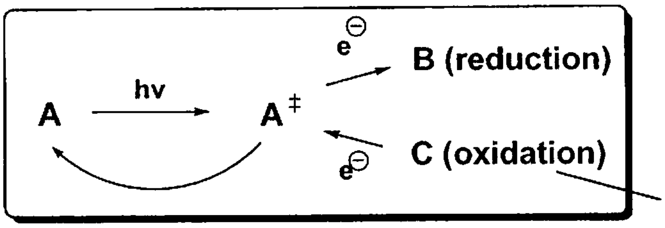
Photocatalyst

Literature Seminar (M2)
Wataru Itano (2005.9.10(Sat.))

Recently, Photocatalyst is applied to many fields in our daily life.

(antibacterial deodrization / sterilization antifogging) *"self-cleaning"*

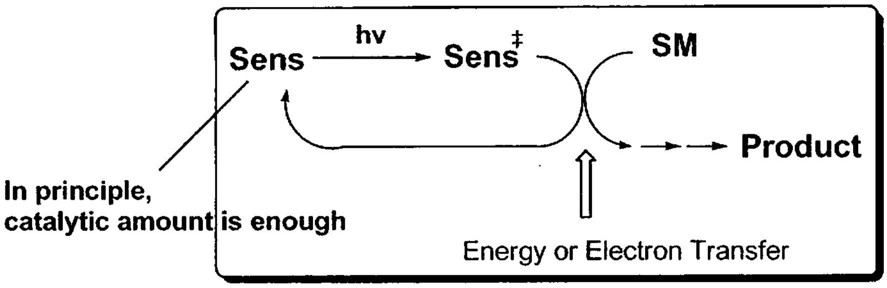
@ The term of "Photocatalyst" is usually used as semiconductor (heterogeneous) catalyst



main force of photocatalytic activity

TiO_2 most successful semiconductor material

@ In (our) organic chemistry field, the molecule named as "Sensitizer" works with the mechanism as shown below



usually "photosensitized"
"photoinduced"
sometimes "photocatalytic"

⇨ They seems to be similar...

(But... actually they are completely different because the adsorption of molecule must be considered in the case of semiconductor catalyst.)

Contents

1. Brief Look of Semiconductor Photocatalyst

(1) About Semiconductor

a solid, whose conductivity is between that of an insulator and a conductive metal

(a) 導体：金属などのように電気をよくとおすもの

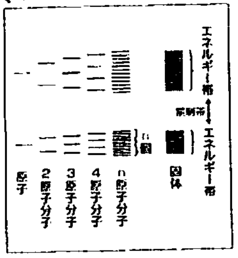
(b) 絶縁体：酸化アルミニウム（アルミナ）や酸化ケイ素（シリカ），あるいは不純物をふくまないダイヤモンドなどのように電気をほとんどとおさないもの

(c) 半導体：ケイ素やゲルマニウムのような単体，酸化チタンのような金属酸化物や，硫化カドミウム のような金属硫化物の一部のように電気伝導性が導体と絶縁体の中間のもの

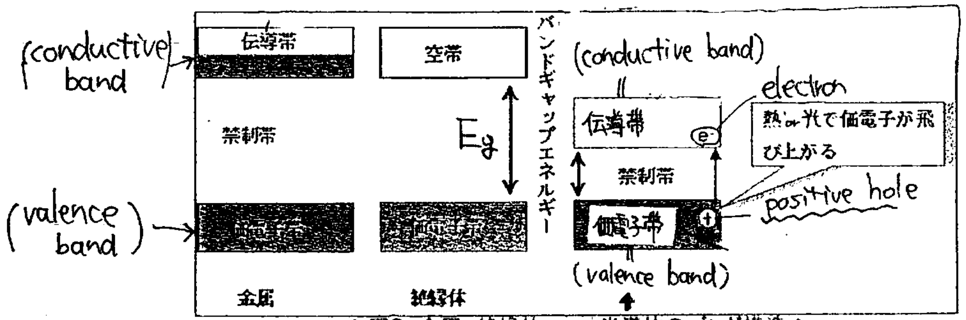
thermally or photonically increasing.

In a solid crystal state, orbitals of each atom are hybridized to a large number of (molecular) orbitals. Therefore, the "band" is formed.

＜図1 エネルギー帯の形成＞



(image)

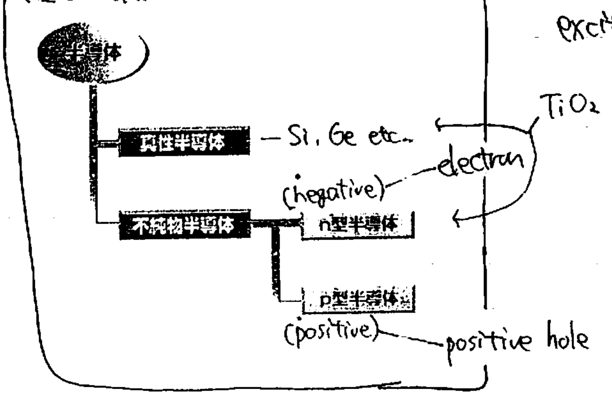


＜図2 金属、絶縁体、 半導体のバンド構造＞

⇓

excited electron or positive hole (p^+) ⇒ electron flow.

＜図3 Classification of Semiconductor＞



$$\begin{cases} \text{Ti} & ((\text{Ar})\,4s^2 3d^2) \\ \text{O} & (1s^2\,2s^2 2p^4) \end{cases}$$

TiO_2 seems to have no remaining of valence electron

? Why does TiO_2 work as n-type semiconductor

This thing is explained by "oxygen vacancies in the crystal"
酸素の結晶欠陥.

(To understand this,) think about crystal structure of TiO_2...

単位格子

At first, crystal is constituted from "unit cell"

cf)

結晶構造

結晶とは空間的に周期的な原子の配列構造をもつもので，周期性の最小単位を単位格子とよぶ．単位格子はかならず平行六面体である（そうでないと単位格子をならべたときにすきまができてしまう）．単位格子の各頂点はかならず原子の中心であるが，それ以外の原子が格子中にふくまれていてもかまわない．図 2-10 のように 3 種類の辺の長さを，a，b，および c，各辺のなす角を α，β，および γ とすることが多い．

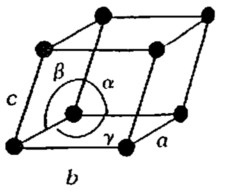


図4　結晶の単位格子

packaging of each molecule is determined by the ratio of ion-radius.

$$\left(\begin{array}{llll} \mathrm{Ti}\ (p: 1.54) \longrightarrow \mathrm{Ti}^{4+} & \sim 0.75\,\text{Å} & \\ \mathrm{O}\ (p: 3.44) \longrightarrow \mathrm{O}^{2-} & \sim 1.4\,\text{Å} & \end{array} \quad r_{\mathrm{Ti}^{4+}}/r_{\mathrm{O}^{2-}} \simeq 0.54 \Longrightarrow \text{八面体六配位}\right)$$

$\Rightarrow$ six O coordinate to one Ti
(one Ti-O bond have $2 \times \frac{4}{6} = 2 \times \frac{2}{3}$ e .)

TiO$_2$ has three crystal structure.

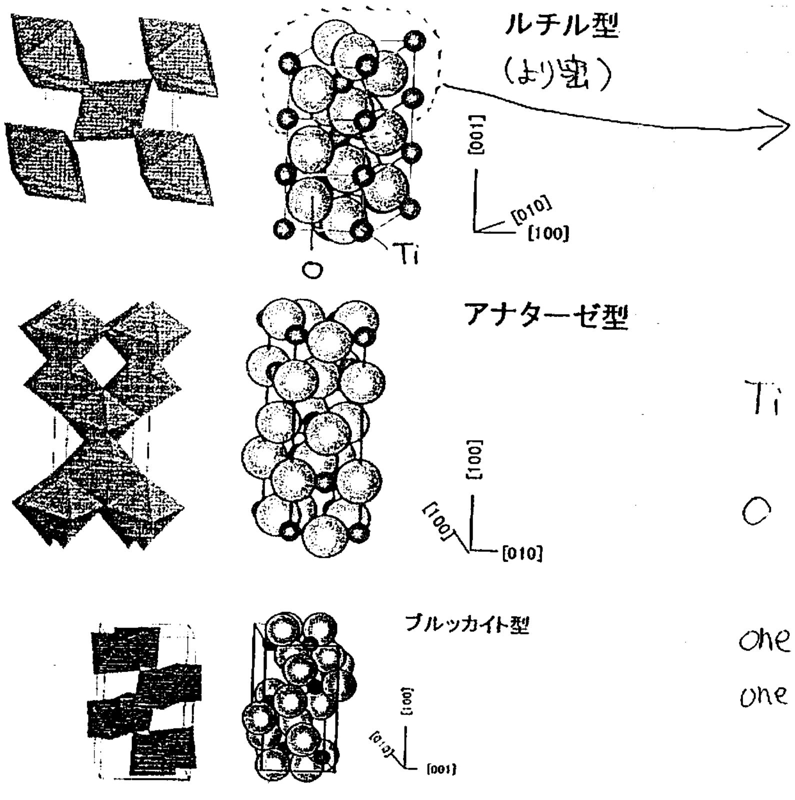
cf)

表1　二酸化チタンの３つの結晶形

	ルチル (6)	アナターゼ (7)	ブルッカイト (8)
	金紅石	鋭錐石	板チタン石
	正方晶系	正方晶系	斜方晶系
	a=b=459 pm c=296 pm ($\alpha = \beta = \gamma = 90°$)	a=b=379 pm c=951pm (　〃　)	a=546 pm b=918 pm (〃) c=516 pm
密度 (g/cm³)	4. 250	3. 894	4. 133
TiO$_2$一分子当たりの体積 (nm³)	0. 0312	0. 0341	0. 0321

ルチル	アナターゼ
塗料	
光触媒 < (?)	光触媒.

図５　二酸化チタンの３つの結晶形、ルチル型は３つの単位格子でも示す。小さい丸でチタン原子を、大きい丸で酸素原子を示す。



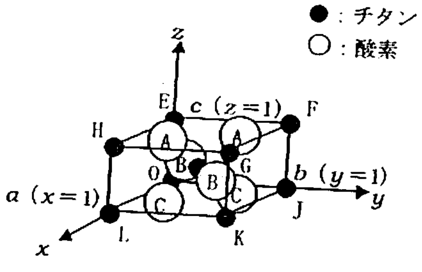
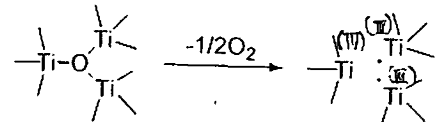


図6　ルチル型酸化チタンの結晶構造の単位格子

$$\left.\begin{array}{l} \mathrm{Ti}: \frac{1}{8} \times 8 + 1 = 2 \\ \mathrm{O}: \frac{1}{2} \times 4 + 2 = 4 \end{array}\right\} \mathrm{TiO_2}$$

one O surrounded by three Ti
one Ti surrounded by six O

To simplify "oxygen vacancies" in the crystal …



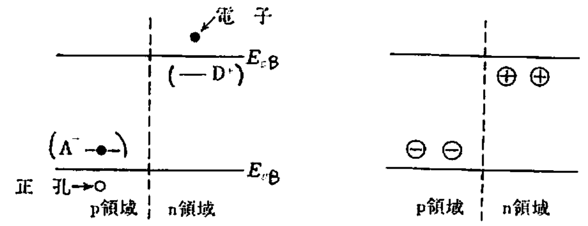
(white) | H₂ red. | (black)

as insulator   as n-type semiconductor

if "oxygen vacancies" occurs.
two electrons are remained among three Ti(Ⅳ)

ⓐ Electron State of semiconductor surface is changed by the interaction of other materials.

<p-n junction>



（a） 電子移動前　（b） 電子移動後

図7　pn 接合の電気二重層の発生

⟹

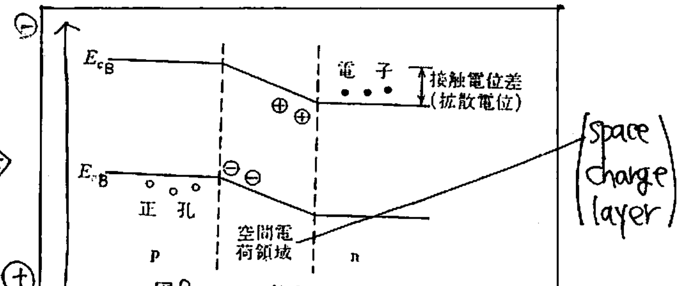


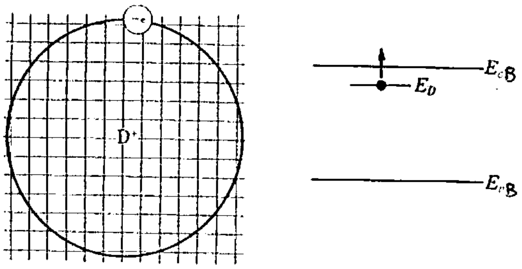
図8　pn 接合のエネルギー図

cf) 多くの場合，半導体の中に適当な不純物（異種原子，格子欠陥）を導入することによって，キャリア密度を増やしたり減らしたりすることができる．伝導帯に電子を供給する不純物をドナー（donor），価電子帯に正孔を供給する不純物をアクセプタ（acceptor）という．

(電流の担い手)
e^{-} → n-type
h^{+} → p-type

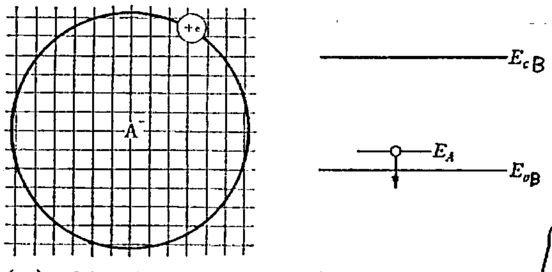
周りより 価電子が1個多い原子
(例えばSiに対し、ドナーとしてPをドーピング)

周りより、1個価電子が少ない原子
(例えばSiに対し、アクセプタとしてAlをドーピング)



（a） ドナーイオンD⁺と電子(−e)と結晶格子　（b） ドナー準位E_D

図9　ドナーとドナー準位



（a） アクセプタイオンA⁻と正孔(+e)　（b） アクセプタ準位E_A

図10　アクセプタとアクセプタ準位

E_{cB} ⟹ Conduction Band edge energy
E_{vB} ⟹ Valence Band edge nergy

(半導体物理の基礎 (オーム社) P2-6)

ⓑ <n-electrolyte junction>

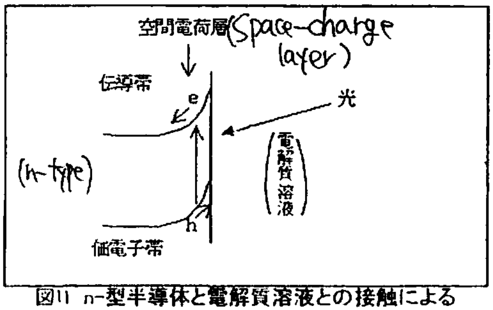


図11 n-型半導体と電解質溶液との接触による空間電荷層の形成と光誘起電子－正孔対の分離

Electrical potential is bent-up
⇓
excited electrons spatially move to the interior
⇓
"Charge-Separation"

b) Historical Aspects of TiO_2

* TiO_2 is used as pigment (顔料) — one of the most basic material in our life.

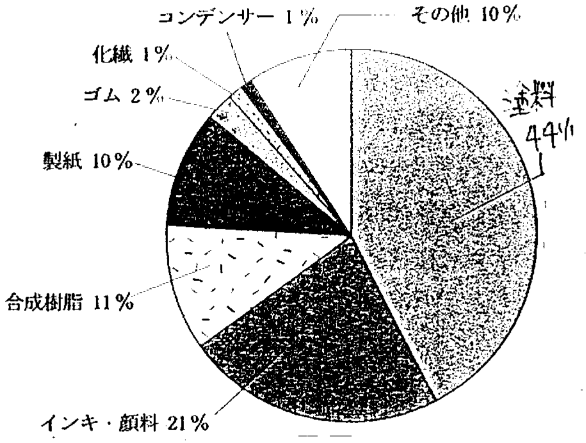


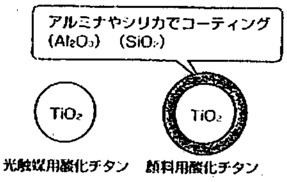
図12 酸化チタンの用途（日本酸化チタン工業会，平成15年度資料

表2 酸化チタン各結晶形の物性値[(2)-(4)]

298Kにおける物性	ルチル	アナターゼ	ブルッカイト
比熱（J℃$^{-1}$·mol^{-1}）	55.06	55.52	
モース硬度	7.0〜7.5	5.5〜6.0	5.5〜6.0
融点（℃）	1870（分解）	ルチルに転移	ルチルに転移
☆ 屈折率（n_D） E// c (589nm) E⊥c	2.616 2.903	2.554 2.493	2.63 2.63
比誘電率	167（//c） 86（⊥c）	48	78（//a）
☆ バンドギャップ Eg (eV)	3.06（直接） 3.01（間接）	3.2	3.2

(from 表2) high n_D → high reflection at surface
high Eg → low adsorption of visible light
) (隠蔽性) untransparentizing agent. (plastic, paper etc..)

additionally { safety for human
inexpensive
chemically highly stable



But... choking (with hν) has been a problematic point.

* 1970's TiO_2 for photochemical solar energy conversion.

- sufficient positive valence band edge (E_{VB}) to oxidise water to oxygen
- extremely stable material in the presence of aq. electrolyte solution.

「Honda-Fujishima effect」
Nature (1972) 238, 37-38

Electrochemical Photolysis of Water at a Semiconductor Electrode

Department of Applied Chemistry, Kanagawa University, Yokohama — AKIRA FUJISHIMA
Institute of Industrial Science, University of Tokyo, Roppongi, Tokyo — KENICHI HONDA

The possibility of $\underline{\text{solar photoelectrolysis of } H_2O}$ was demonstrated for the first time.
「water-splitting」

$$H_2O \xrightarrow{h\nu} H_2 + \tfrac{1}{2}O_2$$

($\Delta G > 0$ ... energy up-take reaction). (such as natural photosynthesis)

It can be applied for efficient solar energy conversion

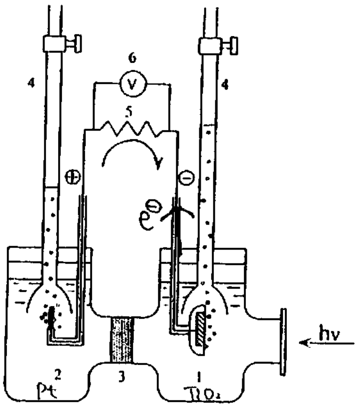


Fig. 1. Schematic diagram of an electrochemical photocell [6]. (1) n-type TiO_2 electrode; (2) platinum black counter electrode; (3) ionically conducting separator; (4) gas buret; (5) load resistance and (6) voltmeter.

$$TiO_2 + 2\,h\nu \rightarrow 2\,e^- + 2\,p^+ \qquad (1)$$
(excitation of TiO_2 by light)

$$2\,p^+ + H_2O \rightarrow \tfrac{1}{2}\,O_2 + 2\,H^+ \qquad (2)$$
(at the TiO_2 electrode)

$$2\,e^- + 2\,H^+ \rightarrow H_2 \qquad (3)$$
(at the platinum electrode)

The overall reaction is

$$H_2O + 2\,h\nu \rightarrow \tfrac{1}{2}\,O_2 + H_2 \qquad (4)$$

this causes "charge separation" after irradiation & driving force for chemical reaction.

space-charge layer

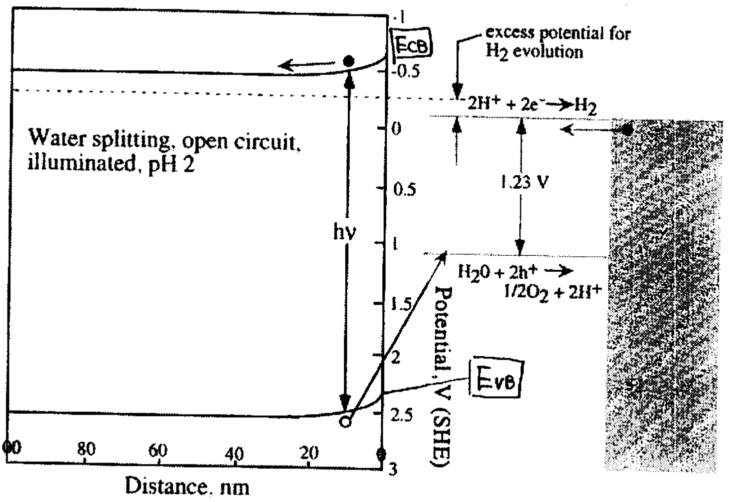


Fig. 2. Schematic representation of photoelectrochemical water electrolysis using an illuminated oxide semiconductor electrode [6]. Open circuit (or small current), pH 2, illuminated conditions are shown for an oxide with an E_{CB} of −0.65 V (SHE) and an E_{VB} of 2.35 V (SHE). With an open circuit, a small excess potential (~0.15 V) is available for H_2 evolution, assuming a reversible counter electrode.

(E_{CB} = −0.65 V (vs SHE), E_{VB} = 2.35 V (vs SHE) の酸化物を用いた場合の. photoelectrolysis of water の模式図)

(About $\boxed{\text{fig 2}}$)

In the case of n-type semiconductor (the reverse process in the case of p-type)

$h\nu \gtrsim E_{gap}$ ⟶ electron-hole pair generates.

⟶ (driven by space-charge layer bias.)

"charge-separation" { electrons toward the interior of the electrode (⟶ the external circuit)
positive-holes toward the solid-liquid interfacial region.

① If the E_{CB} is higher (more negative) than the hydrogen evolution potential

⇓ (depends on pH { −0.4 V (SHE) (in acid solution)
−1.2 V (SHE) (in alkaline solution)

H_2 gas evolution

② If the E_{VB} is lower (more positive) than the water oxidation potential (oxygen evolution)

⇓

O_2 gas evolution.

☆ Semiconductor which can satisfy ① and ②, and also can be stable in that condition, can promote photoelectrolysis of water.

(cf) What is SHE?

a. 標準水素電極

pH = 0の水溶液に白金線を浸し，1 atmの水素 H_2 を吹きこんだ電極系をいう（図 2.4）．英語名は standard hydrogen electrode で，その略号SHEをつかうことが多い．この「標準」は「標準状態」（平衡にあずかる物質の活量 = 1）を意味する．

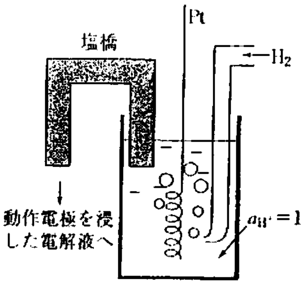
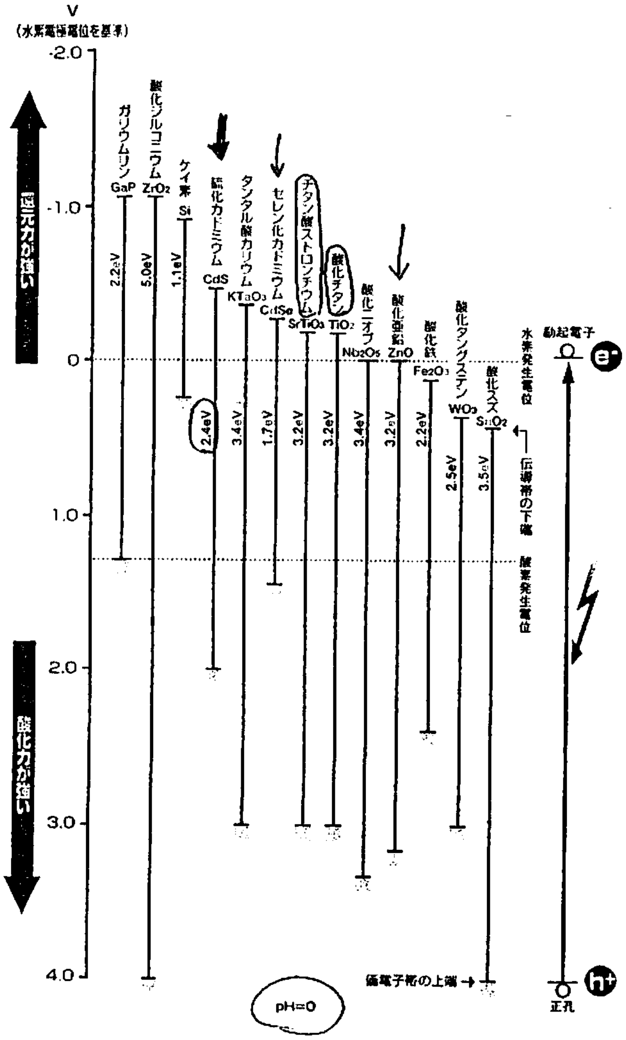


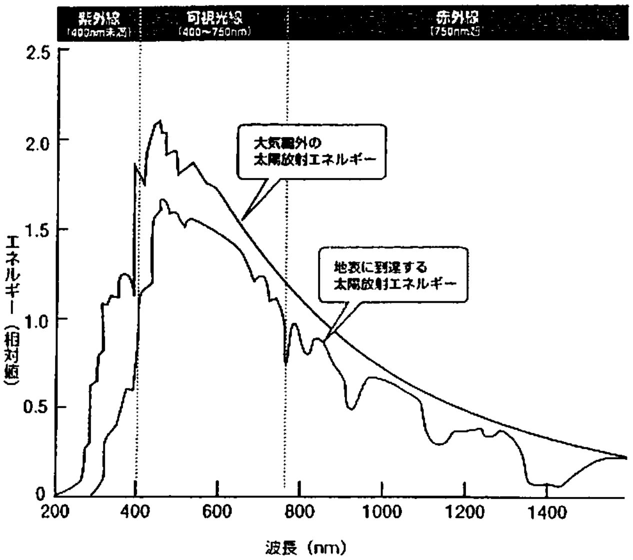
図 2.4　標準水素電極 SHE の構成

⇒ 電位は相対的な値なので、その大小を議論するために設けた基準値

■おもな半導体のバンド構造



■地球を取り巻く光環境



$$\boxed{\lambda\,(nm) = \frac{1240}{E_g\,(eV)}}$$

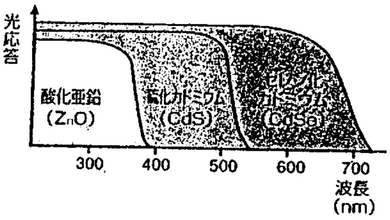
(p4 表2)

$$\left.\begin{array}{l}\lambda_{TiO_2(\text{ルチル})} = \frac{1240}{3.0} = 413\,nm \\ \lambda_{TiO_2(\text{アナターゼ})} = \frac{1240}{3.2} = 380\,nm\end{array}\right)$$

VIS-UV region light need for TiO_2.

So, more appropriate semiconductors are searched.

自身が分解しやすい半導体とその感光域



←

* The more E_g, the shorter λ is needed.
high activity　not preferable

* Semiconductors which have appropriate E_g (CdS etc.) are easily photodissolved

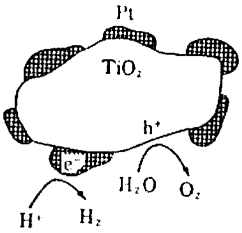
In terms of activity and stability, TiO_2 (or $SrTiO_3$) was the best.

*1980's

⇒ To make this system more practical, so called "catalyst"
a particle (~µm) catalyst was developed

「short-circuited photoelectrochemical cell」
(micro)

(in aquaus solution)



Met : Pt, Rh, Ni

Semiconductor : $SrTiO_3$, ZnO, CdS, CdSe

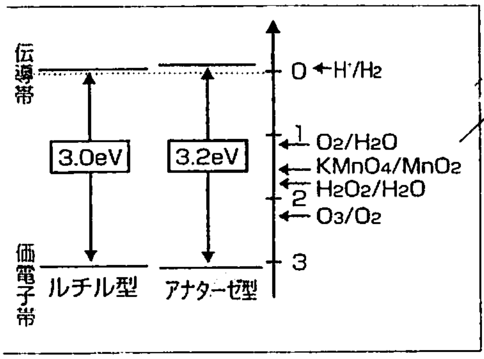
☆ In this case, both electrodes were not separated
So reversal process occur … $H_2 + \frac{1}{2}O_2 \xrightarrow[Met]{} H_2O$ ….

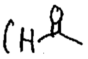
⇒ Many efforts were conducted
But, $\lambda_{TiO_2} \leqq 380$ nm is exclusively problematic point in practical sense.
and so far, water-splitting rate is not satisfactory.

C) Recent Trend of TiO_2

From 1990's, alternatively
the use of TiO_2 as catalyst for decomposing harmful organic compound was beginning.
Fujishima and Hashimoto et al developed this field and made some success.
(Photochem. Rev. I (2000) 1-21)

■バンド構造と酸化還元電位

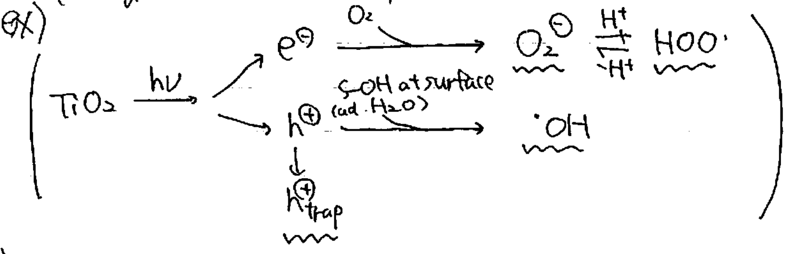


oxidizing power of TiO_2 is stronger than usual oxidants.
- organic compound ( etc..)
- Sterization
- cancer treatment
- ⋮

These effects are usually called "photocatalytic activity" etc..

*Mechanism?
- Many scientists investigates this problem.
- It depends on phase (gas or liquid) or many conditions.
- (Sorry, I cannot investigate (understand) in detail)

ex) (in aquaus)



☆ the adsorption of the molecule usually occurrs.

* In addition to photocatalytic (oxidation) activity, Photo Induced superhydrophilicity at TiO_2 surface was discovered.

(Nature (1997) 388. 431.)

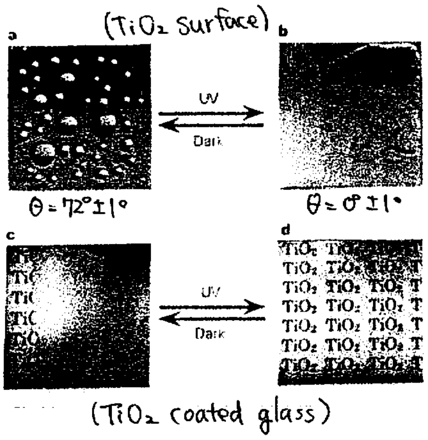
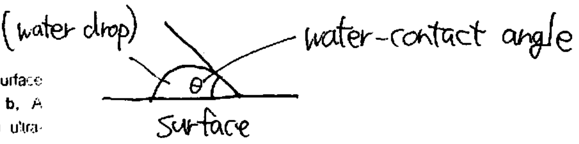
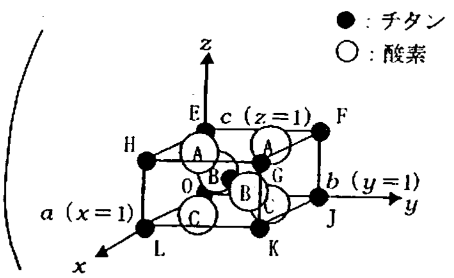


Figure 1 **a**, A hydrophobic surface before ultraviolet irradiation. **b**, A highly hydrophilic surface on ultraviolet irradiation. **c**, Exposure of a hydrophobic TiO_2-coated glass to water vapour. The formation of fog (small water droplets) hindered the view of the text on paper placed behind the glass. **d**, Creation by ultraviolet irradiation of an antifogging surface. The high hydrophilicity prevents the formation of water droplets, making the text clearly visible.



$\theta \lesssim 10° \Rightarrow$ superhydrophilicity.



(P2, 図6)

(110) surface = HFJL面

[001] → $\begin{pmatrix}0\\0\\1\end{pmatrix}$方向

the same direction in which oxygen bridging site align.

bright - hydrophilic.

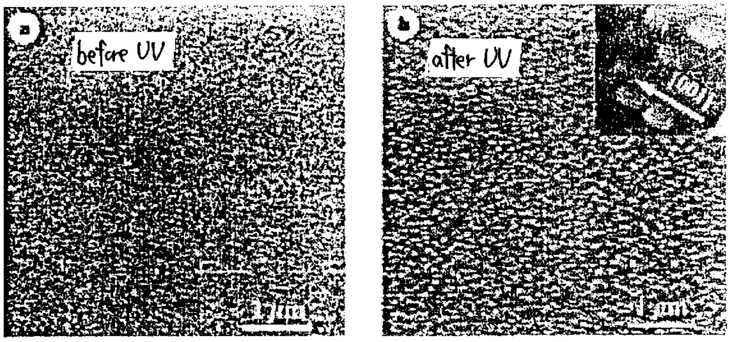
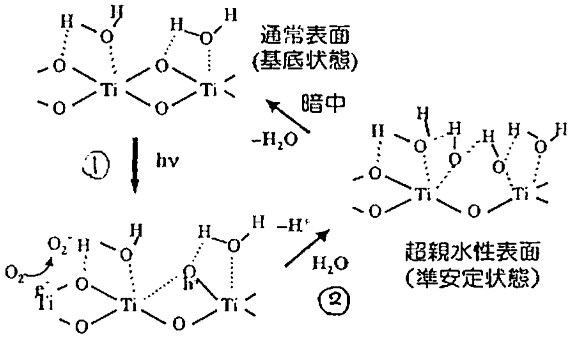


Figure 2 FFM images of a rutile TiO_2 (110) single crystal surface. **a**, A 5×5 μm² image before ultraviolet irradiation. **b**, The same surface after irradiation. Inset, topographic image (245×245 nm) acquired by rotating the sample stage through 45° to the large-scale image. The tip of the Si_3N_4 cantilever is hydrophilic, so hydrophilic areas are bright and hydrophobic areas are dark.



① positive-hole is trapped by oxygen bridging site (Ti–O bond (···) weakened)

② react with adsorbed H_2O in the air then dissociation occurred

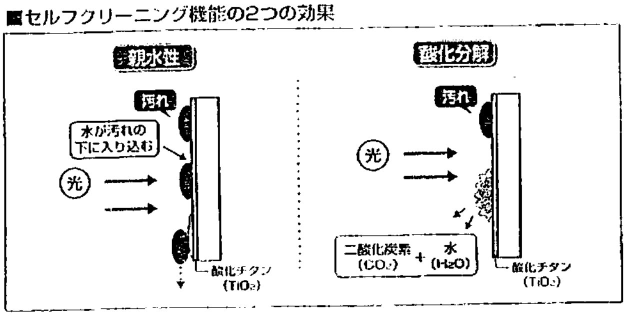
↓

chemisorbed hydroxyl grops

(先端化学シリーズ Ⅱ (丸善) p173)

@ photocatalytic phenomenon and superhydrophilicity can take place simultaneously on the same surface.

■セルフクリーニング機能の2つの効果

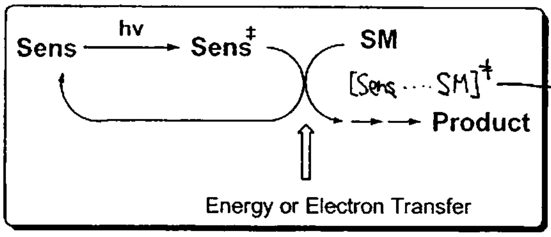


they named as "self-cleaning"

(windows
(mirrors

2. Molecular Photocatalyst (Sensitizer) for Enantioselective Reaction

a) Introduction



Differently from semiconductor photocatalyst, (the adsorption of molecules exist) this interaction is thought to be relatively weak and have short life-time (μs ~ ps)

By the way … How to transfer chirality in photochemical reaction? (especially in solution)

Many strategies have been developed.

- But most methods affording useful ee and yield have been restricted to stoichiometric chirality transfer

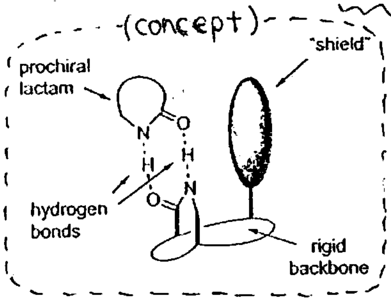
不斉光化学反応の分類

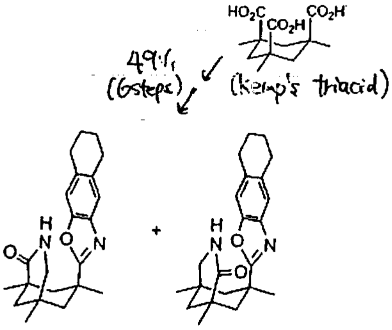
反応媒体	不斉源	励起様式	不斉源/基質比
液相	円偏光	直接	0（円偏光）
	置換基	直接・増感	1
	錯化剤 (complexing agent)	直接	<1
	増感剤 (sensitizer)	増感	<1
	溶媒	直接・増感	>1
	消光剤	直接	>1
	超分子	直接・増感	<1
分子集合系	液晶	直接・増感	>1
	ミセル	直接・増感	>1
	高分子	直接・増感	>1
固相	ホスト分子	直接・増感	1
	ホスト格子	直接	>1
	結晶格子	直接	1
	キラル修飾粘土	直接・増感	>1
	キラル修飾ゼオライト	直接	1

(先端化学シリーズ (丸善/2003) I p96)

so called "absolute asymmetric synthesis"

① with chiral complexing agent — T. Bach et al

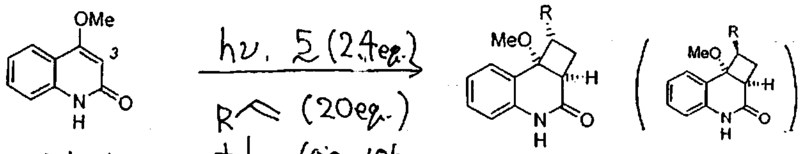




5 ent-5

(for [2+2]-Photocycloaddition (J.A.C.S. (2002) 124. 7982.)

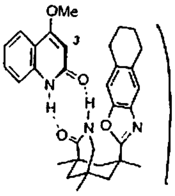
* Intermolecular (J.A.C.S (2000) 122. 11525.)



(2-quinolone)

(R=CH2OAc)
80% (dr >95/5)
92% ee

via



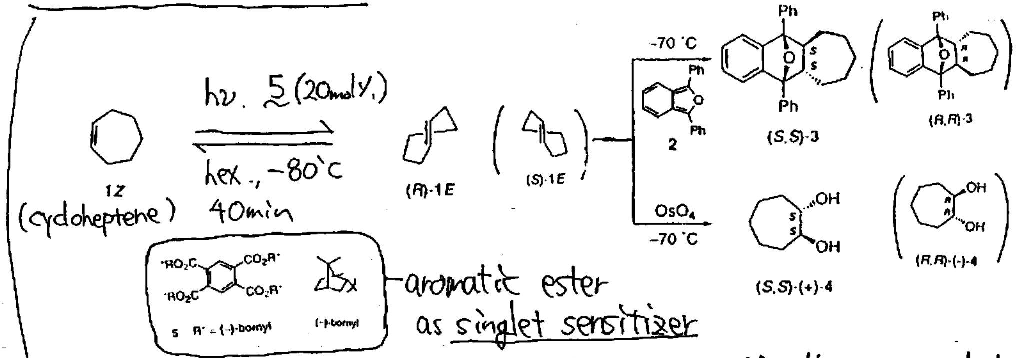
other applications for enantioselective rxn.

- Intramolecular [2+2]-Photocycloadd. (Angew. Chem. Int. Ed. (2000) 39. 2302)
- Norrish-Yang Cyclization (Chem. Eur. J. (2002) 8 2464.)
- Radical Cyclization (Angew. Chem. Int. Ed. (2004). 43. 5849.)

- For substoichiometric chirality transfer,
  chiral photosensitizer seems to be good canditate.

② with chiral sensitizer — Y. Inoue et al

* Z−E Photoisomerization (J.A.C.S. (1999) 121. 10702.)

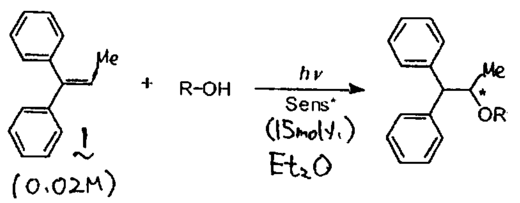


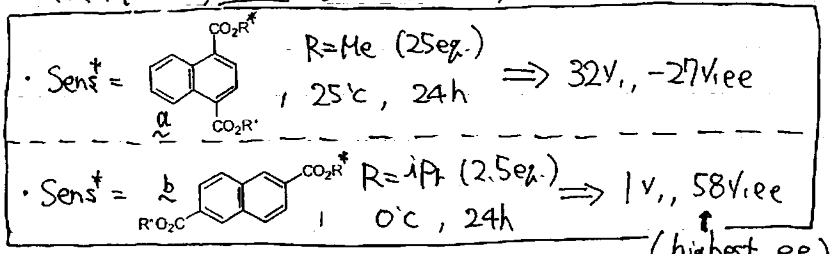
aromatic ester as singlet sensitizer

E/Z ~ up to 0.1 (yield < 10%)
77% ee
was best.

⇒ Product 1-E was subsequently and stereospecifically trapped by Diels-Alder with 2 or OsO₄ oxidation.
↳ very unstable (τ=9.7min at 1°C, 45s at 25°C)

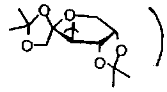
* Anti-Markovnikov Photoaddition. (J.A.C.S. (2003) 125. 3008. etc)





· Sens* = a R=Me (25eq.), 25°C, 24h ⇒ 32%, −27%ee

· Sens* = b R=iPr (2.5eq.), 0°C, 24h ⇒ 1%, 58%ee (highest ee)

(R* =

)

☆ Chirality transfer occurs exclusively in the excited state with chiral sensitizer
(the binding affinity of the sensitizer for the substrate in the ground state is not fatal point.)

[SM ··· Sens*]‡
⇒ but interactions in the excited state is relatively weak and short-lived.

So... why don't you combine these two strategies? (① and ②)
Does it work well??

b) Recent Examples

ⓐ Initial work (?)

Studies on the Enantioselective Catalysis of Photochemically Promoted Transformations: "Sensitizing Receptors" as Chiral Catalysts

David F. Cauble, Vincent Lynch, and Michael J. Krische*
Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas 78712
mkrische@mail.utexas.edu

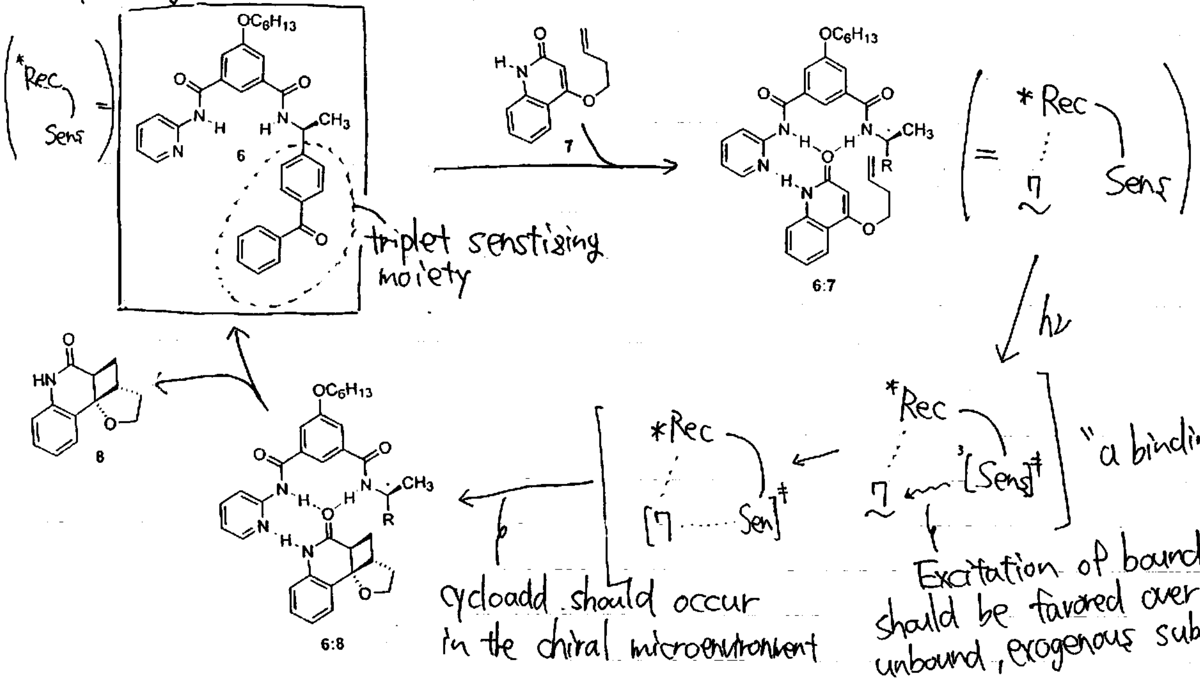
Received October 1, 2002

JOC *Article*

(2003) 68 15-21.

ⓐ well-defined chiral microenvironment
ⓑ kinetic advantage to the transformation of interest
} Chiral molecular receptors that incorporate sensitizing residues

They designed 6 as catalyst for [2+2]-photocycloaddition of 7.



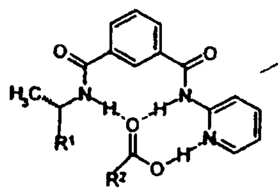
triplet sensitizing moiety

"a binding-induced rate enhancement"

Excitation of bound substrate should be favored over excitation of unbound, exogenous substrate.

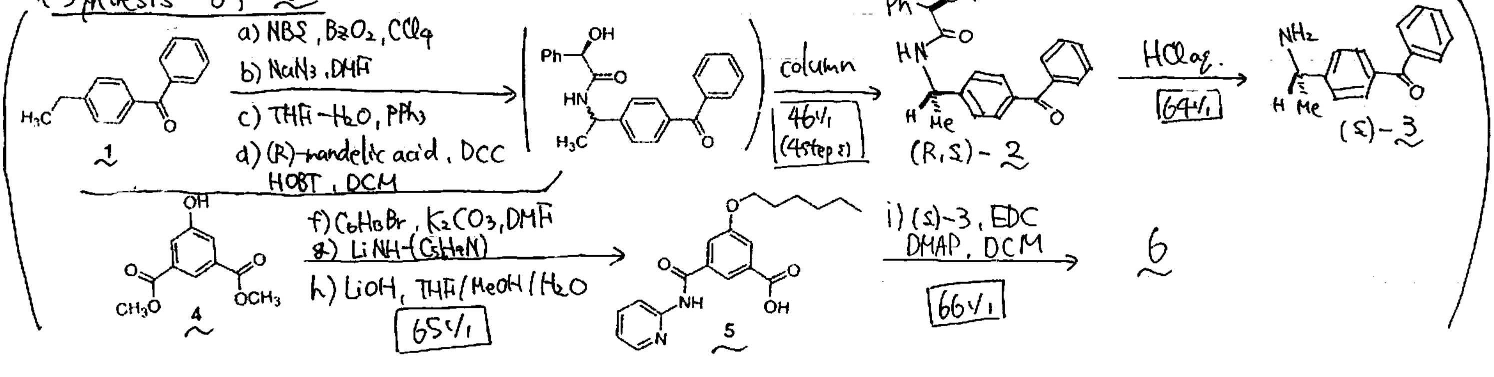
cycloadd should occur in the chiral microenvironment

*structual idea is derived from ... (Tetrahedron: Asymmetry (1997) 24, 3999.)

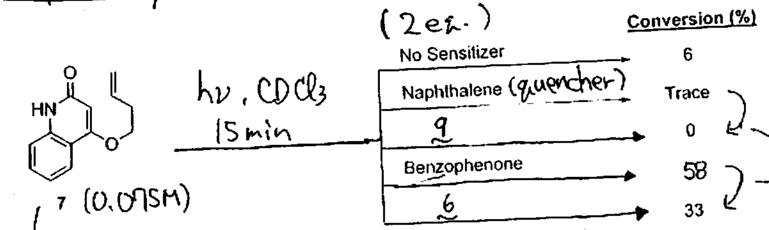


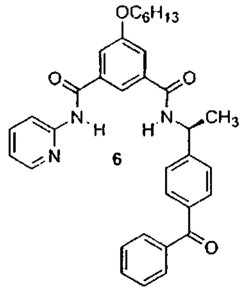
— originally chiral solvating agents for carboxylic acids (for the determination of ee by ^{1}H-NMR)

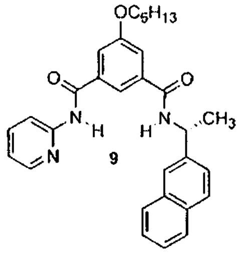
*Synthesis of 6



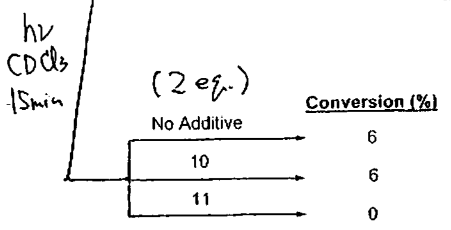
* Capability of 6 for cycloaddition

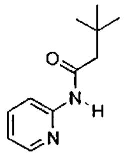






receptor scaffold contain a weakly quenching chromophore ?

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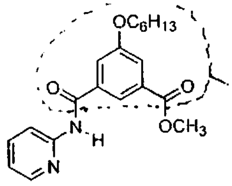
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iso-phthaloyl moiety inhibits the rxn.

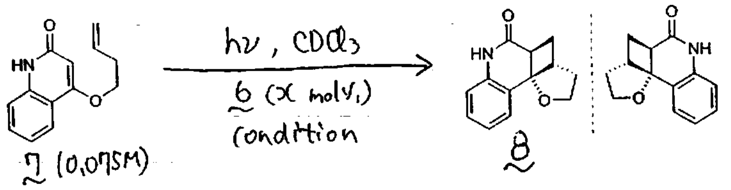
(⇒ "The presence of a weakly quenching chromophore is advantageous" they mentioned. Because ... energy is transferred to the iso-phthaloyl residue rather than to exogenous unbound substrate when 6 binding site is unoccupied or nonproductively occupied by product.

⇓

that will prevent the rate of the background reaction.)

Anyway ...

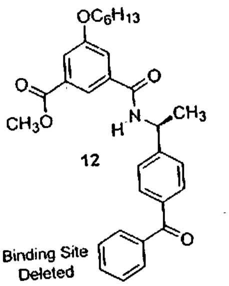
* Enantioselective cycloaddition



entry	x (mol %)	temp (°C)	time (h)	conversion (%)[b]	ee (%)[c]
1	200	30	8	100	0
2	200	−20	12	100	8
3	200	−70	24	100	21
4	100	−70	30	100	22
5	50	−70	40	100	20
6	25	−70	70	100	19

[b] Reactions were periodically monitored by ^{1}H NMR, which enabled a determination of the percent conversion. The formation of byproducts was not observed by ^{1}H NMR. [c] Enantiomeric excess was determined by chiral stationary phase HPLC analysis using a Chiracel OD column.

with



(yield : quant. 0% ee)

⇓

observed ee does not result from only "the association" of 7 to 6

Although the results were not good in terms of ee, this work seems to be an initial attempt for chiral molecular receptor equipped with appendant sensitizing molecule.

⑥ Further Progress

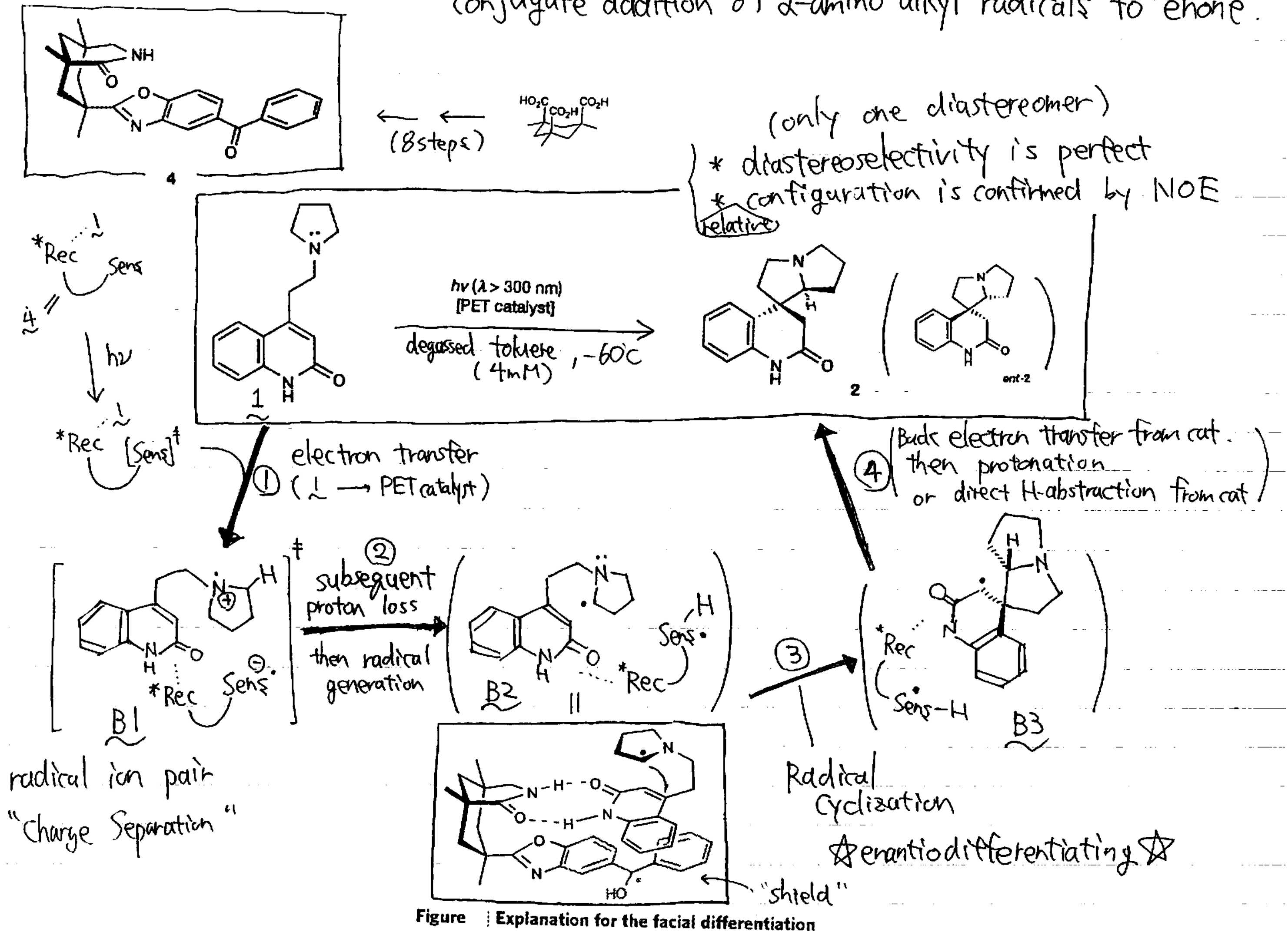
nature
LETTERS
(2005), 436, 1139-1140

Catalytic enantioselective reactions driven by photoinduced electron transfer

Andreas Bauer[1], Felix Westkämper[1], Stefan Grimme[2] & Thorsten Bach[1]

[1]Lehrstuhl für Organische Chemie I, Technische Universität München, Lichtenbergstr. 4, D-85747 Garching, Germany. [2]Universität Münster, Organisch-Chemisches Institut, Corrensstr. 40, D-48149 Münster, Germany.

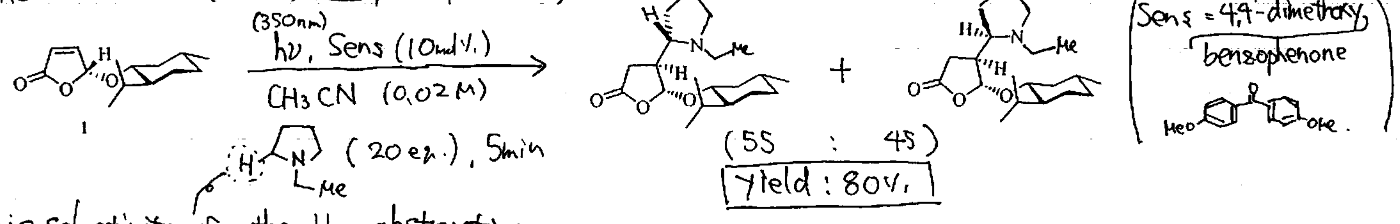
They designed 4 as catalyst and applied for photoinduced electron transfer (PET) catalysed conjugate addition of α-amino alkyl radicals to enone.



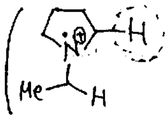
(only one diastereomer)
* diastereoselectivity is perfect
* configuration is confirmed by NOE (relative)

Figure | Explanation for the facial differentiation

* Similar reactions were reported and similar mechanism was proposed (Chem. Eur. J. (2000), 8, 2227-2238)

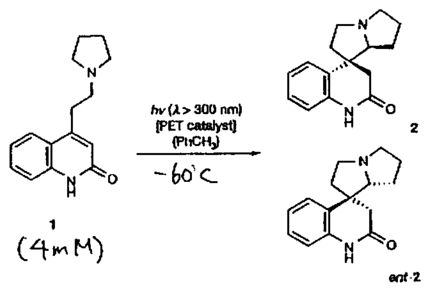


? regioselectivity of the H-abstraction
⇒ might result from better overlap of cleaved C-H bond with the half-filled nitrogen orbital



(kinetically favored)

• Intramolecular case (J.A.C.S. (1991) 113, 8847.)



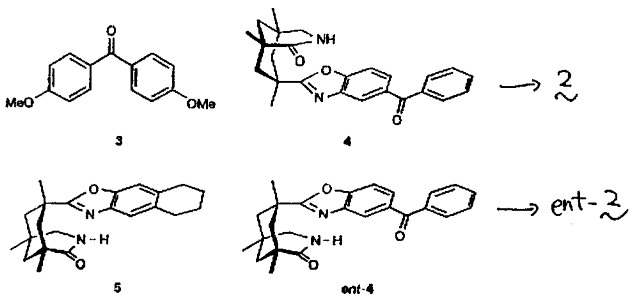


Table 1 | Enantioselective catalytic PET reactions of substrate 1

Entry no	Catalyst	Equiv.*	Time (h)	Product	(e.r.†)	e.e.‡ (%)	Yield§ (%)
1	3	0.1	3.5	2/*ent*-2	50/50	–	7
2	4	0.05	5	2	60/40	20	6
3	4	0.1	2.5	2	69/31	38	55
4	*ent*-4	0.1	3	*ent*-2	31/69	38	52
5	4	0.2	2	2	77/23	54	57
6	4	0.3	1	2	85/15	70	64
7	3/5‖	0.1/1.2	2	*ent*-2	14/86	72	39
8	none		5	2/ent-2		–	25% (1 decomposed)

T.O.N. 12.2

T.O.N. 2.1, Best ee and yield !!

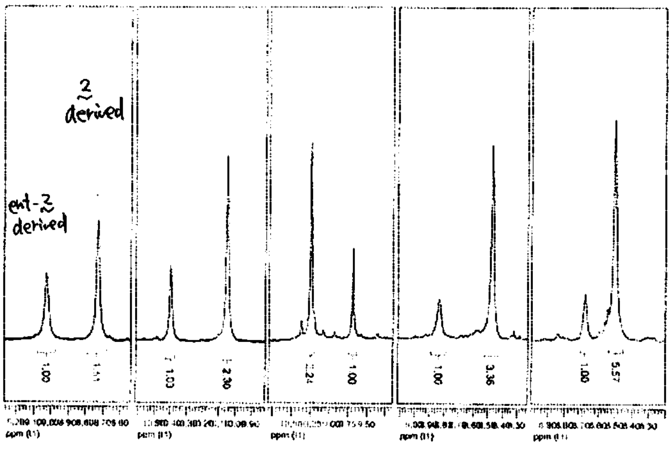
⇒ raising cat. loading (entry 2, 3, 5, 6), ee increased.

⇒ (entry 8) background reaction evidently occurs and decrease ee.

(but, will be increasing suppressed with increasing amounts of 4)

◎ e.r. (enantiomeric ratio) was determined by ¹H-NMR shift experiments using chiral lactam 5 as shift reagent (cf) J.O.C. (2004). 69, 970-973)

product (2 / ent-2) $\xrightarrow{5\ (\sim 1.5\,eq.)}$ the N-H signal of (2 / ent-2) showed strong separation.



Entry 2	Entry 3	Entry 4	Entry 5	Entry 6
0.05 eq. 4	0.1 eq. 4	0.1 eq. *ent*-4	0.2 eq. 4	0.3 eq. 4
e.r. 60/40	e.r. 69/31	e.r. 31/69	e.r. 77/13	e.r. 85/15
20% *ee*	38% *ee*	(– 38% *ee*)	54% *ee*	70% *ee*

⇒ then e.e. was calculated.

(the variance of e.e. data are estimated as ±2%)

◎ Absolute configuration

(entry 7) → tentatively assigned on the basis of their previous result using 5 for radical reaction.

⇓

calculate circular dichroism (CD) spectra

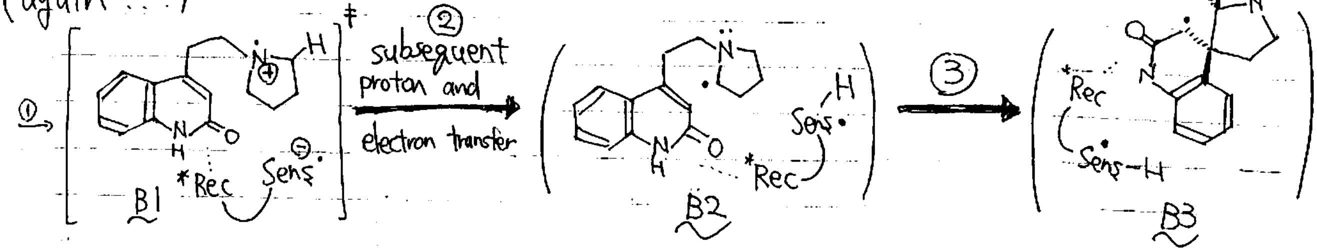
⇓

compare this calculated spectra with experimentally observed one

Q What is good point in this system ?

- more sophisticated structure of catalyst
- more sophisticated reaction system

(again . . .)



radical ion-pair ← stabilized by polar solvent

usually subsequent dissociation or separation (of Sens and substrate) by solvent molecule
(⇒ spoil chiral recognition between Sens and Substrate)

"Trade-off between Ee and Yield" (⇒ T. Inoue's alcohol addition)

In this case, Bach et al use neutral radical species (B3) produced in the sequence of ② and after that, Enantiodifferential cyclization occurred (③))

⇓

So relatively Good results were obtained.

"This is certainly a breakthrough in chiral photochemistry"

— T. Inoue says (Nature (NEWS&VIEWS) (2005) 436. 1099.)

(Appendix)

1-d) Application of Photocatalyst

Usually, TiO_2 is used as thin layer.

◎ Tiles in hospital

antibacterial activity is observed →

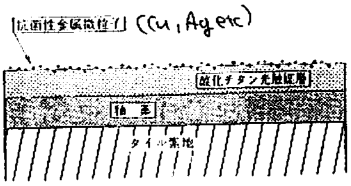
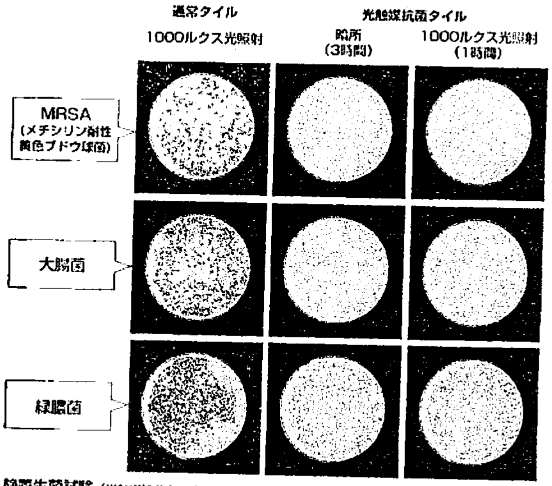


図 4·30 TiO_2 光触媒抗菌タイルの断面

■光触媒抗菌タイルの効果

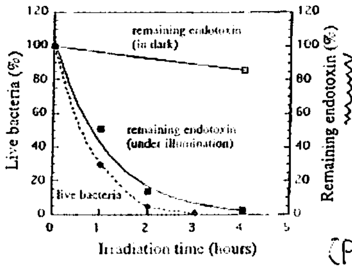


静菌生菌試験（光触媒抗菌タイルの場合、1000ルクスの光をあて、1時間後に観察）

試験菌	MRSA	大腸菌	緑膿菌
滅菌率(%)	99.9	99.9	99.9

(光触媒のしくみ (日本実業出版))

not only bacteria itself,
but also endotoxin can be decomposed
((菌体)内毒素)

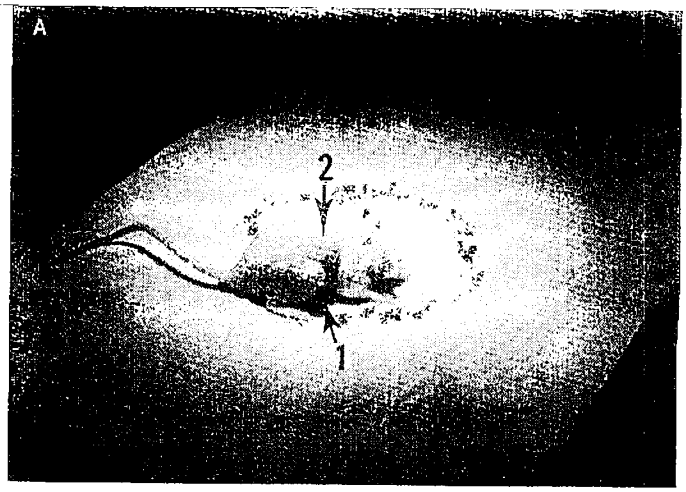


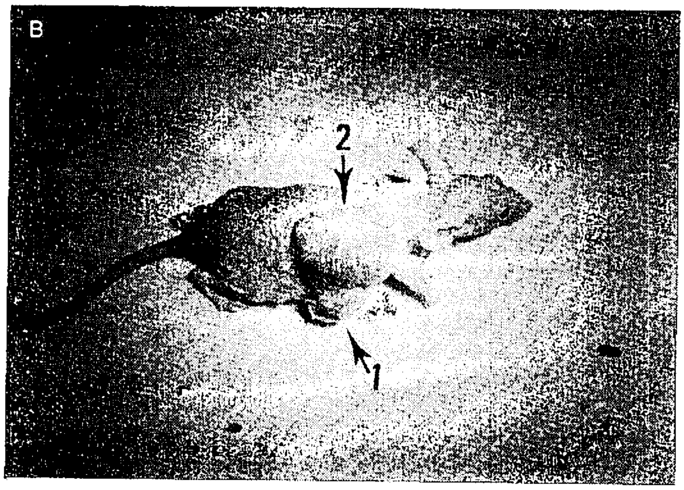
(Photo. Rev. 1 (2000). p12)

Fig. 18. Sterilization of *E. coli* and endotoxin decomposition (endotoxin amount, 3-8 EU/cc=100%) [77]. Both sterilization and endotoxin decomposition commence immediately.

◎ Cancer Treatment

① implant cancer cells under the skin of mice
⇓
② when the size of tumor grew to ~0.5cm,
inject TiO_2 fine-particle solution (only to ↓)
(0.4mg)
⇓
③ After 2-3days, cut the skin to expose the tumor
and irradiate it (Hg lamp, 1h) ⇒
⇓
④ After 4weeks ⇒





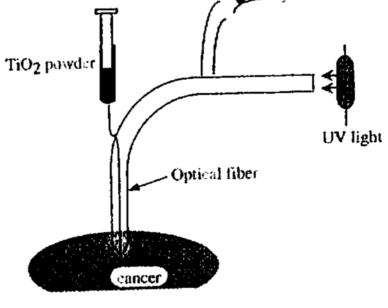
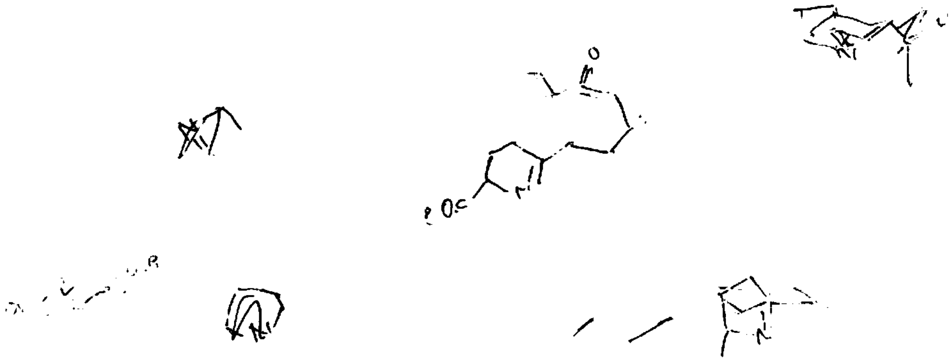


Fig. 20. Future process of photocatalytic cancer therapy [21].

If you have some interests in this field ...
↳ GPJ 国際光触媒展2005
Global Market for Photocatalysis, JAPAN2005
2005年9月14日(水)〜9月16日(金) 東京ビッグサイト

参考図書
a) 光触媒のしくみ (日本実業出版社 / 2000.10)
b) 入門光触媒 (東京図書 / 2004.9)
c) 光触媒標準研究法 (東京図書 / 2005.1)
d) 電子移動の化学 ― 電気化学入門 (朝倉書店 / 1996.4)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