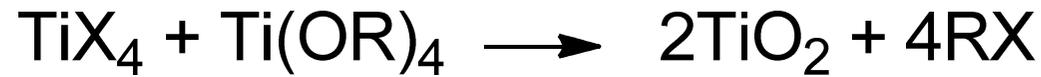
Cheng, H. *et al.*, *J. Mater. Chem.* **2002**, *12*, 3677

- Experimental procedure for the synthesis of TiO₂ nanoparticles using W/O microemulsion-mediated method.

- The values of H₂O/surfactant, H₂O/titanium precursor, ammonia concentration, feed rate, and reaction temperature were significant parameters in controlling TiO₂ nanoparticle size and size distribution.



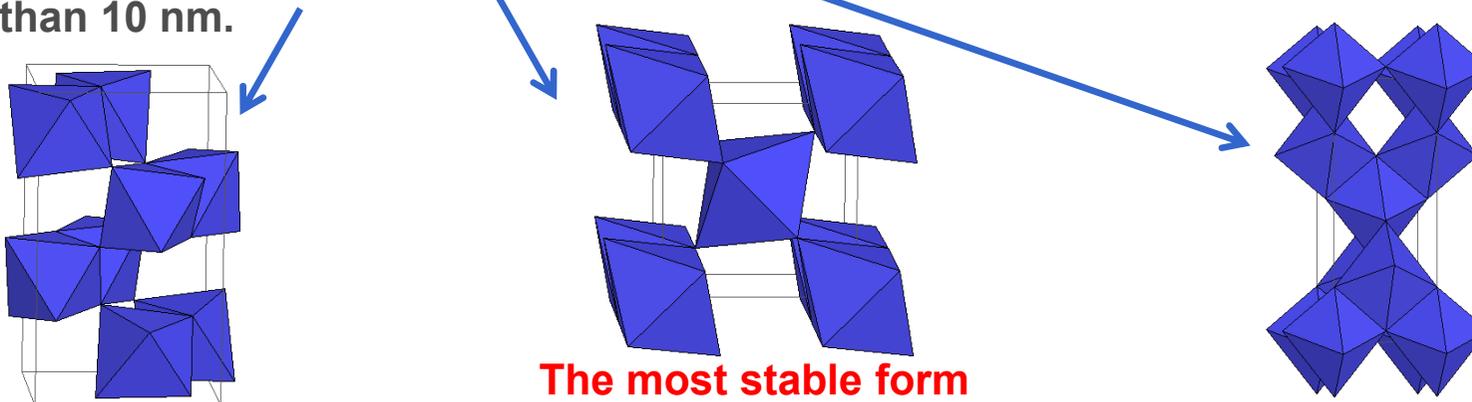
Sol Method



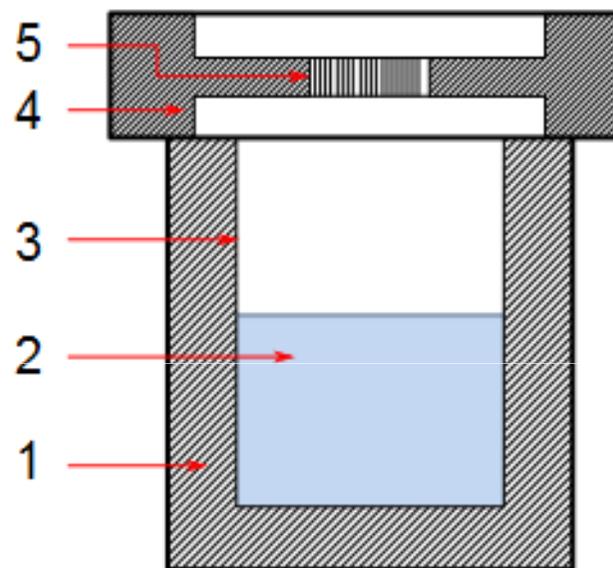
- The sol method is the **nonhydrolytic** sol-gel processes and usually involves the reaction of titanium chloride with a variety of different oxygen donor molecules, e.g., metal alkoxide or an organic ether.

To control particle size

- Increased nucleophilicity (ore size) of the halide resulted in smaller **anatase** nanocrystals, e.g., average sizes ranged from **9.2 nm** for **TiF₄** to **3.8 nm** for **TiI₄**.
- Reaction in pure trioctylphosphine oxide (TOPO) was slower and resulted in smaller particles, while reactions without TOPO were much quicker and yielded mixtures of **brookite**, **rutile**, and **anatase** with average particle sizes greater than 10 nm.



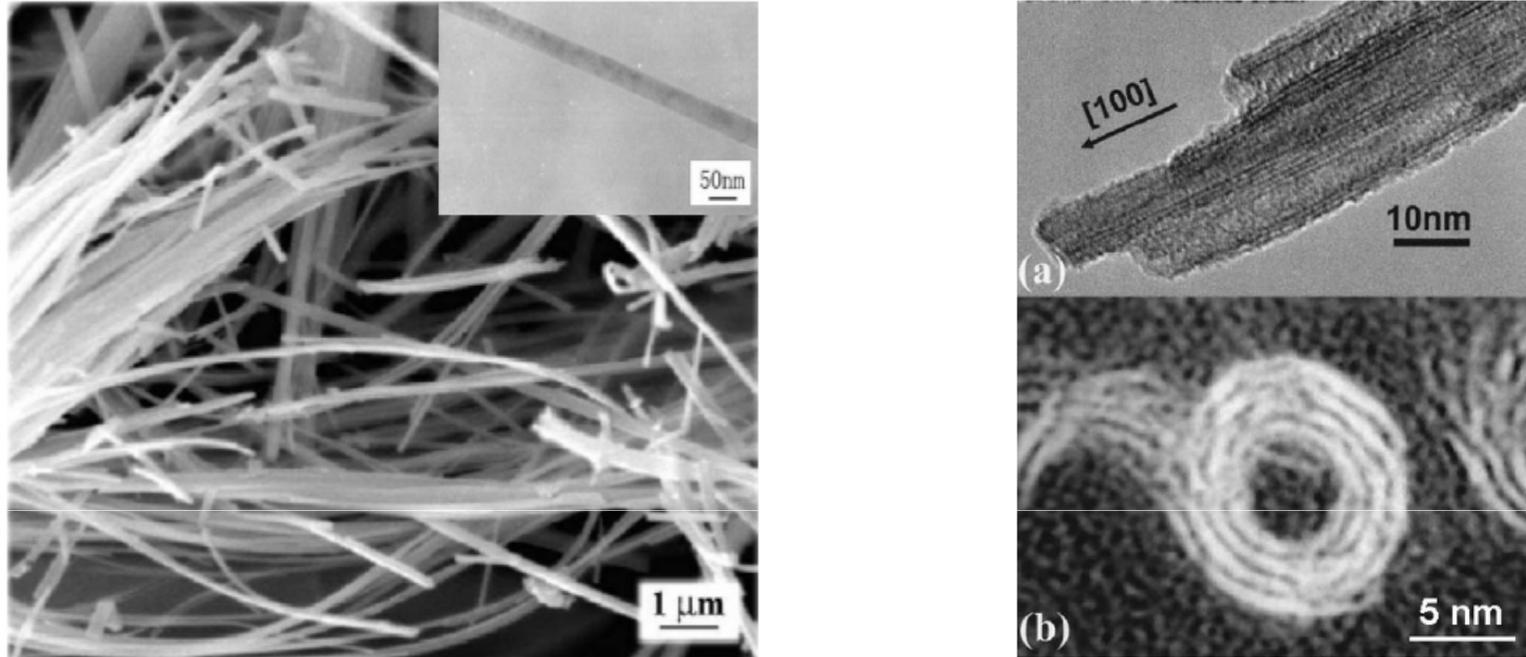
Hydrothermal and Solvothermal Method



Schematic diagram of hydrothermal (solvothermal) synthesis setup: (1) stainless steel autoclave (2) precursor solution (3) Teflon liner (4) stainless steel lid (5) spring



Hydrothermal Method



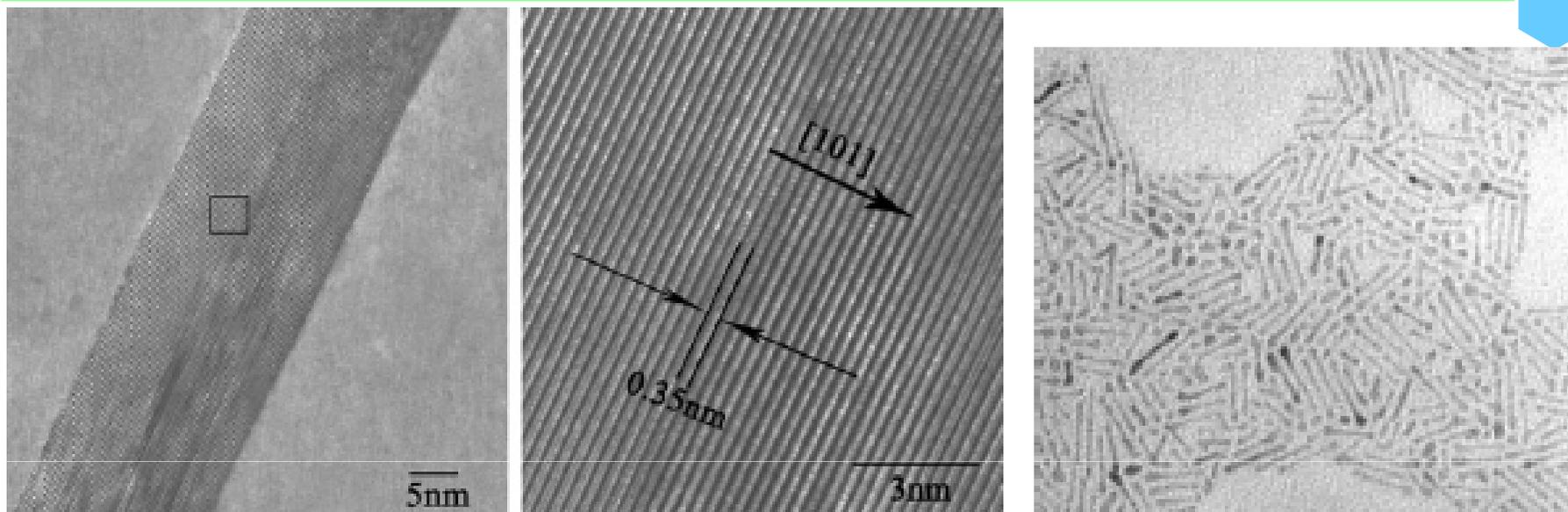
(left figure) SEM images of TiO_2 **nanowires** with the inset showing a TEM image of a single TiO_2 nanowire with a [010] selected area electron diffraction (SAED) recorded perpendicular to the long axis of the wire. Zhang, L. D. *et al.*, *Chem. Phys. Lett.* **2002**, 365, 300.

(a) HRTEM images of TiO_2 **nanotubes**. (b) Crosssectional view of TiO_2 nanotubes. N. Wang, *et al.*, *Applied Physics Letters*, **2003**, 82, 281

- Hydrothermal synthesis is normally conducted in steel pressure vessels called autoclaves with or without Teflon liners under controlled temperature and/or pressure with the reaction in **aqueous solutions**.



Solvothermal Method



(a) HRTEM image of an individual nanowire. (b) The corresponding HRTEM image of the local plane of the nanowire from (a). The fringes with a spacing of 0.35 nm correspond to (101) planes.

Liu, C. *et al.*, *New J. Chem.* **2005**, 29. 969

TEM micrographs and electron diffraction patterns of products prepared from solutions at the weight ratio of (precursor / solvent / surfactant) 1:5:3.

Seo, H. J. *et al.*, *J. Cryst. Growth* **2003**, 257. 309

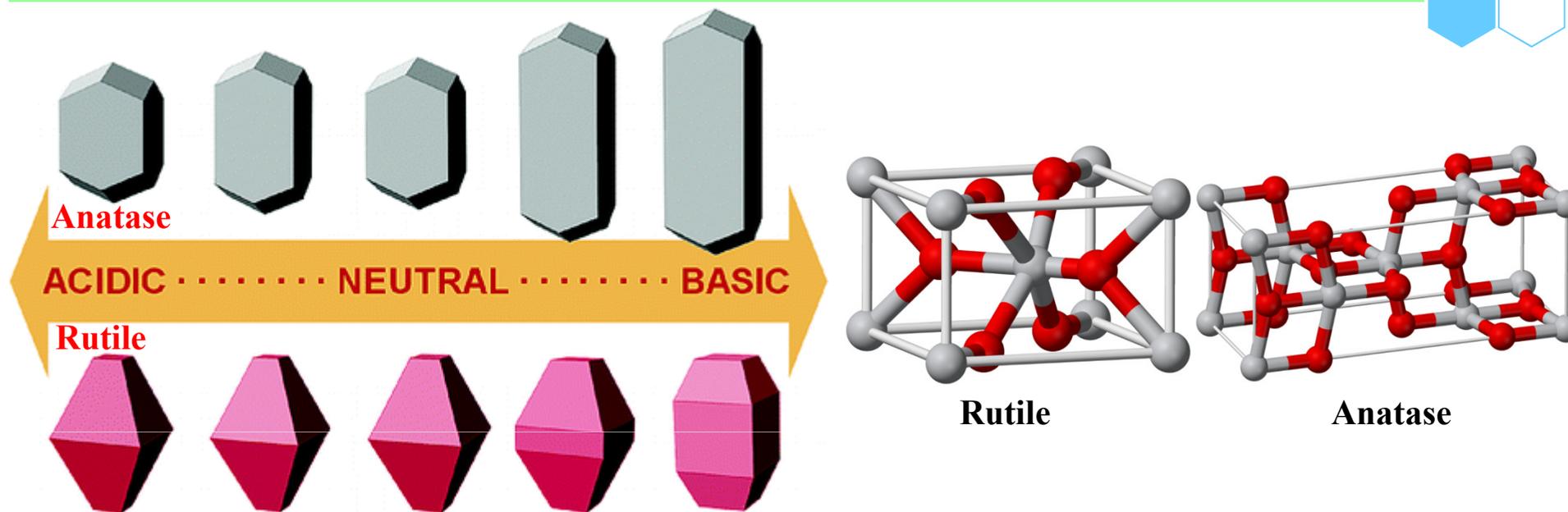
- The solvothermal method is almost identical to the hydrothermal method except that the solvent used here is **nonaqueous**.
- The temperature can be elevated much higher than that in hydrothermal method.
- The solvothermal method normally has better control than hydrothermal method of the size and shape distributions and the crystallinity of the TiO₂ nanoparticles.



iii. Properties

- i. Structural Properties*
- ii. Electronic Properties*
- iii. Photon-Induced Electron and Hole.*

Structural Properties

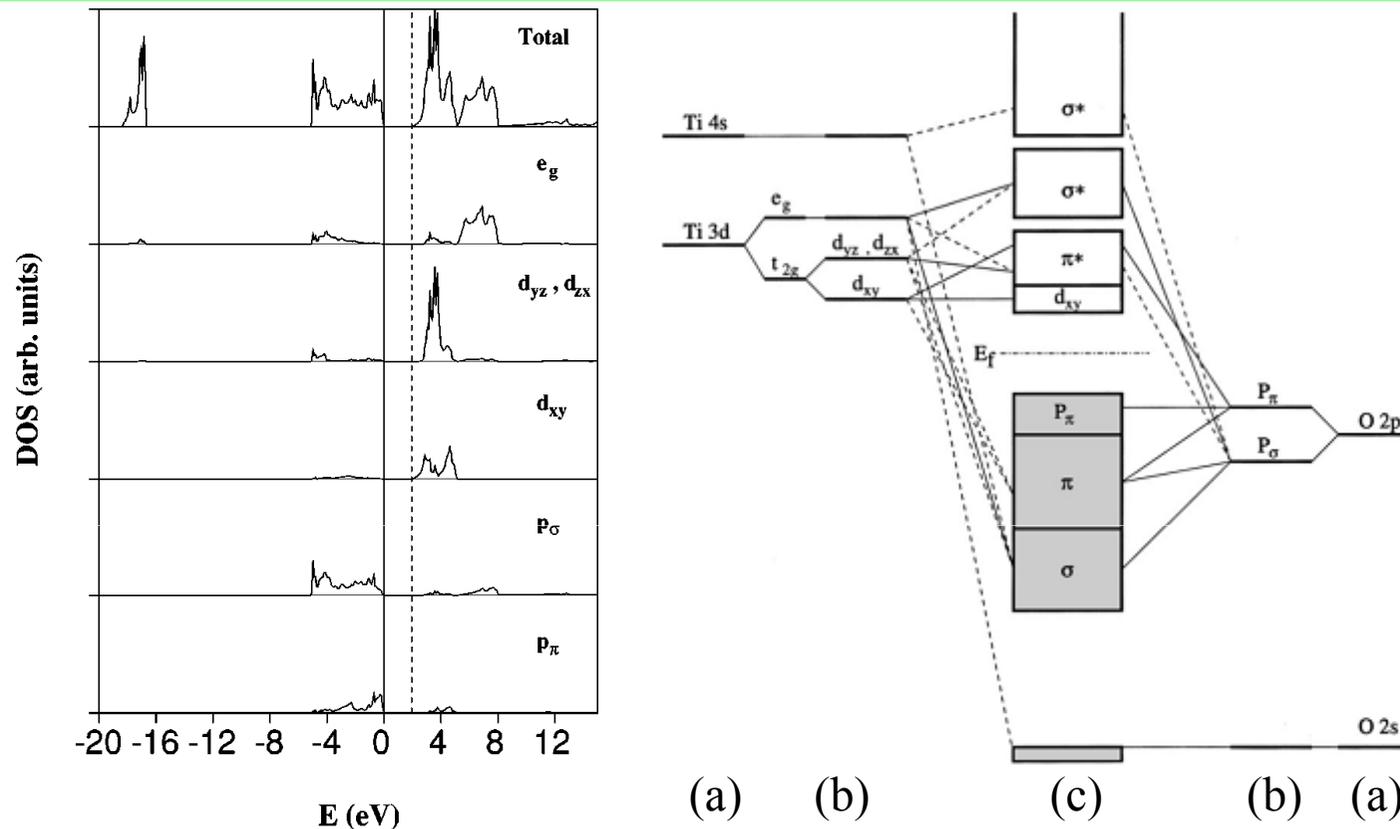


Morphology predicted for **anatase (top)**, with (a) hydrogenated surfaces, (b) hydrogen-rich surface adsorbates, (c) hydrated surfaces, (d) hydrogen-poor adsorbates, and (e) oxygenated surfaces, and for **rutile (bottom)**, with (f) hydrogenated surfaces, (g) hydrogen-rich surface adsorbates, (h) hydrated surfaces, (i) hydrogen-poor adsorbates, and (j) oxygenated surfaces.

- Two structures, rutile and anatase, can be described in term of chains of TiO_6 octahedra, where each Ti^{4+} ion is surrounded by an octahedron of six O^{2-} ions.
- They demonstrated that, under different pH conditions from acid to basic, the phase transition size of a TiO_2 nanoparticle varied from 6.9 to 22.7 nm, accompanied with shape changed of the TiO_2 nanoparticles.



Electronic Properties

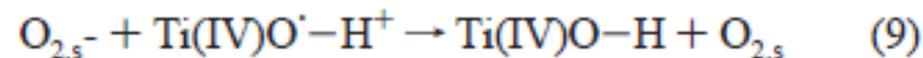
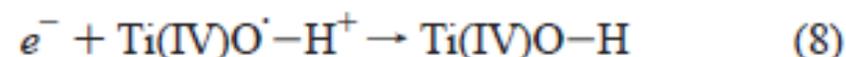
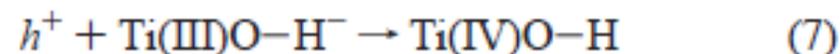
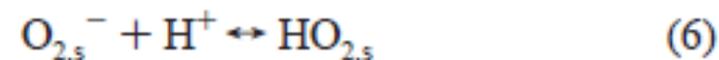
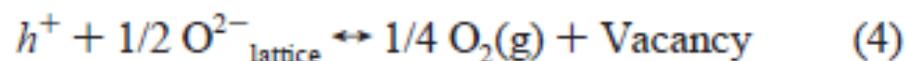
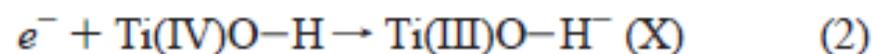
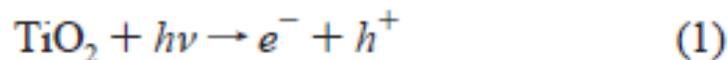


(A) Total and projected densities of states (DOSs) of the **anatase** TiO₂ structure. (B) Molecular-orbital bonding structure for anatase TiO₂: (a) atomic levels; (b) crystal field split levels; (c) final interaction states.

- The DOS (density of states) is decomposed into Ti e_g, Ti t_{2g} (d_{yz}, d_{zx}, and d_{xy}), O p_σ (in the **TiO₃ cluster plane**), and O p_π (out of the **TiO₃ cluster plane**) components.
- It is well-known that for nanoparticles the band gap energy increases and the energy band becomes more discrete with decreasing size.



Photon-Induced Electron and Hole 1

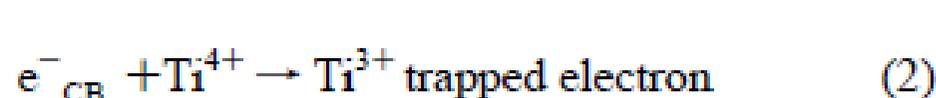
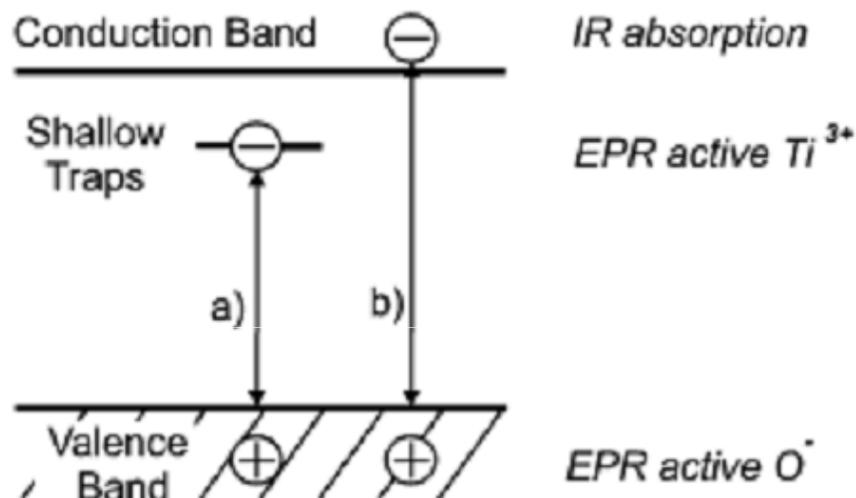


- Reaction (1) is the photon absorption process.
- Reactions (2) – (6) are photocatalytic redox pathways.
- Reactions (7) – (9) represent the recombination channels.
- Reactions (3) & (4) are the competition pathways for holes, leading to bound **OH radicals** and O vacancies, respectively.
- The reverse of reaction (4) generates O adatom intermediated upon exposing defective surfaces to $\text{O}^{2-}(\text{g})$.
- Because photocatalytic TiO_2 surfaces are extensively hydroxylated, the dynamics of defect creation and healing may depend not only on bulk composition and morphology, but also on the nature and density of Ti-OH species.



Photon-Induced Electron and Hole 2

Trapped Charges	Detection By
-----------------	--------------



Scheme of UV induced charge separation in TiO_2 . Electrons from the valence band can either be trapped (a) by defect states, which are located close to the conduction band (shallow traps), or (b) in the conduction band where they produce absorption in the IR region.

- During continuous UV irradiation, photogenerated electrons were either trapped at localized sites, giving paramagnetic Ti^{3+} centers, or remained in the conduction band.
- Photoredox chemistry occurring at the particle surface emanated from trapped electrons and holes rather than from free valence band holes and conduction band electrons.

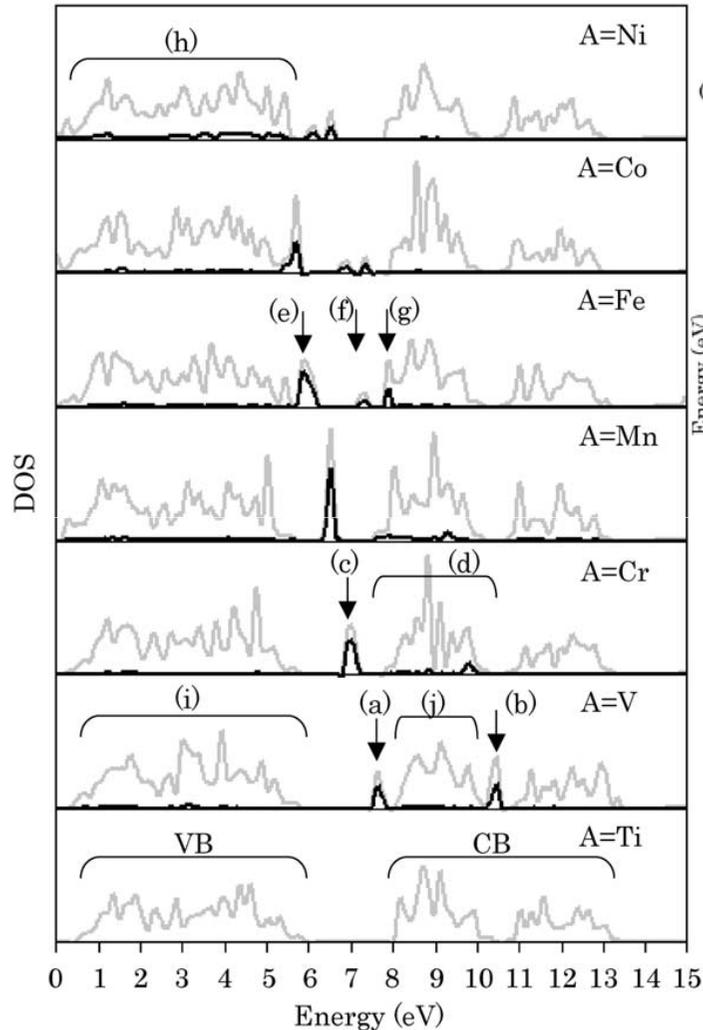


iv. Modifications

- i. Metal-Doped TiO₂ Nanomaterials*
- ii. Nonmetal-Doped TiO₂ Nanomaterials*



Metal-Doped TiO_2 Nanomaterials

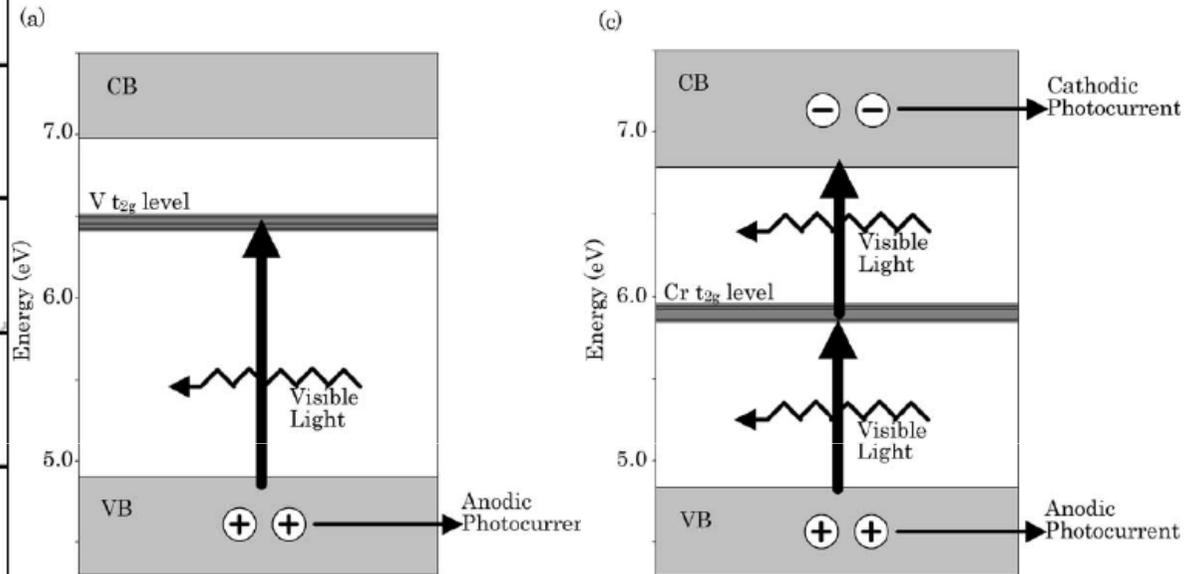


DOS of the metal doped TiO_2

($Ti_{1-x}A_xO_2$: A = V, Cr, Mn, Fe, Co, or Ni)

Gray: total DOS, Black: dopant's DOS

Asai, K. *et al.*, *J. Phys. Chem. Solids* 2002, 63, 3466.

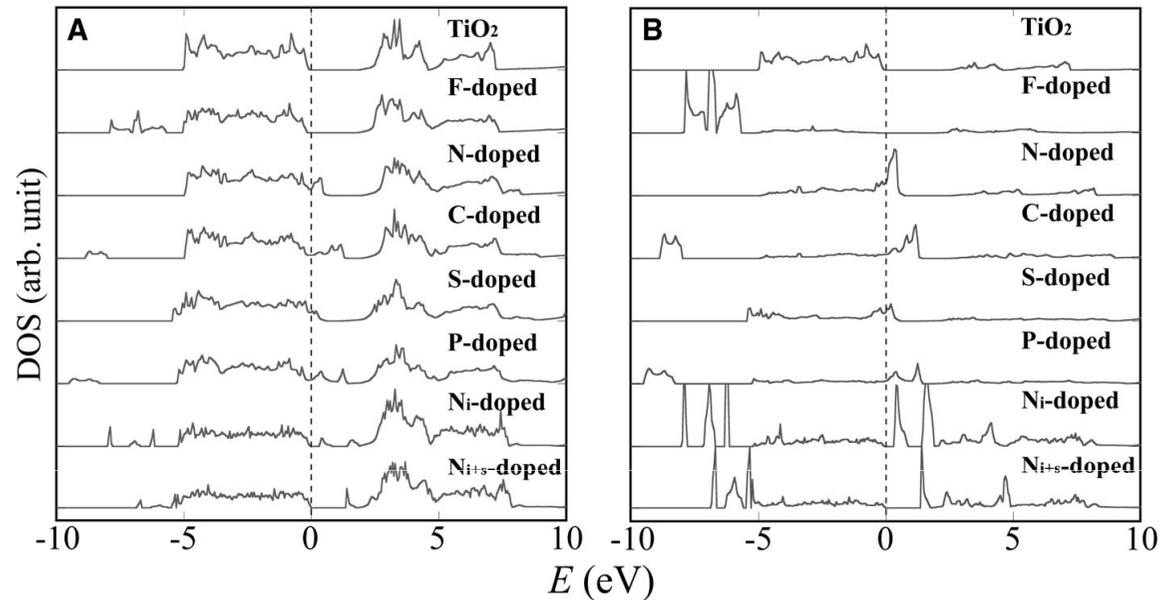


Schematic diagram to illustrate the photoexcitation process under visible light of metal-doped TiO_2

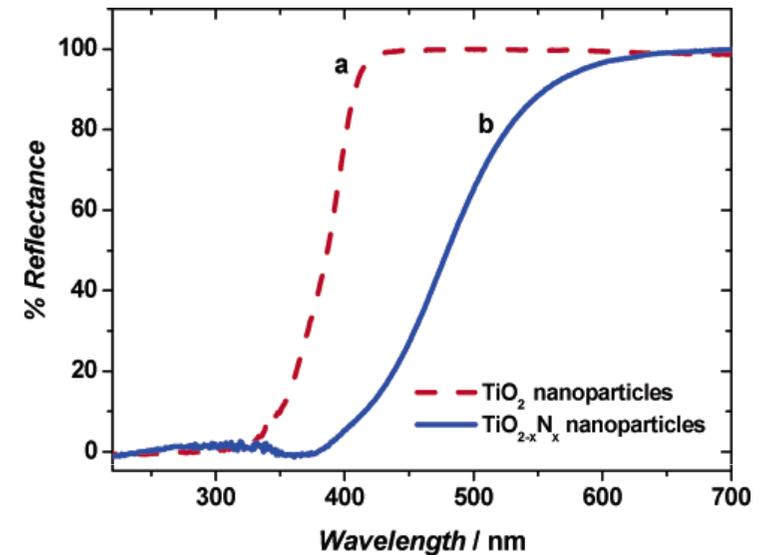
(a) $Ti_{1-x}V_xO_2$, (c) $Ti_{1-x}Cr_xO_2$

- The one of the goals for improvement of the performance of TiO_2 nanomaterials is to increase their optical activity by shifting the onset of the response from the UV to the visible region.

Nonmetal-Doped TiO_2 Nanomaterials



(A) Total DOSs of doped TiO_2 and (B) the projected DOSs into the doped anion site, calculated by FLAPW, for the dopants F, N, C, S and P located at a substitutional site for an O atom in the anatase TiO_2 crystal (eight TiO_2 units per cell). N_i -doped stands for N doping at an interstitial site, and N_{i+s} -doped stands for doping at both substitutional and interstitial sites. R. Asahi, *et al.*, *Science* **2001**, 293, 269.



Reflectance measurements showing the red shift in optical response due to the nitrogen doping of TiO_2 nanoparticles.

Gole, J. L. *et al.*, *Nano Lett.* **2003**, 3, 1049.

- Recent theoretical and experimental studies have shown that the desired band gap narrowing of TiO_2 can also be achieved by using nonmetal dopants.



v. *Applications*

- i. Photocatalytic Applications*
- ii. Photovoltaic Applications*
- iii. Photocatalytic Water Splitting*
- iv. Electrochromic Devices*
- v. Polyfunctional Adsorbent*



Photocatalytic Applications 1

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
----	----	----	----	----	----	----	----	----	----	----	----	----	----

- i)

	: d ⁰ ion
	: d ¹⁰ ion
	: Non-metal

 } to construct crystal structure and energy structure
- ii) to construct crystal structure but not energy structure
- iii) to form impurity levels as dopants
- iv) to be used for cocatalysts

Elements constructing heterogeneous photocatalysts

- Most metal oxide photocatalysts consist of metal cations with d⁰ and d¹⁰ configurations.
- Their conduction bands for the d⁰ and d¹⁰ metal oxide photocatalysts are usually composed of d and sp orbitals, respectively, while their valence bands consist of O 2p orbitals.



Photocatalytic Applications 2

Various parameters and quantum yields of the photocatalytic hydrogenation reactions of CH_3CCH with H_2O over Rutile-Type (top) and Anatase-Type (bottom) TiO_2 at 300 K. Quantum yield = (number of photoformed products) / (number of incident photons).

Rutile

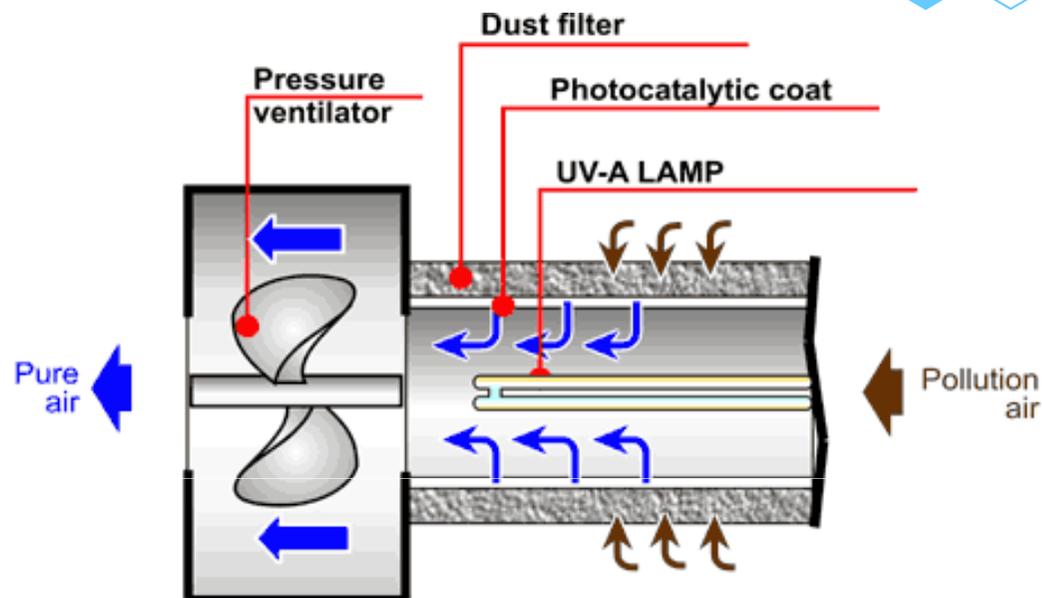
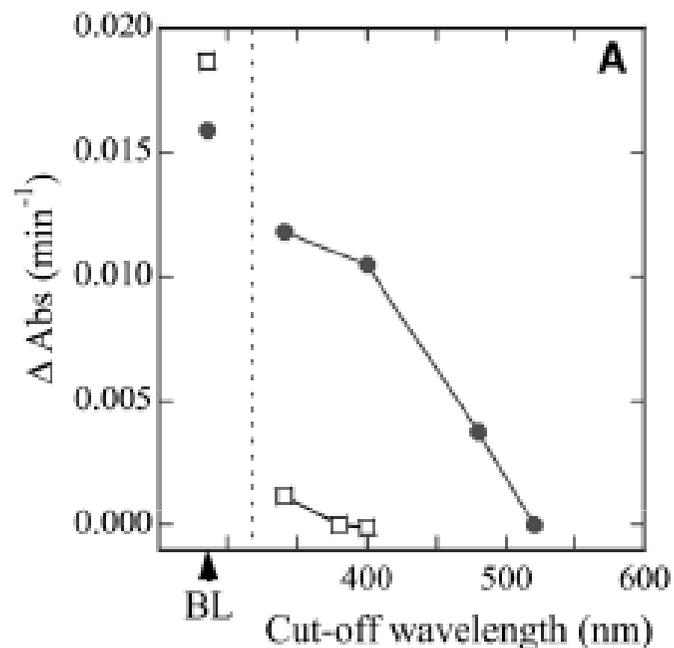
particle size, Å	BET surface area, m^2/g	wavelength at band gap position, nm	magnitude of the shift at band gap, eV	quantum yields, ^b %
55	533	398.0	0.0934	3.6×10^{-2}
120	121	401.5	0.067	0.52×10^{-2}
400	26	409.2	0.01	0.36×10^{-2}
1800	4.7	410.1	0.002	0.12×10^{-2}
2000 ^a	4.0	410.4	0.000	0.10×10^{-2}

Anatase

particle size, Å	BET surface area, m^2/g	wavelength at band gap position, nm	magnitude of blue shift of band gap, eV	quantum yields, ^a %
38	1068	371.5	0.156	7.18×10^{-2}
50	941	375	0.126	7.02×10^{-2}
65	609	380.5	0.079	8.80×10^{-2}
85	430	385	0.041	2.42×10^{-2}
110	312	387	0.024	2.26×10^{-2}
220	137	388	0.016	1.13×10^{-2}
530	26	389.9	0.000	0.264×10^{-2}



Photocatalytic Applications 3

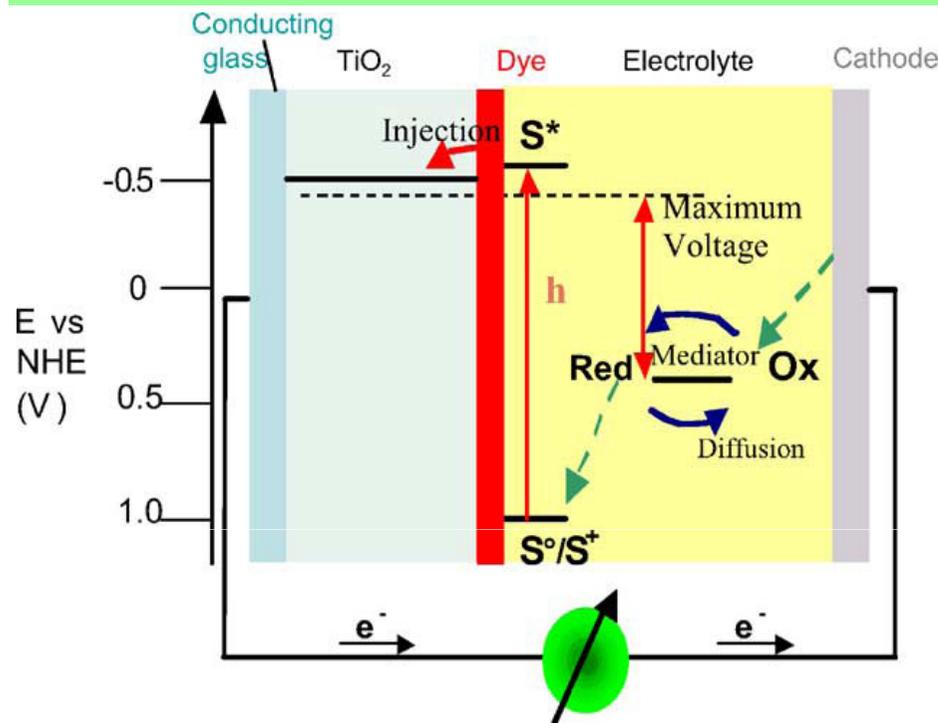


Photocatalytic properties of $\text{TiO}_{2-x}\text{N}_x$ samples (solid circles) compared with TiO_2 samples (open squares). Decomposition of methylene blue as a function of the cutoff wavelength of the optical high-path filters under fluorescent light between **350 and 520 nm**, compared with the results under **BL** illumination with the integrated in the **UV** range.

- The main function of the TiO_2 photocatalyst is to adsorb organic and inorganic contaminants. Under the influence of the UV lamp they later get decomposed into CO_2 and H_2O .



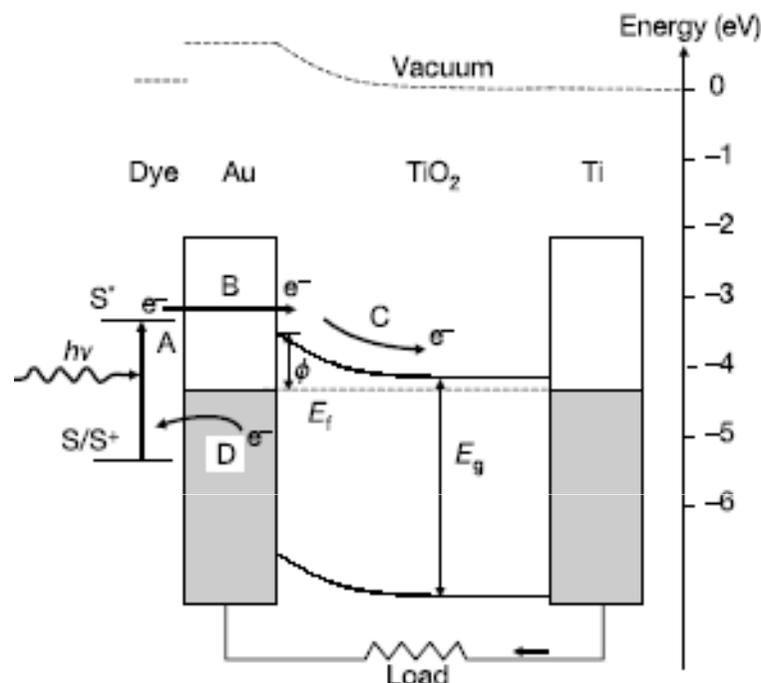
Photovoltaic Applications



Principle of operation and energy level scheme of the dye-sensitized nanocrystalline solar cell.

- **S** : Photoexcitation of the sensitizer
- The dye molecule is regenerated by the redox system, which itself is regenerated at the counter-electrode by electrons passed through the load.

Grätzel, M. *et al.*, *J. Photochem. Photobiol. A: Chem* **2004**, *164*, 3



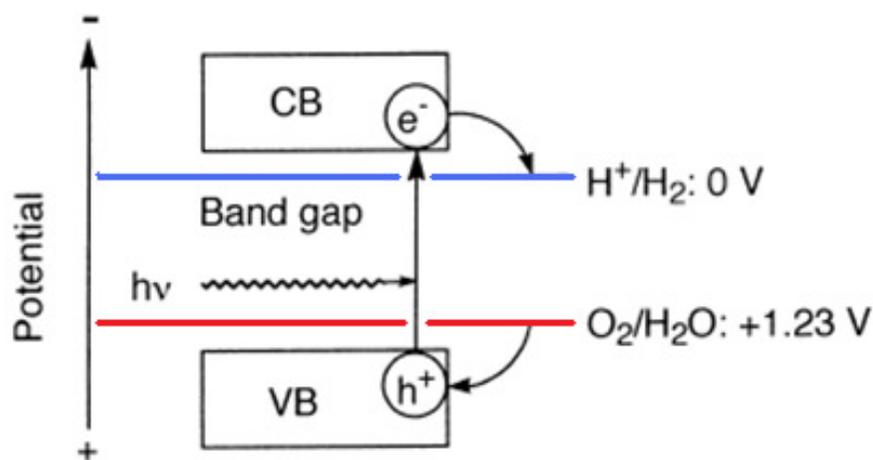
Electron transfer in the operating photovoltaic device.

- **A**: Photon absorption
- **B**: Electron transfer from S^*
- **C**: Electron conduction
- **D**: Reduction of S^*

Tang, J. *et al.*, *Nature* **2003**, *421*, 616

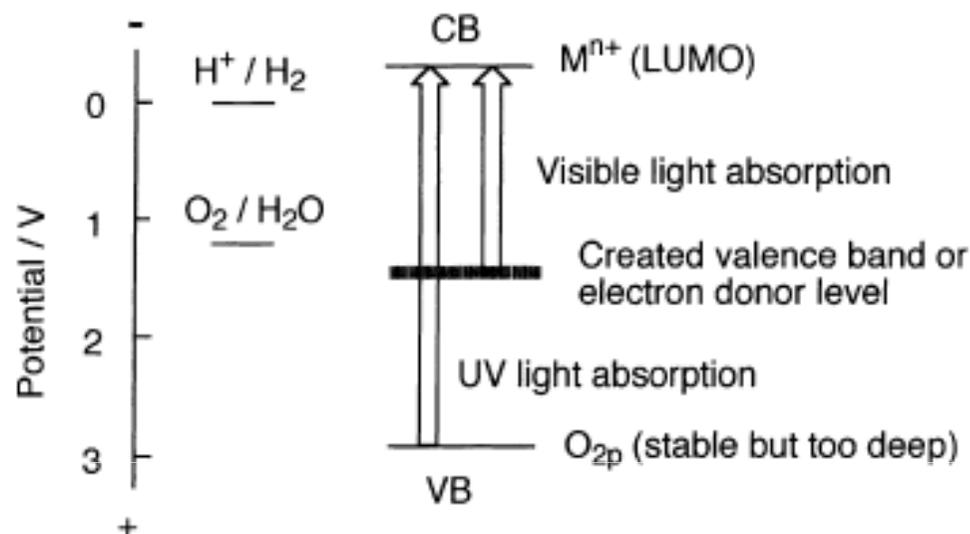


Photocatalytic Water Splitting



The principle of water splitting using a semiconductor photocatalyst.

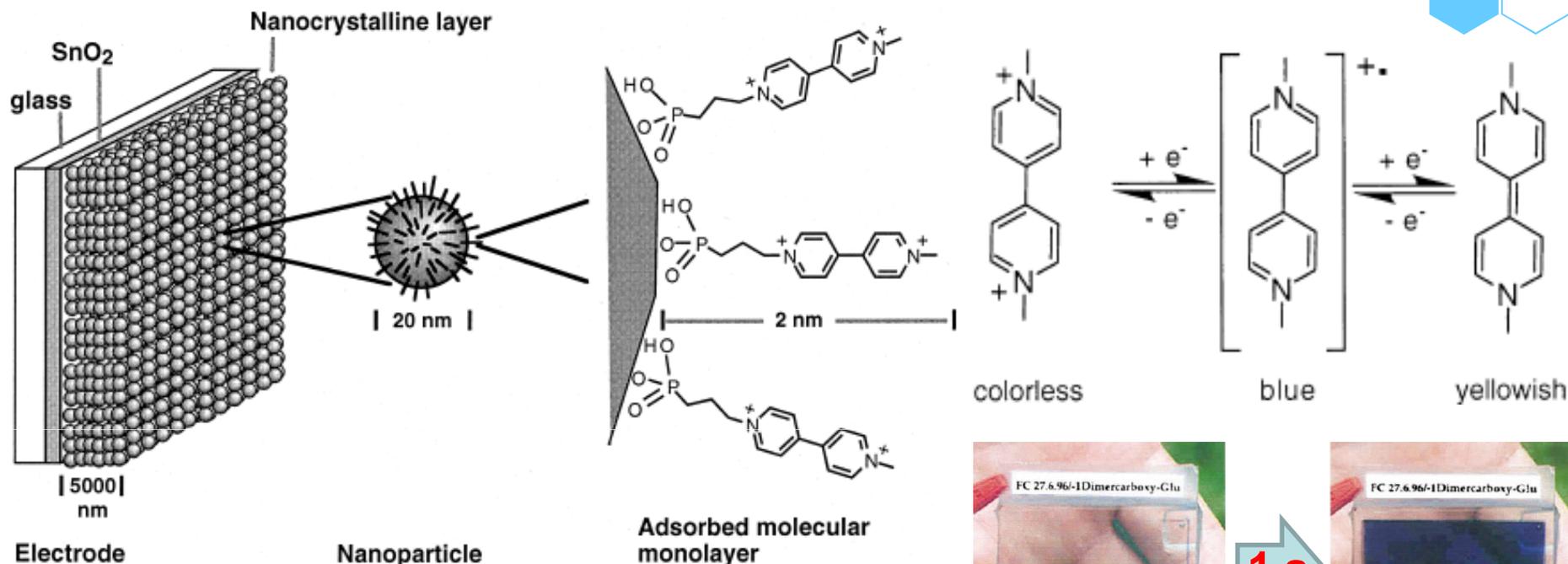
- The bottom level of the conduction band has to be more negative than the reduction potential of H^+ / H_2 (0 V vs. NHE).
- The top level of the valence band has to be more positive than the oxidation potential of $\text{O}_2 / \text{H}_2\text{O}$ (1.23 V).



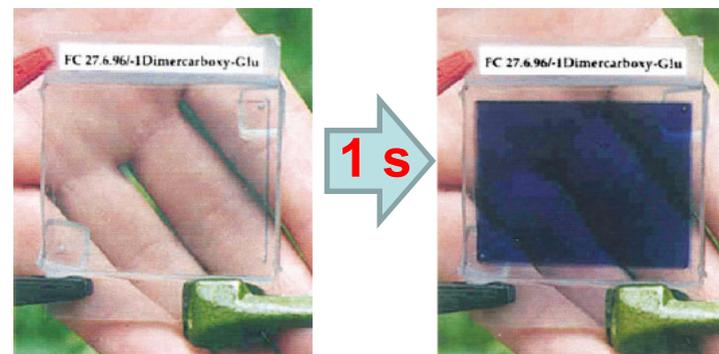
Strategy of the development of photocatalysts with a visible light response.

1. To form a donor level above a valence band by doping some element into conventional photocatalysts with wide band gaps such as TiO_2 .
2. To create a new valence band employing some element.
3. To control the band structure by making a solid solution.

Electrochromic Devices

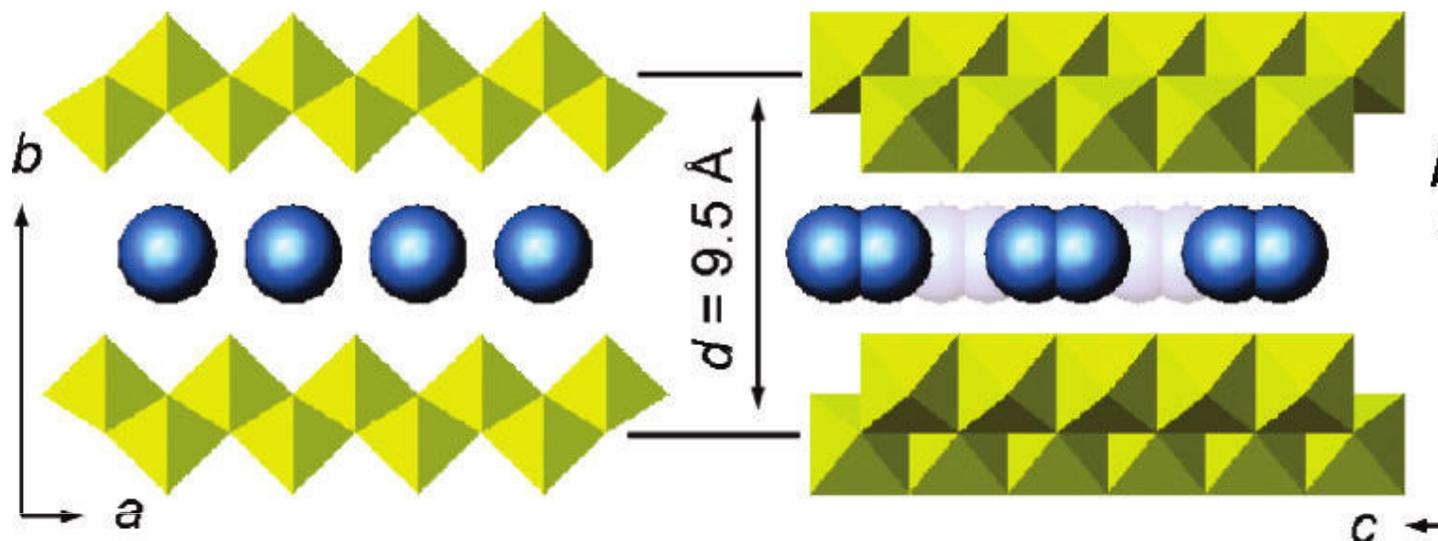


Principle of signal amplification by a TiO₂ nanocrystalline film.



- The device could be switched back and forth between the colorless and colored states within **1 s**.
- **First** reduction potential : **0.2 – 0.6 V**
- **Second** reduction potential : **0.2 – 0.4 V**

Polyfunctional Adsorbent ~Crystal Structure~



Layered Hydrazinium Titanate ($(\text{N}_2\text{H}_5)_{0.5}\text{Ti}_{1.87}\text{O}_4$ (LHT-9))

Projections onto (right) (001) and (left) (100). Edge-faceted stacking of corner-sharing TiO_6 octahedra (yellow) results in the formation of interlayer “pseudochannels” directed along the c axis. These pseudochannels are half-occupied by hydrazinium ions (blue spheres depict the front row and grayish spheres the back row) tailored in such a way that NN bonds are directed along the pseudochannels. The relative sizes of the shown structural units are consistent with their actual size ratios.

- New nanohybrid compound combining the **redox** functionality of hydrazine, the **ion-exchange** properties of layered titanate, the large surface area of quasi-two-dimensional crystallinities, surface **Brønsted acidity**, and the occurrence of surface titanyl bond.
- It possesses a high uptake capacity of **~50 elements** of the periodic table.



Polyfunctional Adsorbent ~Periodic Table~

H																				He	
Li 5	Be																				Ne
Na 8	Mg 11																				Ar
K 22	Ca 13	Sc 13	Ti	V 9 ↓ IV	Cr ^{VI} 22 ↓ III	Mn ^{II} 11	Fe ^{II} 9	Co 9	Ni 9	Cu ^{II} 10 ↓ 0	Zn 10	Ga 22	Ge	As	Se ^{IV} 46 ↓ 0	Br				Kr	
Rb 14	Sr 10	Y 7	Zr 9	Nb	Mo ^{VI} 5 ↓ V	Tc	Ru	Rh 12	Pd ^{II} 15 ↓ 0	Ag ^I 10 ↓ 0	Cd 13	In 7	Sn ^{IV} 35 ↑ II	Sb	Te ^{VI} 28 ↓ 0	I				Xe	
Cs 14	Ba 10	La 9	Hf	Ta	W	Re	Os	Ir	Pt ^{IV} 12 ↓ 0	Au ^{III} 16 ↓ 0	Hg ^{II} 17 ↓ I	Tl 11	Pb 11	Bi	Po	At				Rn	
Fr	Ra	Ac																			
		Ce ^{III} 12	Pr 10	Nd 10	Pm	Sm 9	Eu 11	Gd 7	Tb 10	Dy 9	Ho 10	Er 9	Tm 10	Yb 8	Lu 7						
		Th	Pa	U ^{VI} 13	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr						



Ion exchange or surface complexation



Reduction by LHT-9



Oxidation by LHT-9

Highlighted are the elements that can be adsorbed by nanocrystalline LHT-9 in aqueous solutions. Depending on the nature of each element, different adsorption mechanisms can be proposed. The adsorption capacity of each element is given in atom % relative to Ti.

Wulf, D. *et al.*, *J. Am. Chem. Soc* 2011, 133 (24), 9516.



Polyfunctional Adsorbent ~Functionalities~

◆ *Redox Properties*

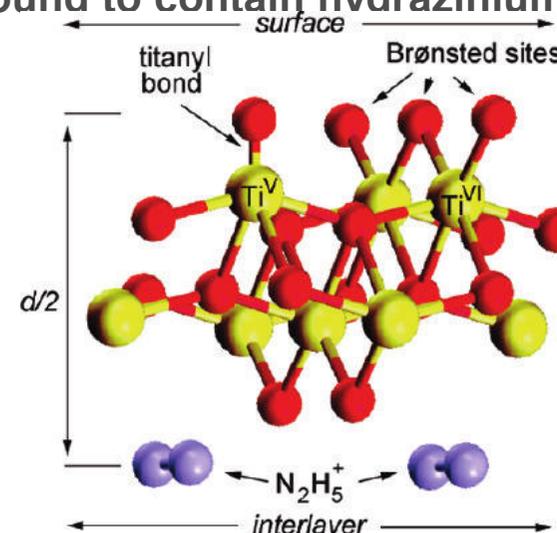
- LHT-9 is an effective reducing agent that has the redox properties of hydrazine superimposed onto the adsorption properties of the nanocrystalline titanate matrix, resulting in the phenomenon of **reductive adsorption**.
- EX) $4\text{HAu}^{\text{III}}\text{Cl}_4 + 6(\text{N}_2\text{H}_5)_{0.5}\text{Ti}_{1.87}\text{O}_4 \rightarrow 4\text{Au}^0 \downarrow + 6\text{H}_{0.5}\text{Ti}_{1.87}\text{O}_4 + 3\text{N}_2 \uparrow + 16\text{HCl}$
- The irreversibility of the majority of reduction reactions under the given redox conditions, LHT-9 can be used for **cumulative extraction of reducible elements** from their solutions.

◆ *Ion Exchange Properties*

- LHT-9 exhibits high rates of ion-exchange and protonation reactions.
- EX) $0.25\text{Rb}^+\text{Cl} + (\text{N}_2\text{H}_5)_{0.5}\text{Ti}_{1.87}\text{O}_4 \rightarrow (\text{N}_2\text{H}_5)_{0.25}\text{Rb}^+\text{Ti}_{1.87}\text{O}_4 + (\text{N}_2) \uparrow + (\text{HCl})$
- The majority of exchange products however, were found to contain hydrazinium.

◆ *Surface Acidity Properties*

- Brønsted acidity is likely caused by protonation of bridging Ti-O-Ti oxygen atoms located at loose corners of TiO_6 octahedra exposed at the surfaces of the titanate layers.





vi. Summary

Summary



- TiO_2 has various functionalities not apply only to be used for white source of paints and cosmetics expected to reflect UV light, they also has **light sensitivity** and modified it has adsorption capacity.
- TiO_2 nanomaterials has significant differences by nanoparticle size and geometry.
- It is necessary to select suitable reaction condition to synthesize objective particle shape materials.
- Photocatalytic and photovoltaic tec. are begun to use various fields, for example, solar panel, pollutant decomposition, superhydrophilic materials and water splitting, etc.
- Although TiO_2 is NOT used industrially since less effectivity, today I introduced, some solubility to improve light effectivity are studying with all one's heart!