Development of Novel Photocatalytic Systems for Photochemical and Photoelectrochemical Energy Conversion

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Development of Novel Photocatalytic Systems for Photochemical
and Photoelectrochemical Energy Conversion

March 2008

Bashir Ahmmad
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This thesis is submitted as a partial fulfillment of the requirements for the award of a PhD in Chemistry

Submitted by-

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(March 2008)
Dedicated to
My Parents
ACKNOWLEDGEMENTS

I will like to extend my gratitude to the Ministry of Education, Culture, Sports, Science and Technology (MONBUKAGAKUSHO) of the Japanese Government for the Scholarship grant.

I am particularly grateful to my supervisor Prof. Yoshihumi Kusumoto of the faculty of science, department of chemistry and bioscience, for his friendliness, encouragement and support while supervising this research work and also for his original ideas. Special thanks go to Prof. Junichi Kurawaki from whom I received theoretical and practical training in chemistry and also for the useful discussions. Special thanks also go to Prof. Yuji Horie of the department of electronics and electrical engineering for the useful advice and permission to use laser machine in his laboratory. I also thank Prof. Kenichi Tanaka for this valuable advice and suggestion during this work.

I am also very thankful to entire staff of the department of chemistry and bioscience; more especially to staff of the Japanese language Center in Kagoshima University. They contributed immensely for my integration in the university as well as in the Japanese community of Kagoshima.

To my laboratory co-workers past and present, especially to Dr. Miyuki Ikeda and Dr. Pascaline Ngweniform, I say thank you for the useful discussions and friendliness. Cordially thank to my classmate and friend Mr. Shouichi Somekawa for his continuous guide and support throughout my Kagoshima University-life. I also thank to my other friends in and out of the Kagoshima University vicinity.

I am thankful to Prof. Ikuo Sakamoto and Dr. AFM Jamal Uddin for their help and support when I came to Kagoshima as a privately financed student. Finally, I pay my gratitude to my Mr. Masao Arima, Ms. Yasuko Arima and Ms. Mika Arima for their kind support and continuous encouragement during my study in Kagoshima University.

Last but not the least; I am very grateful to almighty Allah for his everlasting helps throughout my life.
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GENERAL INTRODUCTION

1.1 BACKGROUND

For reasonable and good life quality fresh water and energy are the two major commodities that furnish every human activity. In the last several decades global energy consumption has increased by about 50%. The two major reasons for the increase in the energy consumption at all times are the steady population increase and strive for better social and economical developments. The world population is expected to double in the next 50 years. Such an increment in the population is expected to consume two-thirds more energy than today, according to the International Energy Agency (IEA).

Presently, approximately 80% of the world primary energy consumption is still dependent on fossil fuel [1]. Extensive fossil fuel consumption in almost all human activities led to some undesirable phenomena such as atmospheric and environmental pollutions, which have not been experienced before in known human history. Consequently, global warming, green house effect, climate change, ozone layer depletion and acid rain terminologies started to appear in the literature frequently. Experts and decision makers widely agree that alleviation of climate change is mankind’s greatest threat and challenge for the 21st century and beyond. In order to avoid further impacts of these phenomena, the two concentrative alternatives are either to improve the fossil fuel quality with reductions in their harmful emissions into the atmosphere or more significantly to replace fossil fuel usage as much as possible with environmentally friendly, clean and renewable energy sources. Among these sources, solar energy comes at the top of the list due to its abundance, and more evenly distribution in nature than any other renewable energy types such as wind, geothermal, hydro, wave and tidal energies [2].
The solar energy impinging on the earth’s surface is about $3 \times 10^{24}$ J / yr, or approximately $10^4$ times the worldwide yearly consumption of energy. In addition, the solar spectrum ranges from ca 400-800 nm (Fig. 1) [3]. In plants and other lower organisms, the natural photosynthetic system successfully converts sunlight into a storable form of chemical fuel called carbohydrates. The total photosynthetic production on the earth is estimated to be $2 \times 10^{11}$ t / yr. This is a huge amount of energy, 6-10 times as much as the total energy demand of mankind. Carbohydrates fuel produced by plants and some lower organisms is not an ideal fuel for our present needs. Acknowledging the abundance of solar energy falling on the earth surface and the large water reserves on the earth crust, researchers have embarked on the search of a suitable fuel that is capable of replacing the now declining and polluting fossil fuel. The most advanced solar energy utilization processes are:

- Conversion of solar light in chemical energy (H$_2$ energy) and
- Conversion into electrical energy (solar cell).

### 1.2 CONVERSION OF SOLAR LIGHT IN CHEMICAL ENERGY

From the viewpoint of solar energy conversion, photocatalytic production of hydrogen by water-splitting has been considered to be a promising approach and one of the
challenging subjects of science and technology.

Hydrogen is one of the most abundant elements found in combined forms in the universe. It is a very light gas and also highly reactive. Hence found in combined form in water (H\textsubscript{2}O), fossil fuels, all plants and animals. It is an odorless, colorless, tasteless and non-poisonous gas [4, 5]. The interest in it comes from the following aspects:
(a) Hydrogen would probably be an ideal future fuel, and water is an inexhaustible natural source.
(b) It is directly related to solar-energy utilization.
(c) It clean (zero-or low-emission), storable and renewable fuel that does not produce pollutants or greenhouse gases.
(d) In a fuel cell hydrogen can directly be converted into electricity.
(e) With a few relatively minor modifications, conventional internal combustion engines (ICE) can be adapted to run on hydrogen.

In the gas phase, water splitting can be carried out only by scission of the H–OH bond, which requires 5.2 eV per molecule or 498 kJmol\textsuperscript{-1} energy. In contrast, electrolysis of water proceeds by combination of two half-cell reactions (in acidic media)

\[ 2\text{H}^+ + 2e^- \rightarrow 2\text{H}_2 \] (1)
\[ \text{H}_2\text{O} - 2e^- \rightarrow \frac{1}{2}\text{O}_2 + 2\text{H}^+ \] (2)

To result in an overall process of
\[ \text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2 \] (3)

The difference in free energy for eq. (1) and (2) amounts to 1.23 eV per electron. Hence the minimum energy required to decompose water to H\textsubscript{2} and O\textsubscript{2} according to Eq. (3) is 2.46 eV per H\textsubscript{2}O molecule, or 237 kJ mol\textsuperscript{-1}. Normally this energy is supplied by electrical power from an external circuit.

In photoassisted water splitting, the driving force for electrons is given by light energy, and the electron should be transferred from the donor (H\textsubscript{2}O) to the acceptor (H\textsuperscript{+}) via an
appropriate mediating species. The later is usually called the photosensitizer. The production of hydrogen by splitting water, utilizing solar energy has been the dream of researchers, and extensive studies have been carried out using semiconductor photocatalysts and metallloporphyrin photosensitizers [6].

(i) Hydrogen evolution from semiconductors

The principle of the semiconductor photocatalyst reaction is simple. Irradiation by light of energy greater than the band gap, separating vacant conduction band (CB) and filled valence band (VB), excites an electron in VB into CB to result in the formation of an excited electron (e\(^-\))-positive hole (h\(^+\)) pair. These e\(^-\) and h\(^+\) reduce and oxidize, respectively chemical species on the surface of photocatalyst, unless they recombine to give no net chemical reaction. The original structure (or chemical composition) of semiconducting materials remains unchanged if equal number of e\(^-\) and h\(^+\) are consumed for chemical reaction and/or recombination, whence the term photocatalyst.

Based on the above consideration, the photocatalytic activity of semiconductor materials must be controlled by three basic parameters: (1) Light absorption property, e.g., light absorption spectrum and coefficient, (2) rate of reduction and oxidation of reaction substrate by respectively e\(^-\) and h\(^+\), and (3) rate (or probability) of e\(^-\)/h\(^+\) recombination [3].

The energy band diagrams of some representative semiconductors are shown in Fig. 2. The lower edge of the conduction band and upper edge of the valence band are presented along with the band gap in electron volts. The energy scale is indicated in electron volts using either the normal hydrogen electrode (NHE) or the vacuum level as a reference. Note that the ordinate presents internal and not free energy. The free energy of an electron–hole pair is smaller than the band gap energy due to the translational entropy of the electrons and holes in the conduction and valence band, respectively. On the right, the standard potentials of several redox couples are presented against the standard hydrogen electrode potential.
In terms of energy usage, the complete electrolytic decomposition of water is possible if the CB energy is at least as negative (i.e., higher in the diagram) as that required to reduce water to hydrogen gas (0.0 V in acid solution), and the VB is at least as positive (i.e., lower) as that required to oxidize water to oxygen gas (+1.23 V). The complete decomposition of water is thus theoretically possible if a semiconductor is illuminated with light that has the minimum band gap energy of 1.23 eV, assuming that the VB and CB energies are placed at exactly the right points. Theoretically, all types of semiconductors that satisfy the above-mentioned requirements can be used as photocatalysts for hydrogen production. However, most of the semiconductors, such as CdS and SiC, that cause photocorrosion, are not suitable for water-splitting [7].

The photosensitized dissociation of water into H$_2$ and O$_2$ and research work in this area has led to the development of many photochemical systems capable of generating either H$_2$ or O$_2$ from water upon irradiation with visible light. Heterogeneously dispersed photocatalyst such as TiO$_2$, ZnO, Fe$_2$O$_3$ and CdS, which are considered as photo semiconductor, have been extensively researched. [8-12]. But most of the
investigations have focused on TiO$_2$ when compared to other photocatalysts. TiO$_2$ is much more promising as it is stable under UV light irradiation, non-corrosive, environmentally friendly, abundant and cost effective. Moreover it shows relatively high activity and chemical stability. TiO$_2$ exist in two major forms, the anatase and the rutile. The anatase form has free electrons in its crystal lattice, hence is an n-type semiconductor [7].

Like other semiconductor photocatalyst, the reduction and oxidation reactions by TiO$_2$ are the basic mechanisms of photocatalytic hydrogen production and photocatalytic water/air purification, respectively. For hydrogen production, the CB level should be more negative than hydrogen production level (E$_{H_2/H_2O}$) while the VB should be more positive than water oxidation level (E$_{O_2/H_2O}$) for efficient oxygen production from water by photocatalysis. But, the energy conversion efficiency from solar to hydrogen by TiO$_2$ photocatalytic water-splitting is still low, mainly due to the following reason:

a. Recombination of photo-generated electron/hole pairs: CB electrons can recombine with VB holes by quickly and release energy in the form of unproductive heat or photons;

b. Fast backward reaction: Decomposition of water into hydrogen and oxygen is an energy increasing process, thus backward reaction (recombination of hydrogen and oxygen into water) easily proceeds;

c. Inability to utilize visible light: The band gap of TiO$_2$ is about 3.2 eV and only UV light
can be utilized for hydrogen production. Since the UV light only accounts for about 4% of the solar radiation energy while the visible light contributes about 50%, the inability to utilize visible light limits the efficiency of solar photocatalytic hydrogen production.

In order to resolve the above listed problems and make solar photocatalytic hydrogen production feasible, continuous efforts have been made to promote the photocatalytic activity and enhance the visible light response. Addition of electron donors (hole scavengers), addition of carbonate salts, noble metal loading, metal ion doping, anion doping, dye sensitization, composite semiconductors, metal ion-implantation etc, were investigated and some of them have been proven to be useful to enhance hydrogen production. The above listed techniques influencing H\textsubscript{2} production have been grouped under two broad classifications, such as ‘chemical additives’ and ‘photocatalyst modification techniques.

\textit{(a) Modification by metal loading}

Conduction band potential of TiO\textsubscript{2} is suitable to reduce H\textsuperscript{+}. However, due to the presence of a large over potential for the evolution of H\textsubscript{2} on TiO\textsubscript{2} surface, TiO\textsubscript{2} alone becomes inactive. Usually, addition of noble metals such as Pt, Pd, or Rh to semiconductors is essential. Nobel metals, including Pt, Au, Pd, Rh, Ni, Cu and Ag, have been reported to be very effective for enhancement of TiO\textsubscript{2} photocatalysis. As the Fermi levels of these noble metals are lower than that of TiO\textsubscript{2} [13, 14], photo-excited electrons can be transferred from CB to metal particles deposited on the surface of TiO\textsubscript{2}, while photo-generated VB holes remain on the TiO\textsubscript{2}. Accumulated electrons on metal particles can then be transferred to protons adsorbed on the surface and further reduce the protons to hydrogen molecules. Therefore, noble metals with suitable work function can help electron transfer, leading to higher photocatalytic activity.

It should be noted that although the loading of noble metal can reduce recombination to
some extent, hydrogen production from pure water-splitting is difficult to achieve, because: (i) recombination cannot be completely eliminated; (ii) backward reaction of H$_2$ and O$_2$ to form H$_2$O is thermodynamically favorable. Therefore, as discussed in the previous sections, electron donors or carbonate salts as well as other mediators are required to avoid the above listed problems. Since Pt is very expensive, more research is needed to identify low-cost metals with acceptable enhancement of photocatalytic activity [15].

(b) Modification by dye sensitization

Dye sensitization is widely used to utilize visible light for energy conversion. Some dyes having redox property and visible light sensitivity can be used in solar cell as well as photocatalytic systems [16, 17]. Under illumination by visible light, the excited dyes can inject electrons to CB of semiconductors to initiate the catalytic reactions as illustrated in Fig. 3.

![Fig. 3: Mechanism of dye-sensitized photocatalytic hydrogen production under visible light irradiation.](image)

Even without semiconductors, some dyes, for example safranine O/EDTA and T/EDTA, are able to absorb visible light and produce electrons as reducing agents strong enough to produce hydrogen [18]. High hydrogen production rate can be obtained by efficient absorption of visible light and efficient transfer of electrons from excited dyes to the CB of
The CB electrons can then be transferred to noble metal particle (Pt) loaded on the surface to initiate water reduction. In order to regenerate dyes, redox systems or sacrificial agents, such as I\(^{3-}/I^-\) pair and EDTA, can be added to the solution to sustain the reaction cycle.

\[
dye \xrightarrow{h\nu} dye^* \\
dye^* \xrightarrow{TiO} dye^+ + e^- \\
dye^+ + e^- \rightarrow dye
\]

As for principles of the improved photocatalyst activity of modified TiO\(_2\), three benefits of modification to the photocatalyst semiconductor system have been studied as follows: Inhibiting recombination by increasing the charge separation and therefore efficiency of the photocatalytic process increased. Increasing the spectrum response range (i.e. excitation of wide band gap semiconductors by visible light) Changing the selectivity or yield of a particular product [15].

(c) **Modification by Ion doping**

Transitional metal ion doping and rare earth metal ion doping have been extensively investigated for enhancing the TiO\(_2\) photocatalytic activities. Choi et al. [19] carried out a systematic investigation to study the photoreactivity of 21 metal ions doped into TiO\(_2\). It was found that doping of metal ions could expand the photo-response of TiO\(_2\) into visible spectrum. As metal ions are incorporated into the TiO\(_2\) lattice, impurity energy levels in the band gap of TiO\(_2\) are formed, as indicated below:

\[
M^{n+} + h\nu \rightarrow M^{(n+1)+} + e^- _{ch} \\
M^{n+} + h\nu \rightarrow M^{(n-1)+} + h^- _{vb}
\]

where, M and M\(^{n+}\) represent metal and the metal ion dopant, respectively. Furthermore, electron (hole) transfer between metal ions and TiO\(_2\) can alter electron-hole recombination as:
Electron trap: \[\text{M}^{n+} + e_{cb}^- \rightarrow \text{M}^{(n-1)+}\]

Hole trap: \[\text{M}^{n+} + h_{vb}^+ \rightarrow \text{M}^{(n-1)-}\]

The energy level of \(\text{M}^{n+} / \text{M}^{(n-1)+}\) should be less negative than that of the CB edge of TiO\(_2\), while the energy level of \(\text{M}^{n+} / \text{M}^{(n+1)+}\) should be less positive than that of the VB edge of TiO\(_2\). For photocatalytic reactions, carrier transferring is as important as carrier trapping. Only if the trapped electron and hole are transferred to the surface, photocatalytic reactions can occur. Therefore, metal ions should be doped near the surface of TiO\(_2\) particles for a better charge transferring. In case of deep doping, metal ions likely behave as recombination centers, since electron/hole transferring to the interface is more difficult. Furthermore, there exists an optimum concentration of doped metal ion, above which the photocatalytic activity decreases due to the increase in recombination. Among the 21 metal ions studied, Fe, Mo, Ru, Os, Re, V, and Rh ions can increase photocatalytic activity, while dopants Co and Al ions cause detrimental effects. The different effects of metal ions result from their abilities to trap and transfer electrons/holes. For example, Cu and Fe ions can trap not only electrons but also holes, and the impurity energy levels introduced are near to CB as well as VB edges of TiO\(_2\). Therefore, doping of either Cu or Fe ions could be recommended for enhancement of photocatalytic activity [20].

The use of anion doping to improve hydrogen production under visible light is rather a new method with few investigations reported in open literature. Doping of anions (N, F, C, S etc.) in TiO\(_2\) crystalline could shift its photo-response into visible spectrum. Unlike metal ions (cations), anions less likely form recombination centers and, therefore, are more effective to enhance the photocatalytic activity. Asahi et al. [21] determined the substitutional doping contents of C, N, F, P and S for O in anatase TiO\(_2\). It was found that mixing of p states of N with 2p of O could shifts VB edge upwards to narrow down the band gap of TiO\(_2\). Although doping of S had resulted in a similar band gap narrowing, the ionic
radius of S was reported to be too large to be incorporated into the lattice of TiO$_2$. Dopants C and P were found to be less effective as the introduced states were so deep that photo-generated charge carriers were difficult to be transferred to the surface of the catalyst. The nitrogen doped TiO$_2$ thin film was prepared by sputtering TiO$_2$ in an N$_2$ (40%)/Ar gas mixture, followed by annealing at 550°C in N$_2$ for about 4 h. N-doped TiO$_2$ powder was also prepared by treating TiO$_2$ in NH$_3$ (67%)/Ar at 600°C for 3 h. The N-doped TiO$_2$ was reported to be effective for methylene blue decomposition under visible light ($\lambda >$ 400 nm).

Additionally, it was reported by Umebayashi et al. [22] that S-doped TiO$_2$ could be prepared by oxidation annealing of TiS$_2$. Annealed at 600°C, TiS$_2$ was partly changed to anatase TiO$_2$. The residual S atoms in the anatase TiO$_2$ formed S-doped TiO$_2$ by Ti-S bonds. Band structures of the S-doped TiO$_2$ were calculated using the super cell approach. It was found that when TiO$_2$ was doped with S, the mixing of S 3p states with the VB of TiO$_2$ increased the width of VB, resulting in band gap narrowing. Since the band gap narrowing was caused by VB upward shifting, the CB remained unchanged. Therefore, the S-doped TiO$_2$ should be able to reduce protons for hydrogen production under visible light. On the other hand, the upward shift of VB may reduce the oxidation ability under visible light.

Also N-doped TiO$_2$ have been extensively investigated. The reported methods to dope N are heating of titanium hydroxide and urea, reactive DC magnetron sputtering, nitriding of anatase TiO$_2$ with alkylammonium salts and treating TiO$_2$ powder in NH$_3$ (80%)/Ar gas flow at 550°C [23-25].

Similar to S-doping, N-doping also caused a VB upward shift resulting in a narrow band gap and less oxidizing holes. Mrowetz et al. [25] reported that N-doped TiO$_2$ was unable to oxidize HCOO$^-$. However, for hydrogen production, electrons are responsible for reducing protons and the ability of oxidation does not affect the performance, since the VB level of TiO$_2$ is far more positive than oxygen evolution energy level. As such CB remains almost
unchanged after N-doping, being at a more negative than hydrogen production energy level. This throws a possibility that N-doped TiO$_2$ should be able to reduce protons for hydrogen production, although no such research has been reported yet. Under visible light irradiation, electrons can be promoted from energy levels in the band gap formed by nitrogen doping to CB. However, electron-hole recombination possibility of N-doped TiO$_2$ was reported to be higher than undoped TiO$_2$ [26]. For efficient photocatalytic reaction, coupling with other technologies, such as noble metal loading or electron donor addition, is necessary.

(ii) Hydrogen production from molecular photocatalytic systems

Molecular photocatalytic systems are based on modeling the scheme of natural photosynthesis. Artificial photosynthetic systems based on molecular photocatalytic or microheterogenous systems have not yet resulted in development of the systems that will provide water cleavage with high efficiency. Nevertheless, the efficiency of natural photosynthesis is quiet high, it is therefore hoped that highly effective photoconverters of this type can be created in the future. Molecular photocatalytic systems involve the use of porphyrins, ruthenium bipyridine complexes and phthlocyanins for the photoreduction of water to hydrogen. In such systems, the photosensitizer is used to photoreduce a suitable electron acceptor such as quinones or methylviologen MV$^{2+}$ in slightly acidic solution (pH < 6), and the oxidized form of the chromophore is reduced with an irreversible, secondary donor such as EDTA$^{2-}$ [27-28]. Thus on steady-state irradiation the reduced form of the viologen builds up in solution, and this species, in the presence of a suitable catalyst, is capable of reducing water to H$_2$ as shown in Fig. 4.

The difficulties involved in carrying out this reaction effectively lies in the charge separation step. That is to suppress the back recombination reaction (rate constant $k_b$) which is a simple exothermic bimolecular process and therefore proceeds much more rapidly than complex catalytic reactions ($k_q$ and $k_l$).
Hydrogen evolution schemes have been extensively studied and proposed mechanisms are based on electron transfer reactions. Quantum yields vary from 0.02-0.3 mol ein⁻¹. After excitation of a photosensitizer S, charge separation takes place. Since the photosensitizer is in its excited state, it is both a stronger oxidant and reductant than in its ground state because of its higher energy content (Fig. 4). After successful charge separation hydrogen gas is formed via the reduced photosensitizer (S⁻) and/or the reduced electron relay R⁻ (equation 6 and/or 7).

\[
\begin{align*}
S^+ + D &\rightarrow S^- + D^+ \hspace{1cm} \text{(4)} \\
S^+ + R &\rightarrow S^+ + R^- \hspace{1cm} \text{(5)} \\
S^- + H^+ &\rightarrow S + H_2 \hspace{1cm} \text{(6)} \\
R^- + H^+ &\rightarrow R + H_2 \hspace{1cm} \text{(7)}
\end{align*}
\]

When hydrogen evolution occurs through the reduced photosensitizer, the mechanism is termed reductive quenching and when it occurs through the reduced relay it is termed oxidative quenching [29,30]. Chl and Ru(bpy)$_3^{2+}$ are known to produce hydrogen via both mechanisms. However, the dominant mechanism for most porphyrins that give high quantum yields is the oxidative quenching. Hydrogen evolution using a four component system made up of a photosensitizer, an electron acceptor, an electron donor and a catalyst.

**Fig. 4:** Energy level diagram for Photoinduced electron transfer. S,photosensitizer; R, electron relay (electron acceptor); $k_q$, rate constant for back electron transfer reaction; $k_f$, rate constant for forward reaction.
for proton reduction has been studied extensively. As photosensitizers the following compounds have been used zinc porphyrins, tin tetraphenylporphyrin complexes, chlorophyll a, Ruthenium polypyridinium complexes such as Ru(bpy)$_3$Cl$_2$ and organic dyes like proflavin or cyanine dyes have been used. To diminish the back electron reaction, sacrificial electron donors such as ethylenediaminetetraacetic acid and triethanol amine are commonly used. Viologen compounds are used as the electron acceptors, with methyl viologen being the most effective in aqueous solution. As catalyst for proton reduction hydrogenase and platinum colloid has been used. Pt is the most used because it is very stable upon long term irradiation. Hydrogen evolution has been investigated under irradiation of mixtures involving EDTA$^{2-}$ as an electron donor, methyl viologen as an electron carrier and hydrogenase or Pt colloid in aqueous micelle solution [3, 27-30] and Langmuir Blodgett (LB) film systems [31] and in polymer matrix system [32]. In order to enhance the hydrogen evolution efficiency, the viologen-linked Zn porphyrin derivatives were synthesized and the photoinduced hydrogen evolution was carried in the presence of 1,4-dihydronicotinamide adenine dinucleotide phosphate (NADH) [33]. The platinum-loaded Langmuir-Blodgett (LB) films of viologen-linked porphyrin also led to the photoinduced hydrogen evolution in the presence of EDTA$^{2-}$ as a sacrificial electron donor. By combining oligosaccharide (sucrose or maltose) degradation with invertase and glucose dehydrogenase, the electron donor, nicotinamide dinucleotide (NADP) is regenerated continuously. It is also possible to regenerate the electron donor by coupling the hydrogen evolution reaction using NADP with the oxygen evolution from grana-ferredoxin-nicotinamide adenine diphosphosphate [34] and hence the electron donor is no more sacrificial. In such a system, an improvement in the yield of hydrogen gas using Chl and zinc porphyrin in aqueous micelle system has been reported in the presence of MV$^{2+}$, and Pt colloid. The effective production of hydrogen gas depends on a number of factors:
a. Photophysical properties of the photosensitizer

No light reaches the earth surface with a wavelength < 400 nm, consequently, the ideal chromophore, or a combination of dyes should have a broad absorption spectrum covering the region 400-850 nm. Porphyrins are capable of collecting up to 45% of the energy available in sunlight. The desired photosensitizer should also have a long singlet or triplet excited state lifetime. This is because the longer lifetime has an advantage since at a given concentration of quencher the number of diffusional encounters between a molecule in an excited state and a quencher molecule will increase when the lifetime of the excited state is extended. Porphyrins are known to have long singlet and triplet lifetimes [35]. However, recent studies have indicated that in organized porphyrin assemblies such as the LB films, porphyrin-polymer systems, hydrogen is produced via the singlet state whereas, in other systems hydrogen was produced via the triplet state. Porphyrins appear to have the most favorable photophysical properties such as high triplet yields, long triplet lifetime, favorable absorption spectra and can easily for organized aggregates such as the one in LB films.

b. Thermodynamic requirements

For a reducing agent to be used in the production of hydrogen from water, its reduction potential must be more negative than the reduction potential of water. This potential depends on the concentration of protons and is given by equation

\[ E_{o'} (H^+/H_2) = 0.059 \text{pH V} \]

At pH 7,

\[ E_{o'} (H^+/H_2) = 0.41 \text{ V} \]

Since kinetic barriers must be overcome, this value is usually greater than 0.41 V (at pH 7). The reduction potential of methyl viologen is 0.455 V and independent of pH. Hence MV\textsuperscript{2+} might be a suitable reducing agent for protons in the presence of a suitable catalyst to overcome the kinetic barriers.
In both the oxidative and reductive quenching mechanisms discussed, the reduction potentials of the ground and excited state of a photosensitizer are related by the one electron potential,

\[
E_{0}(S^{*/S}) = E_{0}(S^{*/S}) - \Delta E \quad \text{(10)}
\]

\[
E_{0}(S^{*/S}) = E_{0}(S^{*/S}) + \Delta E \quad \text{(11)}
\]

Equations 10 and 11, together with the reduction potential for methyl viologen provide rough guidelines when assessing any potential sensitizer. In a reductive cycle, the reduced sensitizer must be capable of reducing water:

\[
E_{0}(S^{*/S}) < \text{ca. -0.41 V at pH 7} \quad \text{(12)}
\]

whereas, in an oxidative cycle, the reduced electron acceptor must be capable of reducing water:

\[
E_{0}(S^{*/S}) < \text{ca. -0.41 V} \quad \text{(13)}
\]

A particular sensitizer with good photophysical properties and thermodynamic properties may still be of no use for hydrogen production due other reasons.

c. Chemical stability

Owing to their high energy content in the excited state, photosensitizers can easily undergo various types of degradation such as hydrolysis and triplet-triplet annihilation with oxygen, forming the highly reactive singlet oxygen that destroys the sensitizer. Electron acceptors such as \(\text{MV}^{2+}\) are also susceptible to hydrogenation reactions through the aromatic structure. The protonation of the reduced viologen cation radical \(\text{MV}^{*+}\) provides another efficient pathway for the decomposition of \(\text{MV}^{2+}\) in a water photolysis system [27-29].

1.3 CONVERSION INTO ELECTRICAL ENERGY (SOLAR CELL)

Photovoltaic devices are based on the concept of charge separation at an interface of two materials of different conduction mechanism. To date this field has been dominated by solid-state junction devices, usually made of silicon, and profiting from the experience and
material availability resulting from the semiconductor industry. The dominance of the photovoltaic field by inorganic solid-state junction devices is now being challenged by the emergence of a third generation of cells, based, for example, on nanocrystalline and conducting polymers films. These offer the prospective of very low cost fabrication and present attractive features that facilitate market entry. It is now possible to depart fully

![Diagram of a dye sensitized solar cell](image)

**Fig. 5:** Principle of a dye sensitized solar cell.

from the classical solid-state junction device, by replacing the contacting phase to the semiconductor by an electrolyte, liquid, gel or solid, thereby forming a photo-electrochemical cell. Contrary to expectation, devices based on interpenetrating networks of mesoscopic semiconductors have shown strikingly high conversion efficiencies, which compete with those of conventional devices. The prototype of this family of devices is the dye-sensitized solar cell (DSC), which realizes the optical absorption and the charge separation processes by the association of a sensitizer as light-absorbing material with a wide band gap semiconductor of nanocrystalline morphology [36]. A schematic presentation of the operating principles of the DSC is given in Fig. 5. At the heart of the system is a mesoporous oxide layer composed of nanometer-sized particles which have been sintered together to allow for electronic conduction to take place. Photo-excitation of the sensitizer (S) is followed by electron injection into the conduction band of the mesoporous oxide
semiconductor. The dye molecule is regenerated by the redox system, which itself is
regenerated at the counter electrode by electrons passed through the load. Potentials are
referred to the normal hydrogen electrode (NHE). The open-circuit voltage of the solar cell
corresponds to the difference between the redox potential of the mediator and the Fermi
level of the nanocrystalline film indicated with a dashed line.

The need for dye-sensitized solar cells to absorb far more of the incident light was the
driving force for the development of mesoscopic semiconductor materials—minutely
structured materials with an enormous internal surface area, which have attracted great
attention during recent years. Mesoporous oxide films are made up of arrays of tiny crystals
measuring a few nanometres across. Oxides such as TiO$_2$, ZnO, SnO$_2$ and Nb$_2$O$_5$, SrTiO$_3$,
In$_2$O$_3$, WO$_3$ or chalcogenides such as CdSe, are the preferred compounds. These are
interconnected to allow electronic conduction to take place. Between the particles are
mesoscopic pores filled with a semiconducting or a conducting medium, such as a p-type
semiconductor, a polymer, a hole transmitter or an electrolyte. The net result is a junction of
extremely large contact area between two interpenetrating, individually continuous
networks [36-39].

1.4 CARBON NANOMATERIALS

Natural carbon can exist in several forms. Most people know about graphite and
diamond, but there is a third type—fullerene or carbon nanotube. By far the most common
fullerene is C$_{60}$. It is also called a "buckyball". But there are some other relatively common
fullerenes such as C$_{70}$, C$_{76}$, and C$_{84}$.

A C$_{60}$ molecule consists of 60 carbon atoms bonded in the nearly spherical configuration
(fig. bellow). If you look carefully, you will see that each carbon atom is equivalent to all
the others (i.e., they all have the same number of neighbors, bonded at the same relative
angles). This shape is called a “truncated icosahedron”, with 20 hexagons and 12 pentagons.
It’s also the shape of a soccer ball. A C$_{60}$ molecule is about 7 Å in diameter which 4.5 times
as large as a hydrogen atom [40, 41].

Carbon Nanotubes, discovered in 1991 by Iijima of NEC Corporation [42], belong to the fullerene family, a molecular form of carbon, quite distinct from diamond and graphite. The easiest way to visualize how nanotubes are built up is to start with graphite, the most stable form of crystalline carbon.

Graphite consists of layers of carbon atoms. Within the layers the atoms are arranged at the corners of hexagons, which fill the whole plane (in the idealized case without defects). The carbon atoms are strongly (covalently) bound to each other (carbon-carbon distance ~0.14 nm), leading to a very large in-plane value for Young’s modulus.

The layers themselves are rather weakly bound to each other (weak long range van de Walls type interaction, interlayer distance of ~0.34 nm). Starting with only one layer of
2-dimensional graphite we end up with a cylinder with only one wall, a single wall carbon nanotube (SWNT). If more layers are taken, cylinders with multiple walls may result, a multi wall nanotube (MWNT) [43].

Thus, cylindrical structures of carbon atoms take two forms: single-walled nanotubes (SWNTs) and multiwalled nanotubes (MWNTs), each of which has its advantages and disadvantages for different applications. SWNTs are essentially single layers of pure-carbon atoms rolled into a seamless tube capped at each end by half-spherical fullerene structures. They measure about 1 nm or $10^{-9}$ m in diameter, and differ from MWNTs in that all of their atoms form a single covalently bound network. This gives SWNTs more distinctive electronic and optical properties. SWNTs tend to aggregate in bundles that are bound by van der Waals attraction. SWNT can be close-end and open-end. In close-end SWNT, the both ends have fullerene structure, i.e. consisting of hexagon and pentagone [44].

Since the invention of Carbon Nanotube, efforts in synthesis, characterization and theoretical investigation on nanotubes has grown exponentially. This is mostly due to their perceived novel mechanical and electronic properties and their tremendous potential for future technological applications.
1.5 REVIEWS ON SOLAR ENERGY CONVERSIONS

In 1972, Fujishima and Honda reported the photocatalytic splitting of water on TiO\textsubscript{2} electrodes resulting in the beginning of a new era in photocatalyst and prompted extensive research concerning solar energy conversion [45].

In the last two decades vast researches have been conducted which can be perceived by several review papers and book related to hydrogen generation [15, 47, 48, 28, 30]. Photocatalytic water splitting into Hydrogen and Oxygen still remains the goal of researchers and scientists in the 21\textsuperscript{st} century.

In 1981 Sakata et al. [48] reported the heterogeneous photocatalytic production of hydrogen and methane from ethanol-water. They found that the quantum yield of hydrogen production was increased greatly by supporting Pt on TiO\textsubscript{2} surface. A mechanism of the photocatalytic reactions was discussed.

Other noble metals, including Au, Pd, Rh, Ni, Cu and Ag, have been reported to be very effective for enhancement of TiO\textsubscript{2} photocatalysis [49-51]. As the Fermi levels of these noble metals are lower than that of TiO\textsubscript{2}, photo excited electrons can transferred from CB to metal particles deposited on the surface of TiO\textsubscript{2}, while photogenerated VB holes remain on the TiO\textsubscript{2}. Anpo and Takeuchi [52] employed ESR signals to investigate electron transfer from TiO\textsubscript{2} to Pt particles. It was found that TiO\textsuperscript{3+} signals increased with irradiation time and the loading of Pt reduced the amount of Ti\textsuperscript{3+}. This observation indicates the occurrence of electron transfer from TiO\textsubscript{2} to Pt particles.

Bamwenda et al. [50] compared hydrogen production from water-ethanol solution using Au-loaded TiO\textsubscript{2} and Pt-loaded TiO\textsubscript{2} as photocatalysts. Different metal particle deposition methods, such as deposition-precipitation, impregnation and photodeposition were also tested. It was found that loading of Pt worked better than loading of Au. Furthermore, Au loading prepared by photodeposition worked better than deposition-precipitation and impregnation. The variations might be explained by the better contact with TiO\textsubscript{2} active
sites for photodeposition method.

Since Pt is very expensive, more research is needed to identify low-cost metals with acceptable enhancement of photocatalytic activity. For example, Dhanalakshimi et al. [17] investigated dye sensitized hydrogen production. When Pt/TiO$_2$ and Cu/TiO$_2$ were used as photocatalysts, enhanced hydrogen production was observed and the effect of Cu loading was almost comparable to Pt loading.

Organic compounds (hydrocarbons) are widely used as electron donors for photocatalytic hydrogen production as they can be oxidized by VB holes. The remaining strong reducing CB electrons can reduce protons to hydrogen molecules. EDTA, methanol, ethanol, CN$^-$, lactic acid and formaldehyde have been tested and proved to be effective to enhance hydrogen production [50, 53]. Nada et al. [46] carried out a qualitative investigation to study the effects of different electron donors on hydrogen production. The rankings in terms of the degree of hydrogen production enhancement capability were found to be: EDTA $>$ methanol $>$ ethanol $>$ lactic acid. It should be noted that the decomposition of these hydrocarbons could also contribute to a higher hydrogen yield since hydrogen is one of their decomposed products. Photocatalytic decomposition of pollutants and photocatalytic production of clean hydrogen fuel can take place simultaneously when the pollutants are acted as electron donors. Li et al. [54] reported enhanced photocatalytic hydrogen production in single component systems and mixture systems of pollutants (oxalic acid, formic acid and formaldehyde) acting as electron donors. Decomposition of the electron donors was reported to be consistent with hydrogen production. Other inorganic ions, such as S$^2-/SO_3^{2-}$, Ce$^{4+/Ce^{3+}}$ and IO$_3^-/I^-$ were used as sacrificial reagents for hydrogen production [15].

Sayama et al. [55] reported that addition of carbonate salts could significantly enhance hydrogen and oxygen production stoichiometrically. Addition of Na$_2$CO$_3$ was found to be effective for enhancement of hydrogen and oxygen production using Pt loaded TiO$_2$
(Pt/TiO₂). Later, various semiconductor photocatalysts including TiO₂, Ta₂ O₅ and ZrO₂ were tested and it was found that the presence of Na₂CO₃ was very beneficial for hydrogen and oxygen production for all the photocatalysts tested. The Infrared (IR) study revealed that the surface of Pt/TiO₂ catalyst was covered by many types of carbonate species, such as: HCO₃⁻, CO₃⁻, H₂CO₃, C₂H₂O₆⁻, HCO₃⁻, CO₃²⁻, HCO²⁺, and C₂O₆²⁻. These carbonate species were formed through the following reactions:

\[
\text{CO}_3^{2-} + \text{H}^+ \leftrightarrow \text{HCO}_3^-
\]

\[
\text{HCO}_3^- + \text{h}^+ \rightarrow \text{HCO}_3^-
\]

\[
\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^-\]

\[
\text{CO}_3^- \rightarrow \text{C}_2\text{O}_6^{2-}
\]

Therefore, photo-generated holes were consumed by reacting with carbonate species to form carbonate radicals, which is beneficial for photo-excited electron/hole separation. On the other hand, peroxy carbonates were easily decomposed into O₂ and CO₂,

\[
\text{C}_2\text{O}_6^{2-} + 2\text{h}^+ \rightarrow 2\text{CO}_2
\]

The evolution of CO₂ and O₂ could promote desorption of O₂ from the photocatalyst surface and thus could minimize the formation of H₂O through the backward reaction of H₂ and O₂. Then desorbed CO₂ soon was dissolved and converted in to HCO₃⁻, in turn effecting H₂ production. Chlorophyll a, which, on the one hand, has primordial biological significance and which, on the other hand, could also play an important role in artificial energy conversion systems.

Many reports exist in which hydrogen gas was produced using Chlorophyll a Chl (a natural green pigment) in microemulsions and in micelle systems in a mixture made up of methylviologen, proton reduction catalyst (hydrogenase, Pt colloid, PtO₂) and a sacrificial electron donor such as ethylenediaminetetraacetic acid (EDTA³⁻), cysteine, and
nicotinamide adenine dinucleotide (NADH) [3, 27, 56-58]. In these systems, the electron donor is sacrificial and the reaction stops immediately after the entire electron donor has been consumed. By combining oligosaccharide (sucrose or maltose) degradation with invertase and glucose dehydrogenase, NADH is regenerated continuously and hence the electron donor is no more sacrificial. In such a system, an improvement in the yield of hydrogen gas using Chl in a micelle system has been reported in the presence of MV$^{2+}$ and Pt colloid [58].

It has also been shown in a series of recent investigations that cobalt porphyrin molecules modified by attachment of ruthenium or osmium complexes to the periphery of the porphyrin ring exhibit the high catalytic activity for the electroreduction of O$_2$ directly to H$_2$O [59]. Co(II)tetraphenylporphyrin (CoTPP) has been used for the selective oxidation of aldehydes in organic solvents. It is used for the selective oxidation of organic substrate owing to its molecular oxygen activating function [60].

Carbon nanotubes also have been attracted interest in the field of catalytic application. Ying Yu et al (61) recently reported the preparation of TiO$_2$/carbon nanotubes composite with the aid of ultrasonic irradiation. The photocatalytic activity of the composite was evaluated by the degradation of acetone and by the detection of the hydroxyl radical (·OH) signals using electron paramagnetic resonance (EPR). This sample have much more highly photocatalytic activity than P25 and TiO$_2$/activated carbon (AC) composite.

Yan Ou [62] et al reported MWNT-TiO$_2$:Ni composite catalyst for the photocatalytic hydrogen production from water under visible light irradiation. The photocatalytic activity of the nanoscaled composite materials were investigated in terms of hydrogen production from water in the presence of methanol as a sacrificial reagent. The rate of H$_2$ evolution was 38.1 $\mu$mol h$^{-1}$ at a weight ratio of MWNT/TiO$_2$ equal to 4.4%. The experimental results were rationalized by assuming that MWNTs serve as photosensitizer, synergetic with metallic Ni, greatly enhancing the activity of visible-responsive photocatalyst.
The development of a novel Ni catalyst supported on CNT (0.5 wt%) for the direct decomposition of ethylene at 400°C to produce CO-free hydrogen has been reported by Savva et al. [63] This catalytic system presented the highest hydrogen yield and carbon capacity for both the ethylene and methane decomposition reactions. In particular, the 0.5 wt% Ni/CNT catalyst exhibited 50 times higher hydrogen yield compared to a 0.3 wt% Ni/SiO₂ catalyst which had been examined under the same experimental conditions.

In the last two decades, much attention has been paid to develop an efficient system for solar energy conversion in electrical energy that can be realized by several review papers and books [36, 37, 64-66, 3, 6]. In a solar cell, can convert solar energy directly to electrical energy. Moreover, the electricity produced in a solar cell can be used to produce H₂ from water in the same system (called Tandem cell) [67].

Carbon nanotube and fullerene have been used widely in solar cell due its extra-ordinary electrical properties. The exploration of new principles and concepts to develop molecular electronic devices for low cost solar cells has been reported by Kymakis et al. [68]. A molecular dispersed heterojunction solar cell consisting of a polymer and dye coated carbon nanotubes blend sandwiched between metal electrodes has been developed. The dye naphthalocyanine (NaPc) was used as the main sensitiser, while nanotubes and poly(3-octylthiophene) (P3OT) act as the electron acceptor and the electron donor, respectively. The incorporation of the NaPc in the P3OT/SWNT composite does dramatically increase the layer absorption resulting in a much higher photocurrent.

Recently, transparent and conductive single-walled carbon nanotube (SWNT) thin films were fabricated onto glass substrates and their optical and electrical properties were evaluated by the same group of researchers. It was shown that solution processed SWNT film can be highly transparent and conductive and can be effectively integrated in polymer-fullerene photovoltaic cells, as the hole collecting electrode, replacing ITO. This application requires composite SWNT film as transparent and conductive as possible, a behavior not
easy to be obtained since there is a trade-off between these two quantities. However, the best photovoltaic characteristics were obtained with a film with only 64% transparency; this can be explained by the 3-D nature of the SWNT film, which significantly enhance the charge transport properties. The best photovoltaic performance was observed for the devices utilizing 80 nm SWNT films with a sheet resistance of 362 Ω/sq, and a transmittance of 64% at 520 nm [69]. Ulbricht et al. [70] has deposited transparent carbon nanotube (t-CNT) on ITO to improve the enhanced role in charge collection and found that the performance is further improved in such a hybrid anode device, in which the part of the t-CNTs collects more charges from the bulk of the organic photovoltaic cell (OPV) and transports carriers to the ITO, while part of the PEDOT:PSS-coated ITO, in contact with P3HT in the pores further collects and transports charges to the current leads. This type of hybrid anode can increase the efficiency of OPVs and allows thicker OPV architectures, and is important for large area OPVs.

1.6 AIM AND OBJECTIVE

Carbon nanotubes (CNTs) combine unique chemical and physical properties. It has attracted the interest of numerous researchers for applications in various fields of research. Catalysis, and in particular heterogeneous catalysis, has also been envisaged as a potential field. For the enhancement of photocatalytic activity of TiO$_2$ usually Pt is used as a co-catalyst. But the use of Pt is not economy way for mass production. Carbon nanotube, which has metallic properties, are quite attractive to replace Pt due to their high electronic conductivity, corrosion resistance toward I$_2$, high reactive for triiodide reduction and low cost. In this research work, carbon nanotube or graphite silica has been used as a replacement of Pt for the enhanced activity of TiO$_2$ in H$_2$ production from alcoholic water solution and in degradation of water pollutants. For the both above photocatalytic reactions an N-doped TiO$_2$ film prepared by laser ablation method was also applied. Moreover, Pt
based counter electrode has been replaced by a CNT one in solar cells using Fe$_2$O$_3$ and TiO$_2$ thin films as working electrodes. In other part of work CoTPP and Chl were solubilized in Pt-loaded polypeptide-surfactant complexes and hydrogen evolution experiments were carried out in the presence of methylviologen as an electron acceptor and ethylenediamine tetraacetic acid, disodium salt (EDTA$^2$) as a sacrificial electron donor.

References


CHAPTER 2

CARBON NANO-MATERIALS SYNERGISTICALLY ENHANCE PHOTOCATALYTIC ACTIVITY OF TiO₂

2.1 INTRODUCTION

As an alternative energy resource for a sustainable environment, scientists all over the world are very interested in H₂ gas as the most promising approach. The photocatalytic decomposition of water into hydrogen and oxygen has been regarded as one of the most potential approaches ever since Fujishima and Honda reported the photoelectrochemical water splitting using a TiO₂ electrode [1]. In the last two decades vast researches have been conducted which can be perceived by several review papers and books related to hydrogen generation published in the past several years [2-5].

Due to their unique chemical and physical properties, carbon nanotubes have attracted the interest of numerous researchers for their application in diverse fields. Catalysis, in particular heterogeneous catalysis, has also been envisaged as a potential field [6]. For the enhancement of the photocatalytic activity of TiO₂, many researchers have used mainly noble metals as co-catalysts. For example, Kawai et al. and Naito et al. [7, 8] report that H₂ is produced high efficiently at room temperature from methanol-water mixtures using a TiO₂ powder deposited with a metal (Pt, Pd), metal oxide (RuO₂), or rhodium complex [(Ph₃P)₃RhCl]. Al-Mazroai et al. [9] showed the enhancement of H₂ production with various noble metals and found an order of Pt > Pd > Ir > Au > Rh ≥ Ru > Ni.

Carbon compound also attracted attention in replacement of novel metals. For example, Ikeda et al. [10] change to full paper] reported the photocatalytic production of hydrogen gas from aqueous methanol solution using powdered mixtures of graphite silica (GS) and platinized TiO₂ (Pt/TiO₂) or those of GS, Pt and TiO₂. GS was added to Pt/TiO₂ and the two-component mixture of TiO₂ and Pt in order to increase the amount of hydrogen
production from aqueous methanol solution. It was found that the addition of GS to Pt/TiO₂ decrease the amount of H₂ gas. On the other hand, in the three-component mixture of TiO₂, Pt and GS, the amount of H₂ gas was strikingly increased. The results on the particle size distribution and SEM images indicate that the particles of TiO₂, Pt and GS clump together by mixing in suspension. The increment of hydrogen gas was attributed to the additional electron-transfer route of TiO₂ to Pt and then Pt to GS.

Although carbon nanotubes (CNTs) can be metallic in nature [11], so far they have been used mainly as a catalyst support. Eswaramoorthi et al. [12] reported partial oxidation of methanol for hydrogen production over carbon nanotubes-supported Cu-Zn catalysts. CNTs were used as a support to Cu-Zn catalysts for H₂ production. The methanol conversion rate and hydrogen selectivity are found to increase with reaction temperature and Cu loading up to the threshold value (12 wt%). Also, a catalyst composed of 12 wt% Cu-9 wt% Zn / CNTs showed good stability in time-on stream studies with suppressed formation of CO. It was found that the use of CNTs as a support enhanced the reducibility of Cu (from Cu(II) to Cu (0)) species at low temperature which in turn increased the rate of H₂ production. Recently, Yu et al. [13] has reported the effect of carbon nanotubes (CNTs) on the adsorption and the photocatalytic properties of TiO₂ (P25) for the treatment of azo dyes including one monoazo dye. The results show that comparing with AC, CNTs can better improve the adsorption capacity of P25 through the strong interaction between P25 and CNTs. Although the adsorption of the azo dyes onto CNTs fit Freudlich adsorption isotherm, those adsorbed onto the mixture of P25 and CNTs show a Langmuir’s pattern. Meanwhile, the photocatalytic activity of P25 for the degradation of the azo dyes in the presence of CNTs also increases more than that with AC. To date CNTs have not been used as co-catalysts. Previously, we have reported the decomposition of diacids and simultaneous production of H₂ using SWNTs and TiO₂ under UV light irradiation [14]. Here, we report photocatalytic H₂ production from aqueous alcohol solution using simple mixtures of TiO₂.
2.2 EXPERIMENTAL

Materials

The photocatalyst was TiO$_2$ (Degussa P25) with mainly anatase structure (ca. 80%) under the shape of non-porous polyhedral particles of ca. 20 nm mean size with a surface area of ca. 49.9 m$^2$/g. SWNTs and MWNTs with a purity of 20-40% were obtained from Materials Technologies Research Ltd. (USA) and were used without further purification. The SWNTs and MWNTs are “as produced” matrix of amorphous carbon soot that contains traces of C-60, C-70 and higher fullerenes in addition to carbon nanotubes. The nanotubes are of 0.7-1.5 nm in diameter and about 10-30 microns in length. CNFs and FLN were of 98 wt% purity and obtained from Frontier Carbon Co. and Showa Denko Co. (Japan), respectively. Powdered Pt (ca. 50 μm) of 99.98% purity (Nilaco) was used without further treatment. Methanol (Wako) of highest grade available and doubly deionized water were used throughout the experiment.

Photo reactor and Light source

A cylindrical flask (so-called Schlenk’s tube) made of Pyrex of ca. 154 cm$^3$ was used as a photoreactor. The top of the flask was sealed with a silicone rubber septum. A super

Digital picture of Schlenk’s tube and super high-pressure mercury lamp.
high-pressure mercury lamp (Ushio 500W USH-500SC) was used as the light source. For filtration of the light a 300-400 nm band pass filter (Toshiba ATG UV-D33S) was used. Care was taken not to heating up the suspension.

**Procedure and Analysis**

Preferred amounts of TiO$_2$ and SWNTs were put into the flask and then water/alcohol mixtures were added. The photoirradiation was carried out under Ar atmosphere for 1 h, maintaining the reaction mixture in suspension by a magnetic stirrer. Prior to irradiation, the suspension of the catalyst was dispersed in an ultrasonic bath for 5 min and Ar gas was bubbled through reaction mixture for 1 h to remove oxygen gas. Gas sampling was made through the silicon rubber septum using a locking-type syringe at a constant time interval, usually 15 min. The quantitative analysis of gas sample was performed by gas chromatography (column packing: MS5Å or porapak N, carrier gas: Ar, detector: TCD). After photoirradiation, the filtrate solution was analyzed by an ion chromatographic analyzer (IC 7000, Yokogawa) equipped with a recorder (SIS chromatocoder 12). The particle size was measured by a laser scattering particle size distribution analyzer (Horiba LA-920).
2.3 RESULTS

Different series of experiments were carried out in order to compare the amounts of H\textsubscript{2} gas evolved by different compositions of TiO\textsubscript{2} and SWNTs. Fig. 1 shows the dependence of the rate of H\textsubscript{2} gas evolution on the SWNTs content to TiO\textsubscript{2} after 1 h irradiation from 50 vol\% methanol-, ethanol- and 1-propanol-water mixtures. We can see a drastic increase in the amount of evolved H\textsubscript{2} gas when a small amount of SWNTs are added to TiO\textsubscript{2}. This is due to the synergy effect of TiO\textsubscript{2} and SWNTs, which emerges from the high electron conductivity of the latter [15]. With an increase in the amount of SWNTs, the surface area for reduction of H\textsuperscript{+} ion increases. A maximum of H\textsubscript{2} gas generation is found around 7-11 wt\% of the SWNTs content. However, larger amounts of SWNTs will impair the absorption of UV light by TiO\textsubscript{2}. This results in a decrease in the evolution rate of H\textsubscript{2} above ca. 11 wt\% of the SWNTs.

![Fig. 1: Plots of the evolution rate of H\textsubscript{2} or CO\textsubscript{2} gas vs. the SWNTs content to TiO\textsubscript{2} (Total amount of catalyst: 30 mg. Alcohol content: 50 vol\%). H\textsubscript{2} from ○methanol, □ethanol, ◇1-propanol aqueous solution.](image)

There are other members of carbon nano-material, such as MWNTs, CNFs, FLN and they are also known to have good electrical properties [6, 15]. Therefore, similar experiments were performed for the production of H\textsubscript{2} gas using MWNTs or CNFs or FLN and TiO\textsubscript{2}. The amounts of carbon nano-materials were changed from 0 to 100 wt\% and the
maximum rate of H\textsubscript{2} evolution were found at 10, 40, 40, 30 wt\% for SWNTs, MWNTs, CNFs and FLN, respectively. The highest rates of H\textsubscript{2} generation with above amounts of carbon nano-materials are shown in Fig. 2. It is seen that the order of H\textsubscript{2} production is SWNTs>> MWNTs> CNFs> FLN.

![Graph showing evolution rate of H\textsubscript{2} gas](image)

**Fig. 2:** Hydrogen generation curves using various nanomaterials (Total amount of catalyst: 30 mg, Methanol content: 50 vol\%).

The comparison of the photocatalytic activity for the production of H\textsubscript{2} gas between Pt/TiO\textsubscript{2} and SWNTs/TiO\textsubscript{2} mixed powders was made by using equal quantity of Pt and SWNTs (9.1 wt\% each) together with TiO\textsubscript{2}, keeping the methanol content constant at 50 vol\% in the solution. The amount of H\textsubscript{2} gas evolved with irradiation time is shown in Figure 3. The amount of H\textsubscript{2} gas evolved from the both systems are nearly same until 1 h irradiation, although after 1 h the amount of H\textsubscript{2} gas in the Pt/TiO\textsubscript{2} system increases a little over the SWNTs/TiO\textsubscript{2} system.

Mechanically blended SWNTs/TiO\textsubscript{2} composite was also used for H\textsubscript{2} generation. For the preparation of the composite, SWNTs and TiO\textsubscript{2} were weighed in different amounts and blended adequately by smashing with an agate mortar. After 1 h irradiation, the hydrogen evolution rate for smashed powder was considerably higher than that of normal powder as shown in Figure 4. For 9.1 wt\% of normal powder of SWNTs to TiO\textsubscript{2} a hydrogen evolution
rate of about 32 \( \mu \text{mol h}^{-1} \) was observed, whereas the same rate was observed for 5.0 wt\% of SWNTs to TiO$_2$ in the case of smashed mixture. For 9.1 wt\% of smashed SWNTs/TiO$_2$ mixture, the highest evolution rate was found to be about 39 \( \mu \text{mol h}^{-1} \).

**Fig. 3**: Plots of amount of H$_2$ gas vs. irradiation time with SWNTs/TiO$_2$ and Pt/TiO$_2$ systems (Total content is 30 mg. Amounts of SWNT and Pt are 9.09 wt\%). ○ SWNTs/TiO$_2$, □ Pt/TiO$_2$.

**Fig. 4**: Comparison curve for H$_2$ production from smashed and non- Smashed mixtures of TiO$_2$ and SWNTs. ○ Smashed, □ Normal powder.
The “as-received” SWNTs contained many aggregates as seen from SEM photo in Fig 5, which were covered by amorphous carbon and shoot. Due to smashing, the aggregates were broken down and the particle size became smaller resulting in increase in the surface area of the catalyst. This fact could be confirmed from the particle size distribution of the mixture of TiO$_2$ and SWNTs, measured after photoirradiation of the mixtures, and the results are shown in Fig 6. We can see that in case of normal mixtures the particle size was found to be inhomogeneous, ranging from about 10 to 400 $\mu$m with the small surface area. But in the case of smashed mixtures the particle size is homogeneous, ranging from about 10 to 50 $\mu$m with large surface areas.

![Fig. 6: Particle size distribution for the normal and smashed SWNTs /TiO$_2$ powder mixtures. ○Normal mixture □smashed mixture, ◇TiO$_2$ only, +SWNTs only.](image)
2.4 DISCUSSION

In the case of noble metal such as Pt, an electron from photoexcited TiO$_2$ is transferred to Pt and then it reduces H$^+$ ion to produce H$_2$ gas [7]. Depending on the tube helicity and diameter Carbon nanotubes can be can be either semi-conducting, semi-metallic or metallic, in nature [16]. Thus, based on the above results, it is possible to propose a mechanism as schematically shown in Figure 7. Photoexcited electrons in TiO$_2$ are transferred to SWNTs through collisions which are then reducing the proton available in the system.

The detail morphological studies of CNTs /TiO$_2$ have been reported by Yu et al. [17] elsewhere. It was found that CNTs can enhance the photocatalytic activity of TiO$_2$ because the presence of CNTs can prevent the e$^-$/h$^+$ pairs produced by TiO$_2$ under UV light from recombination. That is, electrons excited by TiO$_2$ may easily migrate to the nanostructure of the CNTs because of the strong interaction between TiO$_2$ and CNTs. Meanwhile, CNTs raise the band gap of TiO$_2$, which can make the e$^-$/h$^+$ pairs recombination less likely to occur. Moreover, the abundant hydroxyl groups adsorbed on the large surface of the TiO$_2$/SWNTs can lead to the formation of more *OH radicals. Therefore, through the two aspects, i.e. the decrease of the e$^-$/h$^+$ pairs recombination and more hydroxyl group on the surface of the composites, the photocatalytic activity of TiO$_2$ can be greatly enhanced by the presence of CNTs. On the other hand, Prosini et al. [18] have shown that H$_2$ can be produced on the surface of carbon nanotube through reduction of H$^+$ ion. Therefore, it can be concluded that the higher surface area can not be the only factor for the enhancement of the photocatalytic activity of TiO$_2$ by SWNTs.

Considering this mechanism it is easy to understand that the larger the amount of SWNTs in the mixed catalysts, the larger the possibility of contact and interaction between TiO$_2$ and SWNTs becomes, although excess amounts of SWNT will make the UV absorption by TiO$_2$ impair as described above. Thus, more electrons migrating to SWNTs mainly via collision reduce more H$^+$ ions, which is consistent with the result shown in Fig. 1.
This fact can further be confirmed by changing the collision rate between TiO$_2$ and SWNTs. When the mixture of TiO$_2$ and SWNTs was not stirred, H$_2$ gas evolution was very small. Moreover, with the increase in the speed of the stirrer, the amount of H$_2$ gas evolved was increased up to a limit. The appearance of a maximum H$_2$ yield at a relatively lower SWNTs content (9.1 wt%, considering the purity of SWNTs to be 30%) is due to that the specific surface area of TiO$_2$ is 49.9 m$^2$ g$^{-1}$ [10], whereas that of as-grown SWNTs ranges from 400 to 900 m$^2$ g$^{-1}$ [6]. Thus higher loading of TiO$_2$ is required to come into contact more efficiently with the SWNTs surfaces.

On the solid surface with a net positive charge, the adsorption of polar alcohol molecule will be via the negatively charged end (–OH). The hydrogen abstraction rates of different alcohol molecules are related to their adsorption ability on the solid surface, the rupture energy of the α-C–H bond and steric factors (19). The dipole moment of various alcohols are: MeOH (1.70) > EtOH (1.69) > n-PrOH (1.68) [20]. Therefore it can be predicted that MeOH are more strongly adsorbed on TiO$_2$ than EtOH or n-PrOH.

For the Pt/TiO$_2$ or Pt/CdS systems the order of H$_2$ evolution from various alcohols is methanol > ethanol > 1-propanol (19, 20). The rupture energy of α-C–H bond of EtOH is a
little smaller than that of MeOH that causes the above order. But in case of TiO$_2$/ SWNT the order is different as seen from Fig. 1. The reason for such order can be explainable in the following ways: (a) May be in this system the steric factor of alcohol molecules becomes more important that the future energy of $\alpha$-C–H. Due to the small size of MeOH, it can move faster and reach the surface of TiO$_2$ more easily conquering the blockade caused by carbon nanotube and amorphous carbon. Therefore, oxidation process is higher in case of MeOH leading a little higher amount of H$_2$ evolution compared to ethanol. (b) As the number of carbon atoms increases, the non-ionic property of the alcohols increases in the order of 1-propanol > ethanol > methanol. Increasing non-ionic property shows higher affinity towards carbon nanotube and amorphous carbon. For example, Liu et al. [21] shows 90% and 88% recovery of 2-propanol and ethanol, respectively by SWNT. This fact may cause the decreasing of H$_2$ evolution in two ways: (1) increasing attraction of non-ionic SWNTs and amorphous carbon to more non-ionic ethanol and 1-propanol, brings less chance for hydrogen ion to come into contact with the surface of SWNTs resulting the decrease in reduced H$^+$ ions. (2) For the same increasing attraction of alcohol molecules towards SWNTs may cause for insufficient amount of alcohol molecules required for oxidation by holes over the TiO$_2$ surface. The steric and long carbon chain effect can be further confirmed from our previous report where it was found that oxalic acid gives higher H$_2$ evolution than fumaric acid [14]. The present order is consistent with the order of H$_2$ production from various alcohols using TiO$_2$/GS reported by Ikeda et al [22].

However, it was found that in the absence of alcohol, the H$_2$ production was negligible. It is known that Na$_2$SO$_3$ is a good sacrificial agent. But with a similar concentration of Na$_2$SO$_3$ (0.1M) and methanol (0.1M), the rate of H$_2$ production was found to be 0.15 and 5.5 $\mu$molh$^{-1}$, respectively. From this result it can be concluded that H abstraction for the evolution of H$_2$ gas takes place mainly from alcohol molecule.
Although MWNTs have also a larger surface area ranging from 200 to 400 m$^2$g$^{-1}$ [6], it showed a lower effect on the photocatalytic activity of TiO$_2$ than SWNTs did (in Fig. 2). It was found that the rolling direction of simple graphite sheet has a large effect on the electrostatic characteristics of tubes and the presence of defects (other than hexagon) on the tube also affects its electric conductivity considerably [11]. The structures of MWNTs are complex. It is commonly known that there are some defects on the surfaces of the tubes and the direction of the rolled graphite sheets is not controlled [6]. These complexities may affect the photocatalytic effect of MWNTs on TiO$_2$. CNFs have a large surface area but their electrical properties are different from that of SWNTs and MWNTs. Compare to CNFs, FLN has good electrical properties, but it has low surface area (176 gm-1) [23]. It is known that for the enhanced activity of a catalyst, both the surface area and electrical properties of a co-catalyst are important factors.

It is known that Pt itself acts as light reflector and thus can remarkably improve the photocatalytic efficiency [24]. The lower H$_2$ production (Fig. 3) by SWNTs/TiO$_2$ partly attributable to H$_2$ adsorption, due to pressure increase in the gas phase, to carbon nanotubes and amorphous carbon present in SWNTs used [25]. This amorphous carbon contains graphitic carbon and soot that are unavoidable byproducts of the synthesis processes. These impurities also could decrease the amount of hydrogen generation by hindering light absorption of TiO$_2$ photocatalyst. Another impurity in CNTs is metal particle which is used as catalyst during their synthesis process. For the determination of catalytic effect of this amorphous carbon and Ni investigation was carried out with the mixture of TiO$_2$ with active carbon (AC) and graphitic carbon (GC) or Ni. After 1 h irradiation, the amount of H$_2$ gas evolved from the mixtures of TiO$_2$/AC/GC and also TiO$_2$/Ni were 0.45 μmol h$^{-1}$ and 7.6 μmol h$^{-1}$, respectively. The amount of H$_2$ evolution from the TiO$_2$/SWNTs system is 5 times higher that that from the TiO$_2$/Ni system.).

The mechanism for the decomposition of water was suggested by Calvin et al. [26] and
it has also been reported that CH$_3$OH is oxidized to HCHO [27], HCHO to HCO$_2$H, and HCO$_2$H to CO$_2$ on a single crystal TiO$_2$ or ZnO photoanode by a current-doubling process. Since the TiO$_2$ powder can be regarded as a photoelectrochemical microcell, holes generated by the light would oxidize CH$_3$OH, HCHO and HCO$_2$H eventually to produce CO$_2$ [7].

\[
\text{CH}_3\text{OH} \xrightarrow{h\nu, \text{cat.}} \text{HCHO} + \text{H}_2
\]

\[
\text{HCHO} + \text{H}_2\text{O} \xrightarrow{h\nu, \text{cat.}} \text{HCO}_2\text{H} + \text{H}_2
\]

\[
\text{HCO}_2\text{H} \xrightarrow{h\nu, \text{cat.}} \text{CO}_2 + \text{H}_2
\]

In order to confirm the reaction mechanism, the filtrates after the reactions were analyzed. Formic acid and acetic acid (data not shown) were detected in the reaction mixtures of water and various alcohols by ion chromatography. Also a small amount of CO$_2$ was observed after 2 h irradiation. Observed results corresponded to the proposed mechanism.

A noticeable result is seen from the position of the particle size distribution curve in Fig. 6 for SWNTs/TiO$_2$ mixture, TiO$_2$ only and SWNTs only. The particle diameters range 1~10, 10~900 and 10~450 nm for TiO$_2$, SWNTs and SWNTs/TiO$_2$, respectively. But in the mixture of TiO$_2$ and SWNTs, the particle diameter of TiO$_2$ and SWNTs are shifted to the right and left, respectively. From the shift of TiO$_2$ it can be considered that in the mixture the particles of TiO$_2$ are adsorbed on the surface of SWNTs and that of SWNTs it can be consider that the aggregates of SWNTs are partly broken in presence of TiO$_2$. The reason of such effect is not clear yet. But this observation concludes that electron transfer can take place not only during collision between TiO$_2$ and SWNTs but also by the deposition of TiO$_2$ on SWNTs. Due to smashing of the mixture the deposition of TiO$_2$ over SWNTs is higher and thus easier transfer of electron is also higher resulting higher H$_2$ gas evolution.

2.5 CONCLUSION

We have shown that under UV light irradiation, the addition of SWNTs to TiO$_2$ induces a
substantial synergy effect. Deposition of TiO$_2$ on SWNTs surface was expected to give better H$_2$ gas evolution. Therefore, steps were taken for such experiments; unfortunately the result was not as predicted. During the preparation of composite functionalization on the surface of SWNTs is an unavoidable step which may break the hexagon structure of their surface. This functionalization process may lead in a change of their electrical properties giving poor H$_2$ production with TiO$_2$. Other method of composite preparation that does not break the structure of the surface of SWNTs, is under investigation in our laboratory. Moreover, comprehensive studies are underway in our laboratory to further reveal the mechanism for the synergy effect of SWNTs enhancing the photocatalytic activity of TiO$_2$.

References
CHAPTER 3

PHOTOCATALYTIC HYDROGEN PRODUCTION FROM DIACIDS AND THEIR DECOMPOSITION OVER MIXTURE OF TiO$_2$ AND SINGLE WALLED CARBON NANTUBES

3.1 INTRODUCTION

Unique chemistry of semiconductor photocatalysts is being extensively used for a variety of applications. On the other hand, a new and renewable source of energy has been the dreams for generations of scientists and remains as the goal of researchers in the 21$^{\text{st}}$ century. In both these applications, TiO$_2$ has drawn much attention over the last few years resulting in hundreds of article and many reviews related to photocatalytic cleaning of water [1,2] and hydrogen production from water [3,4].

The electronic structure of TiO$_2$ plays a key role in semiconductor photocatalysis. The reaction is initiated by the photoexcitation of TiO$_2$ particles, which leads to the formation of electron($e_{cb}$) - hole($h_{vb}$) pairs

$$\text{TiO}_2 \xrightarrow{h\nu} \text{TiO}_2 (e^{-}_{cb} + h^{+}_{vb})$$

Electrons and holes that migrate to the surface of the semiconductor without recombination can, respectively, reduce and oxidize the reactant adsorbed by the semiconductor. The reduction and oxidation reaction are the basic mechanisms of photocatalytic H$_2$ production and photocatalytic water / air purification, respectively.

In photocatalytic water / air purification, valence band (VB) holes are the key elements that induce decomposition of contaminants. On the other hand, when photocatalysis is applied to perform water-splitting for production of H$_2$, the reducing CB electrons become important as their role is to reduce protons to hydrogen molecules [4]. In order to achieve higher efficiency for photocatalytic water splitting or water / air purification, many
investigators in this field have involved addition of noble metal such as Pt, Cu, and Ag etc. SWNTs have unique electronic and physical properties. In our previous work, we reported a drastic effect of SWNTs on photocatalytic activity of TiO$_2$ in terms of H$_2$ production from water-alcohol mixtures [5]. Another approach for the enhancement of photocatalytic H$_2$ production from water is involvement of an electron donor as sacrificial agents. But, if the sacrificial donors are expensive, the use of electron donor is clearly not of interest. One good way is to use organic wastes and pollutants in water in this role. It is of more interest to combine photocatalytic H$_2$ generation with destruction of pollutants [6].

Photocatalytic decomposition of pollutants and photocatalytic production of clean H$_2$ fuel can take place simultaneously when the pollutants act as electron donors. Li et al. [7] reported enhanced photocatalytic hydrogen production in single component systems and mixture systems of pollutants (oxalic acid, formic and and formaldehyde) acting as an electron donor. Decomposition of electron donors was reported to be consistent with hydrogen production. Furthermore, unlike a single component system, a mixture system involved competition of adsorption on the photocatalyst surface. Li et al. [6] reported photocatalytic hydrogen generation and decomposition of oxalic acid over platinized TiO$_2$. They also reported the effect of some inorganic anions that are commonly found in industrial wastewater, on photocatalytic hydrogen generation from aqueous oxalic acid solution. Despite the limited work on using pollutants as electron donors, the encouraging results show the promise of the integration of pollutant decomposition and hydrogen production.

In this paper we report the photocatalytic degradation of oxalic acid and fumaric acid for the production of hydrogen by using TiO$_2$ and SWNTs mixtures. We chose oxalic acid and fumaric acid as model organic compounds. The aliphatic intermediates most frequently encountered during the degradation of aromatic compounds are short-chain carboxylic diacids such as maleic, fumaric and oxalic acids. Moreover, oxalic acid is highly found in
industrial wastewater and it has strong oxidizing ability [8, 9]. Their decomposition is thus important in the mineralization of a wide variety of pollutants.

3.2 EXPERIMENTAL

a. Materials

The photocatalyst was TiO$_2$ (Degussa P25) with mainly anatase structure (ca. 80%) under the shape of non-porous polyhedral particles of ca 20 nm mean size with a surface area of ca. 50 m$^2$/g. Single walled carbon nanotubes (SWNTs) with a purity of 20-40% was obtained from Materials Technologies Research (MTR Ltd, USA). The SWNTs are “as produced” matrix containing amorphous carbon soot that in turn contains traces of C-60, C-70 and higher fullerenes in addition to SWNTs. The cylindrical tubes are of 0.7-1.2 nm in diameter and about 10-30 μm in length. Oxalic acid of 99.8% (Wako), fumaric acid (Nacalai Tesque Inc.), NaoH of 95% (Wako), KNO$_3$ of 99.9% (Wako), KCl of 99% (Nacalai Tesque Inc.), Na$_2$SO$_4$ of 99% (Wako), KH$_2$PO$_4$ 99% (Wako) and doubly deionized water were used throughout the experiment.

b. Photoreactor and light source

A cylindrical flask (so-called Schlenk’s tube) of ca. 155 cm$^3$ was used as a photoreactor. The top of the flask was sealed with a silicone rubber septum. A super high-pressure mercury lamp (Ushio 500W USH-500SC) was used as the light source. For filtration of the light a 300-400 nm-pass filter (ATG UV-D33S) was used. Care was taken not to heat up the suspension. A pH meter (Horiba, D-51) was used for the measurement of pH of the solution.

c. Procedure and analysis

Preferred concentrations of aqueous solution (20 cm$^3$) of acids were taken into the tube. Mixtures of TiO$_2$-SWNTs of chosen amount in wt% were smashed for 15 min and dispersed
into the acid solution in an ultrasonic bath for 1 min. The photoirradiation was carried out under an Ar atmosphere for 1-4 h, maintaining the reaction mixture in suspension by a magnetic stirrer. Prior to irradiation Ar gas was bubbled through the reaction mixture for 1 h to remove oxygen gas. The number of Ar bubbles was about 10 per second. Gas sampling was performed through the silicon rubber septum using a locking-type syringe at a constant time interval, usually 15 min. Quantitative analysis of gas sample was performed by gas chromatography (column packing: MS5 or Porapak N, carrier gas : Ar, Detector: TCD). Aqueous solutions of preferred concentrations of Na$_2$SO$_4$, KCl, KNO$_3$ and KH$_2$PO$_4$ were added to observe the effect of inorganic anions and NaOH was added to the acid solution in pH controlled experiments.

3.3 RESULTS AND DISCUSSION

The effects of the presence of sacrificial agents, TiO$_2$ and SWNTs are summarized in Table 1. We can see in Table 1 that the presence of a sacrificial agent is necessary for the hydrogen production from wastewater. It is also clear that presence of SWNTs in the system markedly enhances the photocatalytic efficiency of TiO$_2$. This result suggests that oxalic acid is an efficient electron donor to promote the reaction effectively and SWNTs are a good catalyst for hydrogen production.

Table 1: Comparison of effects of diacids and SWNTs on the reaction rate.

<table>
<thead>
<tr>
<th>Acids’ names</th>
<th>Photocatalyst$^{1)}$</th>
<th>Initial concentration of acids (mM$^2)$</th>
<th>Rate of hydrogen evolution (μmol h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>TiO$_2$-SWNTs</td>
<td>0 (Only water)</td>
<td>0.2</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>TiO$_2$-SWNTs</td>
<td>1.0</td>
<td>10.0</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$ only</td>
<td>1.0</td>
<td>Trace</td>
</tr>
<tr>
<td>Fumaric acid</td>
<td>TiO$_2$-SWNTs</td>
<td>1.0</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$ only</td>
<td>1.0</td>
<td>Trace</td>
</tr>
</tbody>
</table>

$^{1)}$ Photocatalyst: 30 mg. $^{2)}$ mM=10$^{-3}$ mol dm$^{-3}$
a. Effect of concentration of acids

Figure 1 shows the effect of concentrations of oxalic acid and fumaric acid on the rate of hydrogen generation. The curves of the plot are attributed to progressive consumption of oxalic acid and fumaric acid in the reactions. Because the concentrations of pollutants vary continuously in the reaction, in order to determine the initial reaction rate, the reaction time interval should be as short as possible. However, it is important that enough change of reactant or product can be determined during the time interval. Therefore, the initial reaction rate determined in the first 30 min was used in the investigation. The rate was found to vary as a function of initial concentrations of acids ($C_0$) according to Langmuir-type isotherm so that it is almost independent of $C_0$ for $C_0>2.0$ mM and decreases sharply for $C_0<0.75$ mM. This result is consistent with the adsorption isotherm of oxalic acid and fumaric acid on TiO$_2$ [10,11] and the rate of H$_2$ gas evolution can be expressed as

$$ r = \frac{dC_{H_2}}{dt} = \frac{kK C_0}{1 + KC_0} $$

where $r$, $k$, $K$ represent the initial reaction rate of the hydrogen generation, the reaction rate constant, and the adsorption equilibrium constant of acids, respectively. $C_{H_2}$ stands for the amount of hydrogen gas. Based on the linear transform of the curve of Fig 1, we can
obtain the slope \((kK)^{-1}\) and intercept \((k)^{-1}\) which yield \(k_1 = 0.5 \times 10^{-7} \text{ mol dm}^{-3} \text{ min}^{-1}\) and \(K_1 = 5.5 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}\) for fumaric acid and \(k_2 = 2.2 \times 10^{-7} \text{ mol dm}^{-3} \text{ min}^{-1}\) and \(K_2 = 6.0 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}\) for oxalic acid. The reaction rate constant \((k_1)\) for oxalic acid is ca. 4 times as large as that \((k_2)\) for fumaric acid.

**Fig. 2:** SEM picture of “as-received” single walled carbon nanotubes with purity of 20-40%.

**b. Effect of content of SWNTs**

For practical application of photocatalytic hydrogen production, it is important for catalysts to have optimum activity. An adequate amount of SWNTs and TiO\(_2\) can give the optimum hydrogen production. It should be noted that the purity of “as-received” SWNTs

**Fig. 3:** Rate of \(\text{H}_2\) gas evolution as a function of SWNTs net content with TiO\(_2\). Acid concentration: 2.0 mM.
were very low (20-40%) and was used without further purification. The SEM image of SWNTs is shown in Figure 2. A small number of rope-like SWNTs are seen together with a large amount of amorphous carbon. To examine the effect of this large amount of amorphous carbon, another experiment was also performed. The results showed that the amorphous carbon has negligible effect on H₂ production. Fig 3 shows the dependence of the hydrogen production on the net content of SWNTs in the mixture. It can be seen that with the increasing amount of SWNTs content, the hydrogen evolution increases and then decreases for both oxalic and fumaric acid solutions.

The highest peaks in the hydrogen evolution are found at 7 and 5 wt% of SWNTs contents for oxalic acid and fumaric acid, respectively. In the plausible mechanism, as described previously [5], it was proposed that photoexcited electrons are transferred to highly electron-conductive SWNTs by collision and then H⁺ ions on the surface of SWNTs are reduced to give H₂. On the other hand, holes in TiO₂ can decompose oxalic and fumaric acids by oxidation. Thus, it is easy to understand that larger the amount of SWNTs in the mixture, the larger the possibility of contact and interaction between TiO₂ and SWNTs. Thus, more electrons migrating to SWNTs reduce the more H⁺ ions as shown in the mechanism [5]. However, the amount of SWNTs cannot be too much due to the reduction of UV light absorption by TiO₂ in the presence of a large amount of SWNTs. Appearance of maximum H₂ yield at relatively lower SWNTs contents (around 5-7 wt%) is due to that the specific surface area of TiO₂ (P25) is 50 m² g⁻¹ whereas that of as-grown SWNTs ranges from 400 to 900 m² g⁻¹ [12]. Thus, higher loading of TiO₂ is required to come into contact with the maximum number of TiO₂ on the SWNTs surface.

c. Effect of pH effect

The pH values of the oxalic and fumaric acid solutions were varied from 2.5 (pure oxalic acid) or 2.55 (pure fumaric acid) to 9.5 (by addition of NaOH). It was found that addition of SWNTs to the mixture did not change the value of pH of the solution. It is seen
from the Figure 4 that photocatalytic activity reached a maximum value around pH 3 and 4 for oxalic acid and fumaric acid, respectively and reaches almost zero at pH 6.5. The pH value

![Graph showing the rate of H₂ gas evolution as a function of pH for oxalic and fumaric acid](image)

**Fig. 4:** Rate of H₂ gas production as a function of different initial pH values of oxalic and fumaric acid solutions. Reaction conditions: acid concentration 2.0 mM; 7 and 5 wt% of SWNTs for oxalic and fumaric acid, respectively.

at a zero point charge (pHzpc) of TiO₂ is 6.25 [13] i.e., till this value the surface of TiO₂ is negatively charged. Thus, repulsion between the surfaces of TiO₂ and oxalate or fumarate ion takes place, resulting in lower H₂ production. For oxalic acid a highest value is observed around pH 3. Draganic et al. [14] have shown that, for the reaction between the radical *OH and three forms of oxalic acid, the reactivity decreases in the order of HC₂O₄⁻ > C₂O₄²⁻ >> H₂C₂O₄. The reaction between *OH and HC₂O₄⁻ is six times as fast as the corresponding reaction with C₂O₄²⁻, which explains the higher rate of hydrogen evolution between pH 3 and 4, where HC₂O₄⁻ is the predominant species of oxalic acid.

d. **Effect of inorganic anions**

Inorganic anions such as Cl⁻, NO₃⁻, SO₄²⁻ and H₂PO₄⁻ are frequently found in industrial wastewater and are likely to retard the rates of oxidation of oxalic acid or fumaric
acid by competing with the active sites of the photocatalyst. Figure 5 and 6 show the effect of some common inorganic anions, Cl\(^{-}\), NO\(_3\)^\(-\), SO\(_4\)^{2-} and H\(_2\)PO\(_4\)^\(-\) on photocatalytic H\(_2\) generation from oxalic and fumaric acid, respectively. For both acid solutions, Cl\(^{-}\) and NO\(_3\)^\(-\) have no effect on H\(_2\) production when acid and anion concentrations were same. Even on doubling the concentration of anions no effect was observed.

NO\(_3\)^\(-\) is adsorbed on TiO\(_2\) more weakly, and it cannot compete with oxalic acid even if its concentration is higher than that of oxalic acid [15]. According to the electrostatic model, Cl\(^{-}\) can only be adsorbed weakly on TiO\(_2\) like NO\(_3\)^\(-\). Oxalic acid or fumaric acid is bidentate ligands, which can form a chelate on TiO\(_2\) [16]; hence oxalic acid or fumaric acid can be more strongly adsorbed on TiO\(_2\) than these anions.

Both SO\(_4\)^{2-} and H\(_2\)PO\(_4\)^\(-\) can be strongly adsorbed on TiO\(_2\) [17] to block the adsorption of oxalate or fumarate. The adsorption of H\(_2\)PO\(_4\)^\(-\) on TiO\(_2\) shows no pure ionic interaction as evidenced by IR spectroscopy [18], which demonstrates that the interaction between them exists as a partly covalent bond. Thus in the presence of SO\(_4\)^{2-} and H\(_2\)PO\(_4\)^\(-\), the rate of H\(_2\) gas generation decreases about 50\% and 75\%, respectively.
When catalytic semiconductor powders, such as TiO$_2$, are suspended in water and irradiated with UV light below $\lambda<385$ nm, free hydroxyl $^\cdot$OH radicals are generated.

$$\text{TiO}_2(h^+) + \text{H}_2\text{O} \rightarrow \text{TiO}_2 + ^\cdot\text{OH} + \text{H}^+$$

The $^\cdot$OH radicals are highly active for the oxidation of organic substances [19].

**Fig. 6:** Plots of amount of H$_2$ gas versus irradiation time in the presence of various inorganic anions. Reaction conditions: fumaric acid concentration 2.0 mM, SWNTs 5 wt%.

Figure 7 and 8 show the relation between the amounts of H$_2$ and CO$_2$ gas evolved respectively from oxalic acid and fumaric acid solutions under 3h UV irradiation. With the increase in the amount of H$_2$ gas, CO$_2$ gas evolution was also proportionally increased. The decomposition reaction of oxalic acid can be shown as

$$\text{H}_2\text{C}_2\text{O}_4 \rightarrow_{\text{hv}, \text{SWNTs-TiO}_2} \text{H}_2 + 2\text{CO}_2$$

Thus it can be concluded that the amount of H$_2$ formed is stoichiometrically ([H$_2$]:[CO$_2$]=1:2) consistent with the amount of oxalic acid decomposed within the experimental error. As can be seen from Figure 6(b), however, the CO$_2$ evolved is much higher than the H$_2$ gas evolved from fumaric acid. Oxalic acid is a two-carbon acid and fumaric acid is a four-carbon acid. Degradation of oxalic acid involves the reaction with holes or $^\cdot$OH radicals releasing two moles of CO$_2$. But Franch et al. [11] reported about 10
Fig. 7: Plots of amounts of H$_2$ and CO$_2$ gas evolved from aqueous solution of oxalic acid.

Intermediate compounds including oxalic acid during the degradation pathway of maleic and fumaric acids and some of these steps involve the reaction with holes or *OH radicals as well as H$^+$ abstraction releasing CO$_2$. This duel effect may be responsible for the unusually low H$_2$ evolution with respect to the unusually high amount of CO$_2$.

Fig. 8: Plots of amounts of H$_2$ and CO$_2$ gas evolved from aqueous solution of fumaric acid versus irradiation time.

3.4 CONCLUSION

Photocatalytic degradation of organic acids and simultaneous production of H$_2$ gas can
be carried out efficiently over TiO$_2$ and SWNTs mixtures even though the purity of SWNTs is very low. The adsorption isotherms of both acids were found to follow the Langmuir-type isotherm. NO$_3^-$ and Cl$^-$ have no effect on photocatalytic H$_2$ production, whereas SO$_4^{2-}$ and H$_2$PO$_4^-$ decrease the rate markedly. The simultaneous degradation of oxalic acid and H$_2$ production are stoichiometrically successful. On the other hand, the degradation of fumaric acid is possible over SWNTs and TiO$_2$ mixtures, but the simultaneous H$_2$ production seems to be comparatively insufficient.

References
CHAPTER 4

PHOPHYSICAL AND PHOTOCHEMICAL STUDIES OF
CHOLOROPHYLL α AND COBALT(II)TETRAPHENYLPOPHYRIN
IN POLY(L-GLUTAMATE)-DECYLAMMONIUM ION FOLLOWED
BY HYDROGEN PRODUCTION UNDER VISIBLE LIGHT

4.1. INTRODUCTION

Porphyrrins belong to a class of cyclic tetrapyrrole compounds that play a vital role in
nature. This is exemplified by the layered thylakoid membranes of chloroplast which
contain chlorophyll molecules bound to proteins to form chlorophyll–protein complexes.
Here, chlorophyll–protein complexes play a central role in the stabilization and
physiological functions of the chloroplast [1–5]. In addition, the biological importance of
vitamin B$_{12}$ has prompted many investigations on the catalytic efficiency of square planar
cobalt porphyrin species [6, 7]. The role of porphyrin is not limited to biological systems,
but includes various fields of science (physics, chemistry, geology and medicine).
Porphyrrins generally have intense $\pi-\pi^*$ absorption bands in the visible region [8]. This
unique property of porphyrins is exploited in the construction of artificial photosynthetic
models and in systems that convert solar light to chemical energy [1, 9].

The conversion of solar energy to chemical energy generally needs porphyrins as well as
suitable catalysts. However, biofunctional molecules such as porphyrins are insoluble in
water or aggregate in aqueous solutions [10, 11]. A number of techniques have been devised
in order to solubilize insoluble porphyrins and also to enhance electron-and/or
energy-transfer reactions between porphyrins and acceptors [10, 12]. Among these
techniques is the use of polymer–surfactant complexes to solubilize dye or porphyrin
molecules [12–14]. This solubilization takes place as a result of the formation of
hydrophobic domains in the polymer–surfactant complex, in which the dye or porphyrin can
reside [12]. The solubilization of chlorophyll α (Chl) into copolypeptide–surfactant complexes has been reported [13–16]. This solubilization leads to the concentration of Chl in the copolypeptide–surfactant complex.

It was also reported previously the photoinduced hydrogen production using cobalt(II)tetraphenylporphyrin (CoTPP) and Chl in a poly(L-glutamate) (Poly(Glu))–decylammonium chloride (DeAC) complex [17,18]. However, the detailed spectroscopic characteristics of the systems were not given in the foregoing studies. In connection with polypeptide–surfactant complexes, it is of interest to investigate in detail the behavior of Chl and CoTPP in the Poly(Glu)–DeAC complexes and also the possible photochemical reaction that may occur in these complexes. The spectroscopic characterization of chlorophyll α and cobalt(II)-tetraphenylporphyrin in a complex system formed between a homopolypeptide, poly(L-glutamate) (Poly(Glu)) which carries a negative charge and a cationic decylammonium (DeAC) chloride surfactant and application of the above systems for H₂ production are reported here. The cooperative binding occurred between the anionic Poly(Glu) and the cationic DeAC, leading to the formation of micelle-like hydrophobic clusters of DeAC and also a change in the conformation of the Poly(Glu) from the random coil to the α-helix. The absorption and fluorescence measurements indicated the existence of equilibrium between the aggregate biofunctional molecules in the bulk phase and the monomeric species in the complex phase of the Poly(Glu)–DeAC system. The fluorescence quenching of the biofunctional molecules by methylviologen (MV²⁺) indicated that the conformation-dependent electron transfer occurred in the Poly(Glu)–DeAC complex system.

4. 2. EXPERIMENTAL

a. General

Chlorophyll α (Chl) from Chlorella, cobalt(II)tetrphenylporphyrin (CoTPP) (Wako,
Osaka, Japan, 99%) and methylviologen (MV$^{2+}$) (Sigma, Kawasaki, Japan, 99%) were used as received. Poly(L-glutamate) (Poly(Glu)) (Peptide Institute, Minoh, Osaka, Japan, molecular weight = 8000) was dissolved in 0.06 M (1 M = 1 mol dm$^{-3}$) NaOH and dialyzed against redistilled water. The concentration of the Poly(Glu) was determined by colloid titration with standard potassium poly(vinyl sulfate) solution [19]. Decylammonium chloride (DeAC) was prepared by titration of decylamine (Nacalai Tesque, Kyoto, Japan, 99%) with hydrochloric acid [20, 21]. The resultant salt was recrystallized twice from ethanol and washed with ethyl ether. Benzene (Wako, Osaka, Japan, 99.8%), ethanol (Wako, Osaka, Japan, 99.5%), 2-methyl-2-propanol (Wako, Osaka, Japan, 99%), acetone (Dotite, Kumamoto, Japan, 99%) were used as received. Laboratory deionized water was distilled twice and used throughout the experiment.

b. **Preparation of the samples for spectroscopic measurements**

Stock solutions of Chl and CoTPP contained in the Poly(Glu)–DeAC complexes and also in the presence of MV$^{2+}$(in some cases) were prepared to give concentrations of 1×10$^{-4}$ M and 1×10$^{-5}$ M for the Poly(Glu) and Chl or CoTPP, respectively, through out the experiment. An aliquot of CoTPP (in benzene) introduced in a 10 mL volumetric flask was dried with nitrogen gas and redissolved in 100 µL of acetone, whereas that of Chl (in ether) was added to 100 µL 2-methyl-2-propanol in a similar flask and the ether was removed by drying with nitrogen gas. To each of the sample solution, Poly(Glu), DeAC and MV$^{2+}$ (fluorescence quenching samples only) were added and the flask was filled to the marked line with redistilled water. The resultant mixture was sonicated for 10 min. The pH of solutions was not controlled but was found to be about 6.5. It is well known that the pheophytinization and allomerization of chlorophylls occur in acidic and basic homogeneous solutions, respectively [22]. Here it should be noted that Chl was stable and did not undergo the pheophytinization or allomerization.
c. Spectroscopic measurements

Circular dichroism (CD) spectra were measured with a JASCO (Hachioji, Tokyo, Japan) J-720 spectropolarimeter and digitized data were transferred to a microcomputer and processed. Absorption and Fourier transformed infrared (FT-IR) spectra were recorded on a Shimadzu (Kyoto, Japan) MPS-2000 and a Perkin–Elmer (Yokohama, Japan) FT-IR spectrophotometer (Spectrum one–B), respectively. Steady-state fluorescence spectra were recorded on a Shimadzu (Kyoto, Japan) RF-5000 spectrofluorophotometer (excitation wavelength: 420 nm for CoTPP and 435 nm for Chl). Relative fluorescence quantum yields of CoTPP were determined indirectly using Chl in ethanol (quantum yield = 0.3) as the reference [23, 24]. Fluorescence lifetime(s) measurements were carried out with a Horiba (Kyoto, Japan) NAES 1100 time-resolved spectrofluorometer that employs a time-correlated single photon counting technique. All measurements were carried out at about 25°C.

4. 3. RESULTS AND DISCUSSION

i. Conformation of Poly(Glu) in aqueous DeAC

Fig. 1a shows the CD spectra of Poly(Glu) in the 190–250 nm region, in the presence of increasing concentrations of DeAC. In the absence of DeAC (spectrum A of Fig. 1a), a small positive band at 217 nm and a strong negative band around 196 nm which are typical of random coil Poly(Glu) are observed. With increasing [DeAC], the CD spectra adopt a double minimum at 222 nm and 209 nm (spectra E and F of Fig. 1a) which is typical of [DeAC] of Poly(Glu) in aqueous DeAC solution α-helix.

The [DeAC] dependence of the molar ellipticities at 222 nm ([θ]222) is shown in Fig. 1b. A decrease in ([θ]222) can be observed as the concentration of DeAC increases. This observation indicates the electrostatic attraction between the anionic Poly(Glu) and cationic DeAC, resulting in the change in the conformation of the Poly(Glu) from the random coil to the α-helix. The change in the conformation occurs at a low concentration of DeAC which is
much below its critical micelle concentration (cmc = 67 mM) [25], indicating a highly cooperative binding between the anionic Poly(Glu) and the cationic DeAC. The addition of Chl or CoTPP to these solutions did not lead to any significant change in the CD spectra; however, some small perturbations associated with insoluble particles of the porphyrin occurred. Satake et al. [20] also reported a similar change in the conformation of Poly(Glu) in aqueous DeAC solutions. In Fig. 1a, an isosbestic point can also be observed around 205 nm, which indicates the one-step transition from the random coil to the \( \alpha \)-helix. FT-IR spectra were also measured to characterize the present systems in detail. FT-IR spectra of the Poly(Glu) were obtained in aqueous DeAC solution. We paid attention to the alkyl chain of DeAC in the 2850–3000 cm\(^{-1}\) region. The peaks in this region are assigned to the C–H symmetric and C–H asymmetric vibrations [26].

Fig. 2 shows the [DeAC] dependence of the C–H symmetric stretching band as well as the asymmetric one. A downshift in the IR frequency was observed above [DeAC] = 0.3 mM, indicating the transformation of the alkyl chain from a less extended form (liquid-like) to a more extended form (solid-like). The concentration of DeAC at which this transformation occurs coincides with that at which a conformation change is indicated from
the CD spectra. This downshift in the C–H stretching mode confirms a highly cooperative binding between the Poly-(Glu) and DeAC.

**ii. CoTPP/Poly(Glu)–DeAC complex**

The absorption spectra of CoTPP consist of a broad Soret band around 400 nm and a weak Q-band around 530 nm, respectively (Fig. 3). The broad Soret band may indicate the presence of aggregated as well as monomeric porphyrins in the Poly(Glu)–DeAC complex. A similar absorption pattern has been observed for the interaction of Ru(bpy)$_3^{2+}$ with sodium hectorite and sodium montmorillonite clay materials [27]. The second derivative absorption spectrum (data not shown) of this system indicated that the Soret band was made up of a combination of two peaks with maxima at 400 nm and 420 nm, respectively. The additional peak at 420 nm may be attributed to the interaction between the hydrophobic clusters of DeAC and the macrocycle ring of CoTPP. To confirm this fact, the absorption spectra of CoTPP in aqueous DeAC (0.4 mM) in the absence of Poly(Glu) were measured. A similar spectral pattern to that of the CoTPP/Poly(Glu)–DeAC complex systems was obtained, confirming the interaction of CoTPP with the hydrophobic tails of DeAC. However, the absorbance was very low compared to the absorbance of CoTPP in the Poly(Glu)–DeAC complex.

The fluorescence spectra of CoTPP in the Poly(Glu)–DeAC complex system consisted of a band around 620 nm. Correcting for changes in absorption cross section, we could obtain the fluorescence quantum yield of CoTPP in Fig. 4. Upon addition of DeAC, the fluorescence quantum yield (excited at 420 nm) was found to increase with increasing concentration of DeAC. The quantum yield of CoTPP is also larger in the Poly(Glu)–DeAC complex than in the colloidal DeAC solution. The increase in fluorescence quantum yields suggests the existence of monomeric CoTPP in the Poly(Glu)–DeAC complex and that of aggregated CoTPP in the colloidal DeAC solution. The excited state lifetimes of porphyrins play a decisive role in the efficiency of
photosensitization reactions. To obtain insight into the solubilization of CoTPP in polypeptide–DeAC complexes, we observed the fluorescence decay curves of CoTPP in the Poly(Glu)–DeAC complex solution. It turned out that the decay curves of CoTPP in the Poly(Glu)–DeAC complex conform to a double-exponential function, denoted by Eq. (1)

\[ I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \] .................................(1)

where \( \tau_1 \) and \( \tau_2 \) denote the lifetime of each component, and \( A_1 \) and \( A_2 \) are pre-exponential factors. In the Poly(Glu)–DeAC solutions, the lifetime of CoTPP is made up of a long component \( (\tau_1) \) whose magnitude increases with increasing concentration of DeAC and a short component \( (\tau_2) \) which disappears above 0.3 mM DeAC (Table 1).

![Fig. 2: The [DeAC] dependence of IR frequencies of C–H (a) symmetric and (b) asymmetric stretching bands of Poly(Glu) in DeAC solution](image)

![Fig. 3: The absorption spectrum of CoTPP in the Poly(Glu)–DeAC (0.4 mM) complex.](image)
The biexponential behavior of fluorescence lifetimes of CoTPP in polypeptide–DeAC solutions can be explained in terms of co-existence of aggregates of CoTPP and monomeric CoTPP in solution. These fluorescence lifetime data are in qualitative agreement with lifetime data for Ru(bpy)$_3^{2+}$ in clay suspensions [28] and also to that of amphiphilic porphyrin molecules in Triton X-100 micelle medium [29]. These authors suggested that the double-exponential decay is due to the presence of two different sites which have different accessibility to the porphyrin or Ru(bpy)$_3^{2+}$. In the present system, we suggest a similar situation in which CoTPP is solubilized in two different sites. The long lifetime component ($\tau_1$) probably can be attributed to the monomeric CoTPP which is incorporated into the hydrophobic clusters of the Poly(Glu)–DeAC complex, whereas the short lifetime component ($\tau_2$) corresponds to CoTPP aggregates in the aqueous bulk phase. The increase in the fluorescence quantum yield and the increase in the longer fluorescence lifetime and its component occur around the [DeAC] range at which the cooperative binding of Poly-(Glu) with DeAC occurs (from CD and IR spectra). This suggests that the cooperative binding of DeAC to Poly-(Glu) leads to the destruction of some aggregated CoTPP, because the monomeric species are incorporated in the hydrophobic clusters of DeAC molecules bound to Poly(Glu).

iii. Chl/Poly(Glu)–DeAC complex system

The absorption spectra of Chl in the Poly(Glu)–DeAC system consist of a soret band at 435 nm and a Q-band at 670 nm, with a shoulder around 710 nm (Fig. 5a). The absorption bands of Chl at 670 nm with the shoulder at 710 nm are characteristic of mixtures containing both the aggregated and monomeric Chl molecules [10, 30]. Upon addition of DeAC solution into this mixture, an increase in the absorbance of the Q-band of Chl (670 nm) occurred with a corresponding decrease in the absorbance of the shoulder band (710 nm). Fig. 5b shows the [DeAC] dependence of the ratio of the absorbance of the shoulder band to the Q-band ($A_{710}/A_{670}$) of Chl in the Poly(Glu)–DeAC complex. The decrease in
$A_{710}/A_{670}$ strongly suggests the equilibrium between the aggregated state and the monomeric state of Chl.

**Table 1:** Fluorescence decay parameters for CoTPP in the Poly(Glu)-DeAC systems at 25°C.

<table>
<thead>
<tr>
<th>[DeAC] (mM)</th>
<th>$\tau_1$ (ns)</th>
<th>$Q_1^a$ (%)</th>
<th>$\tau_2$ (ns)</th>
<th>$Q_2^a$ (%)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>7.5</td>
<td>70.0</td>
<td>0.55</td>
<td>30.0</td>
<td>1.49</td>
</tr>
<tr>
<td>0.1</td>
<td>10.4</td>
<td>79.0</td>
<td>0.72</td>
<td>21.0</td>
<td>1.37</td>
</tr>
<tr>
<td>0.2</td>
<td>10.7</td>
<td>78.0</td>
<td>0.64</td>
<td>22.0</td>
<td>1.10</td>
</tr>
<tr>
<td>0.3</td>
<td>11.0</td>
<td>84.5</td>
<td>0.50</td>
<td>15.5</td>
<td>0.93</td>
</tr>
<tr>
<td>0.4</td>
<td>11.3</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>1.26</td>
</tr>
<tr>
<td>0.5</td>
<td>10.9</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>1.43</td>
</tr>
<tr>
<td>0.6</td>
<td>10.7</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>1.50</td>
</tr>
</tbody>
</table>

The fluorescence emission intensities of Chl excited at the Soret band (435 nm) gave emission intensities around 680 nm with a shoulder band at 730 nm. The fluorescence emission intensity observed is characteristic of monomeric Chl molecules, since aggregated Chl molecules do not emit fluorescence or have very weak fluorescence intensities [2]. Correcting for changes in absorption cross-section of Chl in the Poly(Glu)–DeAC system at various concentrations of DeAC, we could obtain the fluorescence quantum yield of Chl in the various environment as shown in Fig. 6 [23, 24].

The fluorescence quantum yield increases with increasing concentration of DeAC for the Poly(Glu)–DeAC system. The quantum yield is also larger in the Poly(Glu)–DeAC system than in the colloidal DeAC system as shown in Fig. 6. The decrease in the $A_{710}/A_{670}$ ratio and also the increase in the fluorescence quantum yield occur in the [DeAC] range at which the cooperative binding occurs between Poly(Glu) and DeAC. This observation also suggests that a change in conformation of Poly(Glu) induced by DeAC leads to the destruction of some Chl aggregates and the incorporation of monomeric Chl in the Poly(Glu)–DeAC complex.
Fig. 4: Fluorescence quantum yields of CoTPP in (A) Poly(Glu)–DeAC and (B) colloidal DeAC systems (excitation wavelength: 420 nm, excitation and emission slits: 3 nm).

Fig. 5: (a) The absorption spectrum of Chl in the Poly(Glu)–DeAC complex and (b) the [DeAC] dependence of absorbance ratios at 710 nm to 670 nm of Chl in the Poly(Glu)–DeAC complex.

Fig. 6: Fluorescence quantum yields of Chl in (A) Poly(Glu)–DeAC and (B) colloidal DeAC systems (excitation wavelength: 435 nm, excitation and emission slits: 3 nm).
iv. *Electron transfer from the biofunctional molecule to MV$^{2+}$* in the present system

To investigate the electron-transfer reaction from the biofunctional molecule to MV$^{2+}$ in the Poly(Glu)–DeAC complex system, we carried out fluorescence quenching experiments in the absence and presence of MV$^{2+}$. For CoTPP both the fluorescence intensity and fluorescence lifetime were recorded, whereas for Chl only fluorescence intensities were recorded. To prove that the quenching of Chl or CoTPP in the Poly(Glu)–DeAC complex was due to an electron transfer as illustrated in Scheme 1, a sample solution containing either Chl or CoTPP in the Poly(Glu)–DeAC, MV$^{2+}$ and ca. 5 mM EDTA$^{2-}$ as a sacrificial donor was degassed with Ar and irradiated with light (UV and/or visible). EDTA$^{2-}$ reacts with the oxidized Chl or CoTPP and prevents the back-reaction. The blue color of reduced methylviologen (MV$^{-}$) was indeed generated in the above system, confirming that the quenching occurred via the electron transfer.

The Stern–Volmer equation (Eq. (2)) was used to evaluate the quenching efficiency in these systems

$$I_0 / I = \tau_0 / \tau = 1 + K_{sv}[MV^{2+}]$$

Here, $I_0$, $I$, $\tau_0$ and $\tau$ denote the fluorescence intensities and fluorescence lifetimes of Chl or CoTPP in the absence and presence of MV$^{2+}$, respectively. $K_{sv}$ is the Stern–Volmer constant and [MV$^{2+}$] is the quencher (MV$^{2+}$) concentration. However, before the quenching reaction in the Poly-(Glu)–DeAC complex system could be studied, the interaction of MV$^{2+}$
with Poly(Glu) was investigated by using CD spectroscopy. In this case no distinct induced CD was observed upon the addition of MV$^{2+}$ to a solution of Poly(Glu) only. As control experiments, the fluorescence intensity of CoTPP or Chl in the presence of MV$^{2+}$ was measured in another polypeptide–surfactant complex, made up of poly(L-lysine) and SDS (vide infra).

v. Quenching of CoTPP by MV$^{2+}$

Fig. 7 shows the Stern–Volmer plots for the quenching of the fluorescence intensity as well as the fluorescence lifetime of CoTPP by MV$^{2+}$ in the Poly(Glu)–DeAC complex system. The fluorescence intensity as well as the fluorescence lifetime of CoTPP was quenched by MV$^{2+}$, in the present system. We can see in Fig. 7a that the fluorescence quenching of CoTPP by MV$^{2+}$ increases with increasing concentration of DeAC. Also the curves show the downward curvature at higher concentrations of MV$^{2+}$. The downward curves are obtained when a fluorophore is distributed in two or more different environments which have different accessibility to fluorescence quenching [31, 32]. This may be ascribed

![Fig. 7: (a) Stern–Volmer type plots for the quenching of fluorescence intensity of CoTPP by MV$^{2+}$ in the Poly(Glu)–DeAC system: (A) 0, (B) 0.2, (C) 0.4, (D) 0.6 mM DeAC and (b) a comparison of Stern–Volmer type plots for the quenching of fluorescence lifetime (O) and fluorescence intensity (h) of CoTPP by MV$^{2+}$ in the Poly(Glu)–DeAC (0.4 mM) system. Excitation wavelength: 420 nm, excitation and emission slits: 3 nm.](image-url)
to the protected quenching in which one portion of CoTPP is accessible to the quencher while the other is not [31, 32].

The energy transfer between pyrene and proflavin was also reported and similar curves were obtained for this system [12]. Fig. 7b compares the fluorescence lifetime ratio ($\tau_0/\tau$) with the fluorescence intensity ratio ($I_0/I$). The data coincide with each other within the experimental error, suggesting that the quenching process in the Poly(Glu)–DeAC complex is highly dynamic. From Fig. 7b, the bimolecular quenching constant ($k_q$) and the rate of electron transfer ($k_{ET}$) were estimated using Eqs. (3) and (4).

$$K_{SV} = k_q \tau_0 \quad \text{..................(3)}$$

$$k_{ET} = 1/\tau - 1/\tau_0 \quad \text{..................(4)}$$

Here $K_{SV}$ is the Stern–Volmer constant, $k_q$ is the bimolecular quenching constant, $k_{ET}$ is the rate of electron transfer and $\tau_0$ and $\tau$ are lifetimes, respectively, in the absence and in the presence of MV$^{2+}$. The numerical values of $K_{SV}$, $k_q$ and $k_{ET}$ of 152 M$^{-1}$, 1.3×10$^{10}$ M$^{-1}$s$^{-1}$ and 6.6×10$^{7}$ s$^{-1}$ were estimated using Eq. (1) (for the fluorescence lifetime ratio), at the lower concentration range of MV$^{2+}$, where we could obtain an approximately straight line (Fig. 7b). The $k_q$ value for this system is about two times larger than that of the diffusion controlled reaction in water (7.4×10$^9$ M$^{-1}$ s$^{-1}$) [23]. This abnormally high value could be explained by the fact that the electrostatic attraction may occur between the divalent MV$^{2+}$ cation and the –COO$^-$ group of the Poly(Glu), resulting in the partial incorporation of MV$^{2+}$ in the Poly(Glu)–DeAC complex (vide infra). Fig. 8 shows the fluorescence-intensity curves for the quenching of Chl by MV$^{2+}$ in the Poly(Glu)–DeAC complexes. The fluorescence quenching did not occur in the absence of DeAC (Fig. 8A). As the concentration of DeAC increases, the degree of the fluorescence quenching also increased. Also the quenching curves show similar downward curvature at higher concentrations of MV$^{2+}$ which may be attributed
Fig. 8: Stern–Volmer type plots for the quenching of fluorescence intensity of Chl by MV$^{2+}$ in the Poly(Glu)–DeAC system: (A) 0, (B) 0.2, (C) 0.4, (D) 0.6 mM DeAC. Excitation wavelength: 435 nm, excitation and emission slits: 3 nm.

to the protected quenching [31,32]. It should also be noted that the fluorescence intensity ratios for the Chl system are larger than those of the CoTPP system. The facts that fluorescence quenching did not occur in the absence of DeAC and the quenching degree increased with increasing concentration of DeAC suggest that the electron-transfer process in this system is dependent on the change in the DeAC concentration and hence the change in the conformation of the Poly(Glu). The increased quenching rate in both systems can be rationalized by the fact that the incorporation of Chl or CoTPP in the Poly(Glu)–DeAC complex leads to an increase in their local concentrations in the Poly(Glu)–DeAC complex. It was reported that the local concentration of Chl is about 350 times larger than the analytical concentration (1×10$^{-5}$ M), when Chl was solubilized in poly(L-ornithine, L-tyrosine)-sodium dodecylsulfate complex [33]. At pH 6.5 the side-chain group (–COO$^{-}$) of Poly(Glu) is almost fully dissociated (pKa = 4.45) [20], implying that the electrostatic attraction between the side-chain group (–COO$^{-}$) of Poly(Glu) and divalent MV$^{2+}$ may results in the partial solubilization of MV$^{2+}$ into the polypeptide–surfactant complex from the aqueous bulk phase. This interaction is weak since MV$^{2+}$ alone did not induce a
conformation change of Poly(Glu) from the CD studies of solutions containing Poly(Glu) and MV$^{2+}$ only. Hence, MV$^{2+}$ and DeAC may compete for the –COO$^-$ group of Poly(Glu).

**Fig. 9:** Plots of $I_0/(I_0 - I)$ vs. [MV$^{2+}$]$^{-1}$ for (a) the CoTPP–Poly(Glu) system and (b) the Chl–Poly(Glu) system in 0.6 mM DeAC solution

This situation was also confirmed by the observation that the fluorescence quenching by MV$^{2+}$ occurred when CoTPP or Chl was solubilized in Poly(Glu)–DeAC complexes in the presence of MV$^{2+}$, whereas no fluorescence quenching by MV$^{2+}$ occurred when similar experiments were carried out in a complex formed between a cationic polypeptide, poly(L-lysine), and an anionic surfactant, sodium dodecylsulfate, due to the repulsion between the side-chain group (–NH$_3^+$) of poly(L-lysine) and MV$^{2+}$. The above juxtaposition reduces the distance between MV$^{2+}$ and Chl or CoTPP molecules in the Poly(Glu)–DeAC complex, hence increases the rate of electron transfer. In order to analyze the downward-curving plots (Figs. 7a and 8), we employed a modified form of the Stern–Volmer equation [31]. According to this model, two possible sites are assumed for the location of the biofunctional molecule (CoTPP or Chl) in solution. One of the sites is accessible to MV$^{2+}$ quencher (denoted as a) and the other is inaccessible (b). The total fluorescence of Chl or CoTPP in the absence of MV$^{2+}$ ($I_0$) is given by

$$I_0 = I_{0a} + I_{0b}$$

(5)
where $I_{0a}$ and $I_{0b}$ denote contributions from the biofunctional molecule in sites a and b, respectively. In the presence of MV$^{2+}$, the contribution from site b is not affected. Therefore, we obtain

$$I = \frac{I_{0a}}{1 + K_{SVa}[A]} + I_{0b} \text{..........................(6)}$$

where $K_{SVa}$ is the Stern–Volmer constant for site (a) and [A] is the concentration of MV$^{2+}$. Subtracting Eq. (6) from Eq. (5) yields,

$$I_0 - I = I_{0a}K_{SVa}[A]/(1 + K_{SVa}[A]) \text{..........................(7)}$$

From Eqs. (5) and (7) we obtain

$$\frac{I_0}{(I_0 - I)} = \frac{1}{\int_a K_{SVa} + \frac{1}{\int_a}} \text{..........................(8)}$$

$$\int_a = \frac{I_{0a}}{(I_{0a} + I_{0b})} = \frac{I_{0a}}{I_0} \text{..........................(9)}$$

where, $\int_a$ is the fraction of the initial fluorescence of the fluorophore in site a in the absence of MV$^{2+}$. Eq. (8) represents the modified Stern–Volmer equation. The plots of $I_0/(I_0 - I)$ against $1/[\text{MV}^{2+}]$ are shown in Fig. 9 for Chl and CoTPP in the Poly(Glu)–DeAC complex systems. The plots in Fig. 9 show a good linearity between $I_0/(I_0 - I)$ and $1/[\text{MV}^{2+}]$. From the intercept and slope, we obtain $\int_a$ and $K_{SVa}$ values as shown in Table 2. The values of $\int_a$ for Chl are larger than those for CoTPP in the Poly(Glu)–DeAC complex system. The difference between the $\int_a$ values of Chl and CoTPP in the Poly(Glu)–DeAC complex implies that the fraction of Chl incorporated in the Poly(Glu)–DeAC complex is larger than that of CoTPP. The modified Stern–Volmer model is an approximation and assumes that the concentration of MV$^{2+}$ in the assessable site is the total concentration of MV$^{2+}$, because it is difficult to determine the effective local concentration of MV$^{2+}$ that will quench Chl or CoTPP in the complex. Hence the $K_{SVa}$ values estimated here are not the real values. The two site model explains the downward curve obtained in Figs. 7a and 8.
**Table 2:** Modified Stern–Volmer parameters for the fluorescence quenching of Chl and CoTPP by MV$^{2+}$ in the polypeptide–DeAC complex systems

<table>
<thead>
<tr>
<th>Fluorophore</th>
<th>[DeAC] (mM)</th>
<th>$K_{sva}$ (10$^3$ M$^{-1}$)</th>
<th>$f_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chl</td>
<td>0.4</td>
<td>1.9</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>1.8</td>
<td>0.84</td>
</tr>
<tr>
<td>CoTPP</td>
<td>0.4</td>
<td>1.5</td>
<td>0.55</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>3.6</td>
<td>0.56</td>
</tr>
</tbody>
</table>

**vi. Hydrogen production by using CoTPP**

Hydrogen production was performed under visible-light and combined UV/visible-light irradiation by using a system consisting of cobalt(II)tetrphenylporphyrin (CoTPP), methylviologen (MV$^{2+}$), ethylenediaminetetraacetic acid disodium salt and Pt-loaded poly(l-glutamate) (Poly(Glu)) in aqueous decylammonium chloride (DeAC) solution. CoTPP was solubilized in hydrophobic clusters of DeAC induced by its cooperative binding to Poly(Glu). Fig. 10 shows the time course for hydrogen evolution when the sample was irradiated with (a) visible and (b) UV/visible-light, respectively. The amount of hydrogen gas evolved initially increases with time and then becomes nearly constant. As can be seen in Fig. 7 (C and D), the fluorescence quenching, i.e., the quenching due to the electron transfer from CoTPP to MV$^{2+}$, reaches the plateau. This may be responsible for the saturated hydrogen evolution (Fig. 10). Hydrogen gas was not evolved in the absence of either of CoTPP, MV$^{2+}$ or EDTA$^{2-}$ upon irradiation under visible-light as well as UV/visible-light (Figs. 10 and 11), suggesting that these three components are essential for the production of hydrogen in this system and the possible route for electron transfer is via oxidative quenching by MV$^{2+}$. About 0.15 and 3.5μmol of hydrogen gas was obtained after irradiation for 3 h using visible as well as combined UV/visible-light.

The amount of hydrogen gas produced is larger when the sample was irradiated with UV/visible than when irradiated with visible-light ($\lambda >$ ca. 400 nm) only. Under visible-light irradiation, hydrogen gas was produced only when all the components were present
Fig. 10: Time course for hydrogen production under (a) visible and (b) UV/visible-light irradiation. CoTPP (1×10⁻⁵ M), Pt (2.5×10⁻⁶ M), MV²⁺ (2.5 mM), EDTA²⁻ (10 mM), DeAC (0.4mM) and Poly(Glu) (0.1 mM). (a) (A) All components and (B) absence of any of the components. (b) (A) All components, (B) without Pt-colloid, (C) without Poly(Glu) and (D) without EDTA²⁻, CoTPP or MV²⁺. (Fig. 10(a)), whereas under UV/visible-light irradiation, a little mount of hydrogen gas was produced even in the absence of Pt-colloid alone or in the absence of Poly(Glu) alone (Fig. 10(b)). The [MV²⁺] dependence of the rate of hydrogen evolution in the presence of 4×10⁻⁴ M DeAC, 1×10⁻⁵ M CoTPP, 1×10⁻² M EDTA²⁻ and Pt-Poly(Glu) is shown in Fig. 11.

Fig. 11: Effect of [MV²⁺] on the rate of hydrogen production under visible-light irradiation. (a) Visible and (b) UV/visible-light irradiation. CoTPP (1×10⁻⁵ M), Pt (2.5×10⁻⁶ M), EDTA²⁻ (1×10⁻² M), DeAC (0.4×10⁻³ M) and Poly(Glu) (0.1×10⁻³ M).

The rate of hydrogen evolution increases until about 2.5mM (using visible-light) (Fig. 11(a)) and about 5mM (using UV/visible-light) (Fig. 11(b)) and then it decreases through the maximum value. The increase in the rate of hydrogen evolution at lower concentrations of
MV$^{2+}$ is in correlation with that MV$^{2+}$ is closer to CoTPP in the polypeptide–surfactant complex, leading to the effective electron transfer probably via the short-lived singlet state. However, at higher concentrations of MV$^{2+}$ (Fig. 11), the rate of hydrogen evolution decreases. The decrease in the hydrogen gas formation rate at higher MV$^{2+}$ concentrations could be interpreted by the following reasons. A possible side reaction such as the hydrogenation of MV$^{2+}$ in the presence of Pt-colloid may occur. Also the blue color of reduced MV$^{+*}$ can acts as an inner filter and competes with the porphyrin for absorption of the incident light (34). Finally the decrease in the rate of hydrogen production could also be caused by the formation of complex species such as CoTPP–MV$^{2+}$ in the ground state, which is not photoreactive, since they do not yield photoredox products (35, 36). Although the first two factors can also account for the decreased rate of hydrogen evolution, we think that the dominant factor is the formation of ground state complex species such as CoTPP–MV$^{2+}$. Since MV$^{2+}$ is partially incorporated in the Poly(Glu)–DeAC complex probably by bonding to the side chain (–COO$^-$ group) of Poly(Glu), increase in the concentration of MV$^{2+}$ might lead to an additional bonding to CoTPP complicating the electron transfer process. Charge transfer complexes have also been reported to be formed between electron donors (such as pyrene and porphyrins) and the electron acceptor, MV$^{2+}$ (37, 38). Increase in the [MV$^{2+}$] could also lead to ground-state charge transfer complexes between EDTA$^{2−}$ and MV$^{2+}$ which have been reported to occur in alkaline and slightly acidic media (39-41).

The formation of ground state complexes (MV$^{2+}$–EDTA and/or CoTPP–MV$^{2+}$) complicates charge separation and hence decreases the rate of hydrogen production. Similar model systems for the study of hydrogen evolution, but in the absence of a polypeptide–surfactant complex, have been reported. Such model systems consist of zinc tetrakis(N-methylpyridium-4-aryl)porphyrin, EDTA$^{2−}$, MV$^{2+}$ and Pt-colloid, and also zinc tetrphenylporphyrinte-trasulfonate, MV$^{2+}$, triethanolamine and hydrogenase catalyst (34).
In Fig. 12, we show the \([\text{EDTA}^{2-}]\) dependence on the rate of hydrogen evolution. Hydrogen gas was not produced in the absence of \(\text{EDTA}^{2-}\). Below 3 mM \(\text{EDTA}^{2-}\) hydrogen gas was not evolved under visible-light irradiation. On the other hand, irradiating the sample solution with UV/visible-light resulted in trace amount of hydrogen gas below 3 mM \(\text{EDTA}^{2-}\). Above 3 mM \(\text{EDTA}^{2-}\), the rate of hydrogen evolution increases with increasing concentration of \(\text{EDTA}^{2-}\). Hence in this system hydrogen gas was evolved only in excess of \(\text{EDTA}^{2-}\) compared with the concentration of CoTPP. This observation may suggest that \(\text{EDTA}^{2-}\) is not incorporated into the Poly(Glu)–DeAC complex, but is located at the interphase between the bulk phase and the complex phase as well as bulk phase.

\(\text{EDTA}^{2-}\) at the interphase serves as a sacrificial electron donor to the oxidized CoTPP. The effect of \([\text{DeAC}]\) on the rate of hydrogen evolution is shown in Fig. 13. An increase in the rate of hydrogen evolution is observed mostly at \([\text{DeAC}]\) above 0.3 mM under visible as well as UV/visible-light irradiation.

**Fig. 12:** Effect of \([\text{EDTA}^{2-}]\) on the rate of hydrogen production (a) visible and (b) UV/visible-light irradiation. CoTPP (1x10^{-5}), Pt (2.5x10^{-6}), Poly(Glu) (0.1x10^{-3} M) and MV^{2+}: (a) 2.5x10^{-3} M and (b) 5x10^{-3} M.

The results can be associated with the effect of \([\text{DeAC}]\) on the CD spectra of Poly(Glu) and on the fluorescence intensity of CoTPP. This remarkable increase in the rate of hydrogen gas observed above 0.3 mM DeAC (Fig.13) can be ascribed to two possible reasons: the electrostatic repulsion between cationic DeAC and reduced MV^{+} and also the
change in the conformation of Poly(Glu) from the random-coil to the \( \alpha \)-helix. The former reason may be ruled out because in this system the concentration of DeAC (0–0.5 mM) is much lower than its cmc (67 mM) and the cooperative binding between the Poly(Glu) and DeAC is the dominant force in solution (20).

![Fig. 13](image)

**Fig. 13:** Effect of [DeAC] on the rate of hydrogen production under (a) visible and (b) UV/visible-light irradiation. CoTPP \((1 \times 10^{-5})\), Pt \((2.5 \times 10^{-6})\), EDTA\(^{2-}\) \((1 \times 10^{-2} \text{ M})\), Poly(Glu) \((0.1 \times 10^{-3} \text{ M})\) and MV\(^{2+}\): (a) \(2.5 \times 10^{-3} \text{ M}\) and (b) \(5 \times 10^{-3} \text{ M}\).

Fig. 14 summarizes the plausible mode of solubilization of CoTPP in the complex and the reactions leading to the production of hydrogen gas. Initially we have a mixture containing random-coiled Poly(Glu) to which Pt is loaded and also insoluble CoTPP in an aqueous solution containing both MV\(^{2+}\) and excess EDTA\(^{2-}\) in the presence of lower [DeAC]. In the presence of higher [DeAC], however, the cooperative binding of DeAC (above 0.3 mM) to Pt-loaded Poly(Glu) occurs. This leads to the solubilization of CoTPP in the micelle-like clusters of DeAC and the change in conformation of the Poly(Glu) from the random-coil to the \( \alpha \)-helix. The interaction of MV\(^{2+}\) with the side chain group (–COO\(^-\)) of Poly(Glu) brings MV\(^{2+}\) closer to CoTPP. This closeness results in the electron transfer and the formation of the methylviologen radical. This radical transfers the electron to Pt-colloid which in turn is used to produce hydrogen gas. The conformational change of Poly(Glu) might also enhance the separation of charged species formed and leads to the increases of
the hydrogen production. Excess EDTA$^{2-}$ found at the interphase between the bulk phase and the polypeptide–surfactant complex phase donates electrons to the oxidized CoTPP and thus CoTPP is regenerated.

**vii. Hydrogen production by using CoTPP**

Also, hydrogen production was accomplished under visible-light irradiation by using a system consisting of a biomolecule (chlorophyll $a$), methylviologen, ethylenediaminetetraacetic acid disodium salt and Pt-loaded poly(L-glutamate) (Poly(Glu)), in aqueous decylammonium chloride (DeAC) solution.

As shown in Fig. 15, the amount of hydrogen gas produced increases with irradiation time. No hydrogen gas was produced in the absence of any one of Chl, EDTA$^{2-}$, Poly(Glu) or DeAC. On the other hand, a little amount of hydrogen gas was produced when the experiment was carried out in the absence of Pt colloid alone or MV$^{2+}$ alone. This observation suggests that the Poly(Glu)–DeAC complex alone participate in the overall reaction of hydrogen production in this system. The effect of [DeAC] on the rate of hydrogen evolution is shown in Fig. 16.
Fig. 15: The time course for hydrogen evolution in the presence of all components (□), and in the absence of Pt colloid alone (○), MV$^{2+}$ alone (△) or any one of (◊) Chl, EDTA$^{2-}$, Poly(Glu) and DeAC.

Hydrogen gas was not evolved below 0.3 mM DeAC and there was an increase in the rate of hydrogen evolution above this concentration. We also investigated the [MV$^{2+}$] and [EDTA$^{2-}$] dependence on the rate of hydrogen evolution under visible light irradiation, as shown in Fig. 17. In Fig. 17(a), the rate of hydrogen increases until 2 mM and then it decreases slightly through the maximum value, whereas in Fig. 17(b) the rate of hydrogen evolution increases almost linearly with increasing concentration of EDTA$^{2-}$ used in the experiment. No hydrogen gas was evolved in the absence of EDTA$^{2-}$, whereas the hydrogen evolution occurred only in excess of EDTA$^{2-}$ compared with the Chl concentration (Fig. 17(b)).

The increase in the rate of hydrogen evolution at lower concentrations of MV$^{2+}$ (Fig. 17(a)) is in correlation with the fact that MV$^{2+}$ is closer to Chl in the polypeptide–surfactant complex leading to the effective electron transfer. However, at higher concentrations of MV$^{2+}$ (Fig. 17(a)), the rate of hydrogen evolution decreases. The decrease in the hydrogen gas formation rate at higher MV$^{2+}$ The increase in the rate of hydrogen evolution at lower concentrations of MV$^{2+}$ (Fig. 17(a)) is in correlation with the fact that MV$^{2+}$ is closer to Chl in the polypeptide–surfactant complex leading to the effective electron transfer. However, at
higher concentrations of MV$^{2+}$ (Fig. 17(a)), the rate of hydrogen evolution decreases.

**Fig. 16:** The [DeAC] dependence of the rate of hydrogen evolution under visible light irradiation. Chl ($1 \times 10^{-5}$ M), Pt ($2.5 \times 10^{-6}$ M), EDTA$^{2-}$ (4 mM), Poly(Glu) (0.1 mM) and MV$^{2+}$ (2 mM).

**Fig. 17:** Effect of (a) [MV$^{2+}$] and (b) [EDTA$^{2-}$] on the rate of hydrogen production under visible light irradiation. Chl ($1 \times 10^{-5}$ M), Pt ($2.5 \times 10^{-6}$ M), DeAC (0.6 mM) and Poly(Glu) (0.1 mM), (a) [EDTA$^{2-}$] = 4 mM and (b) [MV$^{2+}$] = 2 mM.

The decrease in the hydrogen gas formation rate at higher MV$^{2+}$ concentrations could be interpreted by the following reasons. A possible side-reaction such as the hydrogenation of MV$^{2+}$ in the presence of Pt colloid may occur. Also the blue color of reduced MV$^{+*}$ can serve as an inner filter and competes with Chl for absorption of the incident light (34). Finally the decrease in the rate of hydrogen formation could also be caused by the formation of complex species such as Chl–MV$^{2+}$ in the ground state, which is not photoreactive, since
they do not yield photoredox products (35). Although the first two factors can also account for the decreased rate of hydrogen evolution, we think that the dominant factor is the formation of ground state complex species such as Chl–MV$^{2+}$. Since MV$^{2+}$ is partially incorporated in the Poly(Glu)–DeAC complex by probably bonding to the side-chain of the Poly(Glu), increasing the concentration of this species might lead to a complication in the electron transfer process. Charge transfer complexes have also been reported to be formed between electron donors (such as pyrene and porphyrins) and the electron acceptor, MV$^{2+}$ (38, 39). Since EDTA$^{2-}$ is a sacrificial electron donor, it is reasonable that no hydrogen gas is evolved in its absence.

![Diagram](image)

**Fig. 18**: A simplified representation of the mode of solubilization of Chl in the Poly(Glu)–DeAC complex and the reaction for hydrogen production in the complex system. We omitted DeAC and MV$^{2+}$ in the bulk phase for clarity.

Also the fact that hydrogen evolution can be observed only in excess EDTA$^{2-}$ may suggest that EDTA$^{2-}$ is not incorporated into the Poly(Glu)–DeAC complex, but is located at the interphase between the bulk phase and the complex phase.

Based on the present data, we propose a plausible scheme for the solubilization of Chl in the Pt-loaded Poly(Glu)–DeAC complex and the reactions occurring in solution, as shown in Fig. 18. At low concentrations of DeAC, we have a colloidal mixture containing random-coil type Pt–Poly(Glu) and aggregated Chl in an aqueous solution containing MV$^{2+}$ and
excess EDTA$^{2-}$. Increasing the concentration of DeAC leads to the formation of Poly(Glu)–DeAC complexes and the resultant solubilization of Chl molecules. Another weak electrostatic attraction between MV$^{2+}$ and the side-chain (–COO$^-$ group) of Poly(Glu) may lead to partial incorporation of MV$^{2+}$ into the Pt–Poly(Glu)–DeAC complex. The excited Chl transfer an electron to MV$^{2+}$ resulting to the formation of the MV$^{+*}$ radical. This radical transfers the electron to Pt colloid which in turn is used to produce hydrogen gas. In the absence of Pt colloid or MV$^{2+}$, the α-helix Poly(Glu) may also transfer the electron directly to the nearby protons which are reduced to form hydrogen gas. However, the amount of hydrogen gas formed via this route is very small. The conformation change of Poly(Glu) might also enhance the separation of charged species formed leading to the hydrogen production. Excess EDTA$^{2-}$ found at the interphase between the bulk phase and the polypeptide–surfactant complex donates electrons to the oxidized Chl and thus Chl is regenerated.

4.4. CONCLUSION

Chl and CoTPP molecules were solubilized in the Poly (Glu)–DeAC complexes. The absorption and fluorescence properties of Chl or CoTPP suggest that the aggregated as well as the monomeric species exist in solution. The fluorescence quenching studies show that the electron transfer occurs from Chl or CoTPP to MV$^{2+}$ in the Poly(Glu)–DeAC system. A two-site model was proposed in which the biofunctional molecules are distributed between the aqueous bulk phase of the solution as the aggregate and the complex phase as the monomeric species.

5.5. ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>Chl</td>
<td>chlorophyll a</td>
</tr>
<tr>
<td>CoTPP</td>
<td>cobalt(II)tetraphenylporphyrin</td>
</tr>
<tr>
<td>Poly(Glu)</td>
<td>poly(L-glutamate)</td>
</tr>
<tr>
<td>DeAC</td>
<td>decylammonium chloride</td>
</tr>
<tr>
<td>MV$^{2+}$</td>
<td>methylviologen</td>
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CHAPTER 5

FABRICATION AND EVALUATION OF TiO$_2$/GRAPHITE SILICA TWO-LAYER THIN FILMS BY LASER ABLATION METHOD

5.1. INTRODUCTION

Photocatalysts have attracted much interest due to their numerous applications in the decomposition of pollutants and in the photoinduced hydrogen production. Since Fujishima and Honda discovered the photocatalytic splitting of water on TiO$_2$ electrodes [1], TiO$_2$ has drawn considerable attention. TiO$_2$ is a nontoxic, cheap and very stable compound, which has numerous applications such as production of white pigments and cosmetics. Photocatalytic hydrogen production is a valuable sustainable-energy technology. This is because solar energy is converted to chemical energy in the form of hydrogen. Hydrogen is considered as an ideal fuel for the future because it can be produced from clean and renewable energy sources such as solar energy and water. There have been many reports on the production of hydrogen from water using TiO$_2$ [2-7]. When TiO$_2$ is exposed to light, it absorbs the UV portion of light. This leads to the generation of electrons (e$^-$) and holes (h$^+$) at the conduction band and valence band, respectively. The electrons found in the conduction band of TiO$_2$ can reduce protons from water to produce hydrogen gas. This process is usually catalyzed by platinum catalyst. The addition of a sacrificial electron donor such as alcohols can enhance hydrogen production by preventing the reverse reaction which is the recombination of electrons and holes.

TiO$_2$ has also been extensively used for the decomposition of organic wastes [8-10]. The surface properties of TiO$_2$ such as pH, surface defects and crystalline phase are important parameters in determining the photocatalytic activities because that photocatalytic reaction
occurs on the surface of TiO$_2$. The modification of the surface charge of TiO$_2$ by nafion has been reported [11] and led to enhance the photocatalytic activities for the decomposition of charged organic compounds. It was found in our laboratory that graphite silica (GS) has the ability to enhance the hydrogen production as a co-catalyst due to its property to enrich the hydrogen ions [12, 13]. In these previous papers, we proposed the mechanism of the synergy effect between GS and TiO$_2$ as follows. (1) The clay components in GS particles have the ability to elute several kinds of metal ions and exchange for hydrogen ions in the suspension. The resultant GS surface becomes more hydrophilic and hydrogen-ion-rich. (2) The pH values of the suspension increase to ca. 8 by adding GS. At pH values higher than 6.6, the –TiO– groups dominate on the TiO$_2$ surface [14]. The negatively charged TiO$_2$ clamps together with GS. (3) The hydrogen production is therefore increased by the photocatalytic reduction of hydrogen ions held in the clay in GS.

In this paper, we report the fabrication and characterization of two-layers thin film composed of GS and TiO$_2$ (GS / TiO$_2$) prepared by the layer ablation method. A laser ablation method has several advantages [15-18]: high purified thin films can be prepared because of its simple system, many experimental parameters we can control and any materials from pure elements to multicomponent compounds can be used as a target. In this study, we attempt to enhance the photocatalytic activity of TiO$_2$ thin films by using GS as a co-catalyst.

5.2. EXPERIMENTAL

The experimental setup for the laser ablation is illustrated in Fig.1. Two types of target were used, one containing only TiO$_2$ and another containing only GS. The targets were prepared by mixing either 5.5 g of TiO$_2$ (Degussa P25) with 0.55 g of paraffin (10%) or a similar amount of GS with paraffin to prevent cracking. The mixed powder was pressed at
20 MPa for 1 h and calcined at 400 °C for 6 h to form TiO$_2$ and GS pellets.

**Fig. 1:** Schematic image of the laser ablation system.

The pellet was introduced into the chamber and the experimental conditions were adjusted. A laser power of 2.8 J / (pulse cm$^2$) was used throughout the experiment. The wavelength of laser is 532 nm (Nd-YAG Laser). The distance between the substrate and the target was 3 cm when TiO$_2$ was used as the target, whereas it was 7 cm when GS was used as the target. O$_2$ gas was flowed into the chamber through a mass flow meter to control the pressure at 133.8 Pa when TiO$_2$ pellet was used as the target. Substrate temperature was 600 °C when TiO$_2$ was used as the target. The laser irradiation time was 12 min when TiO$_2$ was used as the target, whereas it was changed for adjusting the GS thickness when GS was used as the target.

Irradiation of the target with a laser beam melted the target to form a plume. The plume accumulated on the quartz substrate to form the TiO$_2$ thin film. The process was repeated using the TiO$_2$ film as the substrate and GS as the target. Upon irradiation of the GS target with laser light, GS melted and accumulated on the TiO$_2$ -film surface to form the GS / TiO$_2$ thin film. The thin films prepared were characterized by X-ray diffraction (XRD) using an X-ray diffractometer (Rigaku) with Cu K$\alpha$ radiation. Scanning electron microscopy (SEM) images of the thin films were also taken using a Hitachi S-4100 microscope.
The photocatalytic activity of the prepared thin films was evaluated by measuring the rate of decomposition of methylene blue and also the production of hydrogen in water-methanol mixture. The thin film was fixed on a stand and placed in a 50 cm$^3$ beaker containing $1 \times 10^{-5}$ mol / dm$^3$ methylene blue. This solution was irradiated from the top of the beaker under UV light by using a super-high-pressure mercury lamp (Ushio 500 W). A UV-D33S filter was used to cut-off visible light. The rate of decomposition of methylene blue was determined by measuring the change in absorbance of methylene blue during irradiation, using a Shimadzu MPS-2000.

For hydrogen production, the thin film was inserted in a 10 cm$^3$ water-methanol mixture contained in a 40 cm$^3$ cylindrical flask. The top of the flask was sealed with a silicone rubber septum. To remove oxygen gas, the suspended solution was bubbled with Ar gas (about 5 ml / min) for 1 h with stirring. Then photoirradiation was carried out under an Ar atmosphere of about 1 atm with stirring. The evolved gas was sampled through the silicone rubber septum by using a locking-type syringe at a constant time interval and the sampled gas was quantitatively analyzed by a gas chromatograph (detector; thermal conductivity detector (TCD), column packing; molecular sieve 5 Å, carrier gas; Ar). A super-high-pressure mercury lamp (Ushio 500 W) was also used as a UV light source with a UV-D33S filter.

5.3. RESULTS AND DISCUSSION

Initially the properties of TiO$_2$ thin films prepared by the laser ablation method were studied. The epitaxial growth occurred at 600 °C and resulted in the rutile and anatase forms of TiO$_2$. The peaks of TiO$_2$ (rutile and anatase) decreased with decreasing substrate temperature. At room temperature (about 25 °C), the XRD spectrum of the TiO$_2$ thin film did not show any peak. It suggests that the film is amorphous. The absence of XRD peak at
room temperature and its presence at higher temperatures can probably be attributed to that there is no sufficient energy to crystallize TiO$_2$ at room temperature, whereas at higher temperatures, the energy is sufficient to crystallize TiO$_2$ (rutile and anatase) in the thin film. In previous study, it was found that the amorphous TiO$_2$ thin film had no photocatalytic activity for the hydrogen production, and under the condition of O$_2$ atmosphere and high temperature of the substrate, the anatase was easy to form. Therefore, 600 °C (the maximum temperature of our apparatus) and O$_2$ 1 Torr was used as substrate temperature for the preparation of the TiO$_2$ thin film. XRD patterns of the TiO$_2$ thin film is shown in Fig. 2c.

![XRD patterns](image)

**Fig. 2:** XRD patterns of the (a) GS powder, (b) GS film (c) TiO$_2$ film (d) GS/TiO$_2$

Next the preparation of the GS thin film on the quartz substrate was tried by the laser ablation method. GS is mainly composed of quartz and clay components [12, 13]. The XRD peaks of GS powder are almost composed of crystal peaks as shown in Fig. 2a. Whereas the thin films of GS did not show any peak corresponding to the quartz contained in GS. No growth of the crystal was observed even if substrate temperature was high. We show the XRD patterns of the GS thin film (laser power: 2.8 J / pulse cm$^2$, distance between substrate...
and target: 7 cm, irradiation time: 30 min, atmosphere: \( \text{O}_2 \) 1 Torr, substrate temperature: 600 °C) in Fig. 2b as the representative of these GS films. This observation suggests that the laser ablation is responsible for the generation of amorphous quartz in GS. It was found that the clay portion in GS mainly contribute to activity of hydrogen production in the previous papers [12, 13]. Therefore it was suggested that the GS film which had no quartz peaks of XRD was also effective.

**Fig. 3:** SEM views of (a) the TiO\(_2\) thin film and (b) the GS / TiO\(_2\) thin film.

The preparation of tow-layers film (GS / TiO\(_2\)) was tried on the basis of these results. The XRD pattern of the GS / TiO\(_2\) film is shown in Fig. 2d. We can find only TiO\(_2\) crystal peaks because that the quartz crystal in GS changed to amorphous. Fig. 3 shows the SEM images of (a) TiO\(_2\) and (b) GS / TiO\(_2\) thin films (laser irradiation time of GS target is 2 min). The particle size of the TiO\(_2\) thin film ranged over 50 nm - 1 nm. In Fig.3b, the smaller sized particles (50 nm - 1 nm) are mainly attributed to TiO\(_2\), while the particles of 500 nm - 1 nm are attributed to GS which was deposited on the surface of TiO\(_2\) thin films.

We also attempted to deposit TiO\(_2\) on GS film (TiO\(_2\)/GS film). However the GS film was easy to peer as increasing the thickness of the GS film. It is suggested that the clay in GS prevents the connection of Si-O bonds in quartz when the thickness is large. Therefore we used the GS/TiO\(_2\) film (GS is deposited on the TiO\(_2\) film) for the hydrogen production and
the decomposition of the organic compound.

![Graph showing the effect of GS loading on degradation rate of methylene blue.](image)

**Fig. 4:** Effect of GS loading on degradation rate of methylene blue.

Fig. 4 shows the effect of GS loading on the rate of degradation of methylene blue. This kind of the reaction can be represented as follows.

\[-d[MB]/dt = k [MB]\]  \hspace{1cm} (1)

and after integration of equation (1):

\[\ln ([MB] / [MB]_0) = -kt\]  \hspace{1cm} (2)

where \([MB]_0\) is the initial concentration of methylene blue, \([MB]\) is the concentration of methylene blue after time \(t\) of photocatalytic decomposition and \(k\) is a rate constant related to the reaction properties of the solute. The rate constants \(k\) for the pseudo first order reaction were obtained from the initial linear portion using equation (2). The rate of degradation of methylene blue increases up to GS loading of 200 nm and decreases through the maximum. GS deposited on the TiO\(_2\) thin film is probably responsible for the increase in the rate of degradation of methylene blue. This is because the clay portion of GS has an ion-exchange property which creates an excess of OH\(^-\) in the solution as shown in Fig.6 (a). These OH\(^-\) ions may be adsorbed on the TiO\(_2\) surface giving the GS/TiO\(_2\) thin film an overall negative charge. Since methylene blue is cationic, it can be easily adsorbed to the
surface of the TiO$_2$ thin film. A similar mechanism has been proposed for the surface modification of TiO$_2$ by an anionic Nafion-polymer [7]. The hydroxide ion (OH$^-$) can be changed to hydroxide radical (OH·) by giving electron to hole in TiO$_2$ under UV light. Hydroxide radical (OH·) can attack organic compounds. It is also one of the reasons of enhancement of photocatalytic activity for the decomposition of methylene blue.

Fig. 5: Effect of GS loading on H$_2$ production rate.

Fig.5 shows a similar trend on the rate of hydrogen evolution which also increases up to 200 nm and decreases through the maximum. The increase in the rate of hydrogen production is also related to the presence of GS in the film. It was found that the clay potion in GS enhances the activity of the production of hydrogen [12, 13]. The clay has an ion-exchange property which exchanges cations between the metal ions in the clay and protons (H$^+$) in water. The proton reacts with the electron in the conduction band of TiO$_2$ in the thin film as shown in Fig. 6 (b).

The fact that there was an optimal GS loading for the degradation of methylene blue and the H$_2$ production indicates that excessive GS loading on the TiO$_2$ thin film inhibits the overall photocatalytic activity. It seems that higher GS coverage on TiO$_2$ blocks the active sites for the photocatalytic activity.
5.4. CONCLUSION

The photocatalytic activity of TiO$_2$ thin film for hydrogen production and decomposition of organic compound is enhanced by the deposition of GS which has property of clay. The experimental results obtained showed that the clay in GS was a key component. It was concluded that the enhancement is attributed to the enrichment of hydrogen ions in the clay components of GS. The present study may be expected to contribute to the novel development of the practical co-catalyst in the usage thin films.

References

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6.1. INTRODUCTION

Co-catalysts are indispensable for the hydrogen production using photocatalytic semiconductors. At present, expensive noble metals such as platinum (Pt) and ruthenium (Ru) are used as the co-catalysts. The Pt metal shows especially outstanding performance for photocatalytic hydrogen production, but it is a fairly rare metal. To realize a hydrogen-based society, the co-catalysts derived from abundant natural minerals seem to be interesting and important as a co-catalyst in low cost.

We are strongly concerned with graphite silica (GS, also called “black silica” and “silica black”), one of natural minerals, as a low cost co-catalyst. Here, it should be emphasized that the GS is much cheaper and more abundantly available than metals such as Pt. The GS is siliceous ore containing several percent of carbon in a black mudstone of pre-tertiary. It is mainly composed of quartz, clay and carbon. The GS is usually used as an addition to concrete blocks and an adulterant for soil improvement or snow melting. In industrial application, it has been studied as a source for the preparation of β-SiC or α-Si₃N₄ whiskers [1, 2].

Generally, co-catalysts are roughly classified into two types. One is a support-type in which co-catalysts are deposited on photocatalysts. The other is a mixing-type in which co-catalysts are mixed with photocatalysts in suspension. The support-type has high efficiency, but the supporting process is complicated. The mixing-type has lower efficiency than the support-type, but the mixing process is very easy and convenient for practical use.
For the support-type, many metals such as Pt, Ni and Ru are used [3-8]. On the other hand, Cu, Ni, Ag, Co, etc. are known as mixing-type co-catalysts [9,10]. For both types, roles of the co-catalysts are summarized as follows. 1) The co-catalysts efficiently accept electrons or holes from TiO\textsubscript{2} to avoid recombination of the electron and hole. 2) The co-catalysts adsorb reactants on the surface which is the reaction field of electrons (or holes) and the reactants. In case of the mixing-type, the frequency of collisions and the degree of aggregates are important factors. Moreover, it is needed that the co-catalysts hold the reactants sufficiently.

In this chapter, the co-catalytic ability of GS itself and its components were studied. We obtained the following significant results. The clay component in GS showed good co-catalytic performance close to that of powdered GS. The pH values of water increased by adding GS, irrespective of whether the TiO\textsubscript{2} powder was present. Both TiO\textsubscript{2} and GS particles were aggregated in suspension. On the basis of these experimental results, we here report the role of GS as a co-catalyst for the hydrogen production from water-methanol suspension containing powdered GS and TiO\textsubscript{2} and propose a plausible mechanism of the synergy effect between GS and TiO\textsubscript{2}.

6.2. EXPERIMENTAL

a. Reagents and materials

The photocatalyst was TiO\textsubscript{2} (Degussa, P 25) with a mainly anatase structure (ca. 80%) under the shape of non-porous polyhedral particles of ca. 20 nm mean size with a surface area of 49.9 m\textsuperscript{2}/g. The GS powder was obtained from Nishi-nihon Environmental Engineering Inc. The GS powder has a surface area of 11.1 m\textsuperscript{2}/g. The typical composition of GS is shown in Table 1. It was estimated by using the norm method based on X-ray diffraction and X-ray fluorescence analysis [11,12]. Main components are quartz, carbon, and several kinds of clay such as sericite and kaolinite.
Fig. 1 shows a typical example of thermogravimetry-differential thermal analysis (TG-DTA) curves of GS. A weight loss of about 4% was observed at around 923 K on the TG curve. One exothermic peak was observed on the DTA curve, which was accompanied by the weight loss. The loss mainly corresponds to the total mass of carbon in GS as seen in Table 1. These results suggest that most of carbon was removed by heat treatment at around 923 K. As shown in Fig. 2, the GS color changed from black to pale-pink after the measurement of TG-DTA.

**Table 1:** A typical example of composition of GS.

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical formula</th>
<th>Content /wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>SiO₂</td>
<td>67.9</td>
</tr>
<tr>
<td>Sericite</td>
<td>K₂Al₆Si₆O₂₂</td>
<td>18.9</td>
</tr>
<tr>
<td>Carbon*</td>
<td>C</td>
<td>5.80</td>
</tr>
<tr>
<td>Dolomite</td>
<td>(Ca, Mg)CO₃</td>
<td>3.50</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>Al₂SiO₂</td>
<td>1.77</td>
</tr>
<tr>
<td>Hematite</td>
<td>Fe₂O₃</td>
<td>0.87</td>
</tr>
<tr>
<td>Rutile</td>
<td>TiO₂</td>
<td>0.77</td>
</tr>
<tr>
<td>Pyrite</td>
<td>FeS₂</td>
<td>0.48</td>
</tr>
</tbody>
</table>

*a contain graphite

The calcined GS was obtained by heat treatment for 5 h at 923 K in air. The pale-pink colored GS contains negligible carbon, as mentioned above. The clay fraction in the calcined GS was separated by the following method [13]. The calcined GS powder was dispersed in water by ultrasonication for 30 min. After the suspension was allowed to stand in a dark place for 6 h, its suspension was separated into two layers of the supernatant and the sediment. The supernatant was centrifuged at 3500 rpm for 15 min. After the precipitate was dried on standing, the pale-pink colored clay was obtained.
Fig. 1: Typical DTA-TG curves of GS.

Fig. 2: The color change of GS by heat treatment. Left and right: before and after heating at around 923 K, respectively.

After the supernatant was removed, the sediment was washed to remove the clay fraction remaining on the GS surface. The sediment was then treated ultrasonically for 20 min in water of 160 cm$^3$. The obtained suspension was centrifuged at 3500 rpm for 15 min, and the supernatant was removed. This process was repeated 19 times. The ash-like colored powder was obtained after drying. The powder containing mostly quartz was thus obtained from the calcined GS.

Other reagents such as graphite (99%, Nacalai Tesque), activated carbon (for chromatography, Wako), quartz (99%, Wako), and platinum (99.98%, Nilaco) were used without further purification. Methanol (Wako) was of the highest grade available and was used as received. Laboratory deionized water was distilled twice.
b. Method of Hydrogen production

The amount of hydrogen gas evolved photocatalytically from water-methanol mixtures was measured by following procedures. 1) A mixture of powdered TiO$_2$ and an additive such as GS, several kinds of GS components, or Pt powders was added to aqueous methanol (20 cm$^3$) in a batch photoreactor of a cylindrical flask (154 cm$^3$) whose top was sealed with a silicone rubber septum. 2) To remove oxygen gas, the suspended solution was bubbled with Ar gas (about 1 ml/min) for 1 h with stirring after ultrasonication for 1 min. 3) Photoirradiation was carried out under an Ar atmosphere of about 1 atm with stirring. 4) The evolved gas was sampled through the silicone rubber septum by using a locking-type syringe at a constant time interval. 5) The sampled gas was quantitatively analyzed by a gas chromatograph (detector; thermal conductivity detector (TCD), column packing; molecular sieve 5 Å or Porapak N, carrier gas; Ar). The photoirradiation was provided by a super-high-pressure mercury lamp (Ushio, 500-W USH-500SC) with an optical band pass filter (300-400 nm, Asahi Techno Glass, UV-D33S).

c. Hydrogen production using recycled TiO$_2$ and GS

The co-catalytic properties of recycled GS were examined in the following manner. After the hydrogen production experiment was finished, the suspension used was centrifuged at 1000 rpm for 7 min, and then the supernatant was removed. A fresh water-methanol mixture was added to the remaining sediment. Again, the hydrogen production experiment was performed. These recycling processes were repeated consecutively five times.

d. pH of GS suspension and eluting metals from GS

The variations of pH and the eluting metals from GS in water were measured by following procedures. Proper amounts of GS were added to 50 cm$^3$ of water with or without
TiO$_2$. The suspension was stirred for 20 min. The pH of the suspension was measured using a pH meter (Horiba, D-51). Then the suspension was filtered and the filtrate was analyzed by inductively coupled plasma emission spectroscopy (Thermo Elemental, IRIS).

**e. Size distribution of particles and aggregates in suspension**

To investigate the aggregation of TiO$_2$ and GS particles in water, the size distribution of particles was measured by a laser diffraction particle size analyzer (Shimadzu, SALD-3100). The measurement was carried out with and without ultrasonication. The images of aggregates of TiO$_2$ and/or GS were taken with a scanning electron microscope (Hitachi S-4100).

**6.3. RESULTS AND DISCUSSION**

Fig. 3 shows the GS-content dependence of the evolution rate of hydrogen gas from 40 vol% aqueous methanol suspension. The GS content of the GS-TiO$_2$ mixture was varied in the range of 0 to 100 wt%, keeping the total amount of the mixture at 30 mg. The maximum production rate of hydrogen gas, 22.3 μmol h$^{-1}$, was observed at a GS content of 50 wt%. On the other hand, TiO$_2$ or GS only resulted in 0.23 μmol h$^{-1}$ and 0.03 μmol h$^{-1}$, respectively. By adding GS to TiO$_2$ suspension, the amount of hydrogen gas was increased by a factor of ca. 100 (a ratio of 22.3 and 0.23 μmol h$^{-1}$). These results show that the photocatalytic hydrogen production was enhanced by the synergy effect of GS and TiO$_2$.

Fig. 4 shows the hydrogen production by recycled TiO$_2$ and GS. The amount of hydrogen gas under 1 h irradiation in the 2nd cycle was larger approximately two times than that in the initial cycle. Furthermore, the amount of H$_2$ gas was larger than that of the initial cycle in all runs. The cleaning effect of the GS and TiO$_2$ surfaces in the recycling process may be responsible for the increment of hydrogen production.
Fig. 3: The GS-content dependence of the evolution rate of H$_2$ gas from water-methanol mixtures containing 40 vol% methanol under UV irradiation (35 mW cm$^{-2}$).

Fig. 4: Hydrogen production by recycled TiO$_2$ and GS. Methanol: 40 vol%, UV strength: 15 mW cm$^{-2}$.

Fig. 5 shows the irradiation–time course of hydrogen production from suspension of TiO$_2$ with GS or Pt powder. The hydrogen evolution from platinized TiO$_2$ (0.3 wt% Pt/TiO$_2$) was also studied for comparison [14]. The amount of H$_2$ gas evolved with the powdered GS–TiO$_2$ mixture was about one–eighth of that evolved with 0.3 wt% Pt/TiO$_2$. Since GS could not be deposited to TiO$_2$, the mixture of powdered Pt and TiO$_2$ was also examined. The synergy effect by the powdered GS was comparable to that by the powdered Pt. Therefore, the GS powder is considered to bear comparison with the co-catalytic Pt in the photocatalytic activity.
Fig. 5: Comparison of hydrogen production from various kinds of suspensions: ○; Pt/TiO₂, □; Pt and TiO₂, ◊; GS and TiO₂. Methanol: 40 vol%, UV strength: 15 mW cm⁻². Note the logarithmic ordinate.

Fig. 6: Comparison of hydrogen production. Each powdered additive (15 mg) was added to powdered TiO₂ (15 mg). For TiO₂ alone and GS alone systems, the total amount of 30 mg was used. Methanol: 40 vol%, UV strength: 15 mW cm⁻². Note the logarithmic abscissa.

Fig. 6 shows the amount of hydrogen gas evolved from various suspended mixtures of TiO₂ with untreated GS, SiO₂, graphite, activated carbon, calcined GS, clay from GS, or quartz from GS. An addition of powdered SiO₂ to TiO₂ suspension did not enhance the photocatalytic hydrogen production, but it was rather detrimental. The quartz from GS was also insufficient to enhance the hydrogen evolution. These indicate that the SiO₂ fraction is not effective for the photocatalytic reaction.
The suspended mixture of TiO$_2$ with graphite or activated carbon (Fig. 6) showed no enhancement effect for hydrogen production. However, the calcined GS with negligible carbon maintained ability to enhance the hydrogen gas evolution. The ability was almost equal to that of the untreated powder of GS. These results strongly suggest that the carbon in GS does not play an important role in the synergy effect between GS and TiO$_2$.

The clay fraction separated from GS showed the synergy effect comparable to both powders of untreated and calcined GS as shown in Fig. 6. This fact indicates that the clay in GS is mainly responsible for the synergy effect of GS and TiO$_2$ for the hydrogen production.

Table 2 shows the metal species eluted from GS. We can see that various metal species are eluted from GS. As shown in Fig. 6 (see “GS-filtered suspension”), the presence of these metal species alone in the absence of the GS particles was not effective in the photocatalytic hydrogen production by TiO$_2$. This means that the interaction between GS and TiO$_2$ particles is important for the synergy effect.

**Table 2:** Metal species eluted from GS (30 mg) in water (50 cm$^3$).

<table>
<thead>
<tr>
<th>Eluting species</th>
<th>Amount / μmol</th>
<th>Eluting species</th>
<th>Amount / μmol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>2.44</td>
<td>Al</td>
<td>0.28</td>
</tr>
<tr>
<td>K</td>
<td>1.46</td>
<td>Mg</td>
<td>0.16</td>
</tr>
<tr>
<td>Ca</td>
<td>1.20</td>
<td>Nb</td>
<td>0.08</td>
</tr>
<tr>
<td>Ga</td>
<td>0.68</td>
<td>Mn</td>
<td>0.07</td>
</tr>
<tr>
<td>Si</td>
<td>0.61</td>
<td>Hf</td>
<td>0.05</td>
</tr>
</tbody>
</table>

$^a$ Main species are listed.

Fig. 7 shows the time variation of pH after adding 30 mg of GS to 40 cm$^3$ of water containing no TiO$_2$. The pH values increased with time and reached equilibrium pH of about 8 after ca.10 min from starting pH of 6, resulting in pH increments of about 2. The very similar pH increment by the presence of GS was also observed in water containing TiO$_2$. The pH increment and the elution of metal ions strongly suggest that GS particles exchange their metal ions for hydrogen ions in water.
Fig. 7: Time course of pH variation of 40 cm$^3$ water containing 30 mg of the GS powder.

Fig. 8 shows the GS-amount dependence of both the equilibrium pH and the exchanged hydrogen ions per 1-mg GS ($C_p$) which were estimated from the equilibrium pH. The $C_p$ decreased steeply by the addition of GS and became nearly constant at around 0.1 μmol mg$^{-1}$ at around 600 mg of GS. This suggests that most metal ions at active ion-exchange sites are replaced by the hydrogen ions in the suspension used for hydrogen production.

Sayama and Arakawa reported that an addition of carbonate salts to Pt-loaded TiO$_2$ suspensions leads to highly efficient stoichiometric photocatalytic decomposition of liquid water into H$_2$ and O$_2$ [15]. They found that neither the pH nor cation directly contributes to the water splitting, but the presence of a high concentration of carbonate ions is essential for the catalytic photodecomposition of water. This also strongly suggests that a simple shift of pH to higher values and the presence of cations are not effective, but the coexistence of GS and TiO$_2$ powders is essential for the photocatalytic hydrogen production in the present system.

Fig. 9 shows the particle size distribution of various suspensions. Fig. 9 (a) and (b) are size distributions of GS and TiO$_2$ particles, respectively, which were added to water and allowed to stand for 1 day. It is considered that some particles of GS or TiO$_2$ are
self-agglutinated. The size distribution of the GS–TiO₂ mixture is shown in Fig. 9 (c). The pattern of distribution differs from a simple composite of those shown in Fig. 9 (a) and (b). This result shows that self-aggregates of GS or TiO₂ were reconstructed to co-aggregates of GS and TiO₂ by mixing them together. Fig. 9 (d) shows the size distribution of the GS–TiO₂ mixture after ultrasonication. Some of the co-aggregates were separated into small particles below around 1 μm in diameter by ultrasonication. Fig. 10 shows SEM images of samples after drying suspensions. Fig. 10 (A) and (B) are photographs of GS and TiO₂ samples, respectively. The SEM images of the GS-TiO₂ mixture are shown in Fig. 10 (C) and (D). We can see that TiO₂ particles agglutinate with certain parts of GS surface, especially as seen in Fig. 10 (C). All the obtained data reveal that there is the strong interaction between GS and TiO₂.

Scheme 1 shows a plausible aggregation process between GS and TiO₂ in a stirring step before irradiation. The GS particles elute several kinds of metal ions and exchange them for hydrogen ions in suspension. The ion–exchange makes the surface of GS to a more hydrophilic and hydrogen-ion-rich one. The surface of a TiO₂ powder (Degussa, P 25) is hydroxylated (–TiOH) at around pH=6.6 [16,17]. However, the –TiO⁻ groups coexist and

---

**Fig. 8:** The dependence of both the equilibrium pH and the exchanged hydrogen ions per 1-mg GS on the amount of GS. Various amounts of GS were added to 50 cm³ of water.
become dominant at pH values higher than 6.6. Hence, GS clumps together with negatively charged TiO$_2$ to give the particles centered at a particle size of about 4 μm.

**Fig. 9:** Particle size distribution of several kinds of powders in water. a; GS alone, b; TiO$_2$ alone, c; GS–TiO$_2$ mixture, d; after ultrasonication of GS–TiO$_2$ mixture. Note the logarithmic abscissa.
Fig. 10: SEM images of samples after drying suspensions. A: GS, B: TiO₂, C, D: GS-TiO₂ mixture.

Scheme 1: a: Ion exchange between metal ions and hydrogen ions by the clay in GS. b: Aggregation of both particles of GS and TiO₂.

Scheme 1 shows a plausible aggregation process between GS and TiO₂ in a stirring step before irradiation. The GS particles elute several kinds of metal ions and exchange them for hydrogen ions in suspension. The ion–exchange makes the surface of GS to a more hydrophilic and hydrogen-ion-rich one. The surface of a TiO₂ powder (Degussa, P 25) is
hydroxylated (–TiOH) at around pH=6.6 [16,17]. However, the –TiO\(^{-}\) groups coexist and become dominant at pH values higher than 6.6. Hence, GS clumps together with negatively charged TiO\(_2\) to give the particles centered at a particle size of about 4 \(\mu\)m. Taking these results into consideration, the reaction model is illustrated as shown in Scheme 2. It is considered that the hydrogen ions held in the clay are the main source of hydrogen gas evolved. Though 15 mg of GS contains the clay components of about 3 mg, the co-catalytic property of GS itself was comparable to that of 15 mg of the clay. This suggests that the synergy effect of GS and TiO\(_2\) is not fully induced by the clay alone.

\[\text{Scheme 2: Increment of hydrogen production by the photocatalytic reduction of hydrogen ions held in the clay in GS.}\]

In this connection, we also studied the addition effect of commercially and naturally available clay to TiO\(_2\). The addition of the clay such as Kunipia F (99% sodium montmorillonite), Kunigel-V1 (natural Na-type bentonite) and Sumecton SA (synthesized smectite) of Kunimine Industries Co. Ltd., Bengel A (purified montmorillonite, Hojun Co. Ltd.) and kaolin (natural clay, mostly kaolinite) instead of GS to TiO\(_2\) did not enhance the hydrogen production at all. This suggests that clay itself may not have the active sites for the
hydrogen production and also that the clay may play the lead in the hydrogen production when it is in GS. Further studies are needed to clarify all aspects of the mechanism of the synergy effect and the detailed surface structure of GS.

6.4. CONCLUSION

A drastic synergy effect for hydrogen production from water-methanol mixtures was found for GS in collaboration with photocatalytic TiO$_2$. The amount of evolved hydrogen gas was increased by a factor of ca. 100 simply by mixing GS with TiO$_2$. To reveal the key component of the drastic synergy effect, the amount of evolved hydrogen gas was measured from various suspended mixtures of TiO$_2$ with untreated GS, SiO$_2$, graphite, activated carbon, calcined GS, clay from GS, or quartz from GS. The experimental results obtained showed that the clay in GS was a key component. It was concluded that the synergy effect is attributed to the enrichment of hydrogen ions in the clay components of GS and aggregation of GS and TiO$_2$ particles. The present study may be expected to contribute to the novel development of the practical co-catalyst in the photocatalytic production of hydrogen gas.

References
SINGLE WALLED CARBON NANOTUBE BASED COUNTER ELECTRODE FOR Fe₂O₃ and TiO₂ FILM SOLAR CELLS

7.1. INTRODUCTION

For the gratification of increasing world energy demand and the protection of the environment from pollution renewable resources of energy are urgently needed. The search for such energy resources has led to an increasing interest in photoelectrochemical cells which take advantage of the fact that photons falling on a semiconductor can create electron-hole pairs, which may result in setting up of an electric potential difference across the interface at a junction between two different materials [1]. For the last twenty years much attention has been paid on the metal oxide-based thin film as a working electrode. Among the oxide semiconductors, TiO₂, ZnO, SnO₂, Nb₂O₅, SrTiO₃, In₂O₃ and WO₃ have been studied elaborately [1-3]. Semiconducting iron oxide (Fe₂O₃) is suitable to use as a photoelectrode because of its low cost as well as its small band gap energy of ~2.0 eV [4] which enables it to absorb of the photons of solar spectrum. Recently, in our laboratory a porous thin film of Fe₂O₃ was utilized in a new type of solar cell [5]. It was found that bilayered Fe₂O₃ film prepared by laser ablation and squeegee method gives better physical stability and stable I-V curve under visible light irradiation with Pt as a counter electrode. But the use of Pt is not economic way for mass production. Carbonaceous materials are quite attractive to replace Pt due to their high electric conductivity, corrosion resistance toward I₂, high reactivity for triiodide reduction and low cost [6].

Suzuki et al. [7] examined three kinds of nano-carbon materials for the search of an efficient counter electrode for dye-sensitized solar cells (DSC): SWNT, multi walled carbon nanotube (MWNT) and nano horn. They prepared the carbon nano material and Pt film over
FTO glass by a repeated deposition and drying process. Among three electrodes the highest efficiency was found for SWNT, which was 4.5%. MWNT and nanohorn showed low efficiencies of 0.2 and 0.04%, respectively. Moreover, they found that SWNT shows 85% efficiency of that in Pt electrode. However, they did not report the efficiency of SWNT electrode in Fe₂O₃ film solar cell and also the effect of Pt loading over SWNT electrode. In this paper we report the effect of Pt loading over SWNT films when used in Fe₂O₃ as well as dye-sensitized TiO₂ films solar cells.

7.2. EXPERIMENTAL

a. Materials

The photocatalysts were Fe₂O₃ (Wako, 99.5%) and TiO₂ (Nippon Arosol, P25) with mainly anatase structure (ca. 80%). EtOH (Wako, 99.5%), dicyclohexylcarbodiimide (DCC, Wako, 95%), γ-aminopropyltriethoxysilane (Alfa Aesar), Tetrahydrofurane (THF, Wako, 99.5%), Eosin Y (EY, Wako, 85%), single-walled carbon nanotubes (MTR Ltd, 20-40%), Pt (Nilaco, 99.98%), All films were prepared on indium-tin Oxide (ITO, Aldrich) coated glass which has a resistance of 8-12 ohm.

b. Preparation of dye-fixed TiO₂ film

In the first step, the TiO₂ film was prepared by the pulse laser ablation method. TiO₂ targets were prepared by mixing 5.5 g of TiO₂ with 0.55 g of paraffin (10%) to prevent cracking. The mixed powder was pressed at 20 MPa for 1 h and calcined at 400 °C for 6 h to form a TiO₂ pellet. The pellet was introduced into a vacuum chamber (O₂ atmosphere), where the laser pulse enters through a window and impinges on the target materials to be deposited. A laser power of 2.8 J / (pulse cm²) was used throughout the experiment. The wavelength of the laser was 532 nm (Nd-YAG Laser). The substrate temperature and time of laser irradiation were 600 °C and 24 min, respectively. Irradiation of the target with a laser
beam melted the target to form a plume. The plume was accumulated on the ITO coated glass to form the TiO$_2$ thin film.

Structure of dicyclohexylcarbodiimide and Eosin Y.

In the second step, the TiO$_2$ film was fixed with EY using a silane-coupling reagent as described by Ryo et al. [8]. The silane-coupling reagent was stirred in aqueous EtOH solution for 1 h at room temperature. After the stirring, the TiO$_2$ film was dipped into the solution under stirring for 1 h using a magnetic stirrer. The film was dried by heating at 100 ºC for 15 min. The propylamine modified TiO$_2$ film was dipped into a solution containing 100 ml of THF, EY and DCC and the mixture was stirred for 6 h. The film was then air-dried and stirred twice into aqueous EtOH (pH=12, adjusted by NaOH) for 24 h and twice in distilled water for 12 h to remove excess dyes which physically adsorbed or attached with ester bond on the TiO$_2$ surface.

c. Preparation of Fe$_2$O$_3$ film

The bilayered Fe$_2$O$_3$ film was prepared by the laser ablation and the squeegee methods. Initially, a compact thin film of Fe$_2$O$_3$ was deposited on ITO coated glass with the same method as for TiO$_2$ film preparation. This time the substrate temperature into the laser chamber was set at room temperature. The compact thin film was further coated with porous Fe$_2$O$_3$ by the squeegee method. The preparation method of the Fe$_2$O$_3$ paste is as follows: Fe$_2$O$_3$ powder (2 mg) was mixed with nitric acid (0.1 ml) and water (2 ml). After well
mixing, 2 ml of Triton X-100 were mixed to get a paste. The paste was then used to prepare the film by the squeegee method. Finally the film was heated at 450 °C for 1 h in air environment. The total thickness of the film was about 10 μm.

d. Preparation of counter electrode films

Film of SWNT was prepared by the doctor-blade technique. First, 5 mg of SWNT was smashed softly for 2 min. 1 ml of a surfactant (Triton X-100) was added and mixed to get a paste. The paste was spread over an ITO glass to get a thin film (a) which was then heated at 450 °C for 1h at oxygen atmosphere (1 atm). Another SWNT film (b) was heated comparatively at lower temperature (250 °C) for 30 min in N₂ gas atmosphere (1 atm). Hereafter, the films (a) and (b) are indicated as O-SWNT and N-SWNT, respectively. Another type of Pt-loaded SWNT film was prepared by the following method: 5 mg of SWNT and 0.4 ml of ethanol was put into a mortar and mixed well to get a paste-like suspension. The paste was spread almost homogeneously over ITO glass and dried at room temperature for two days. Then a layer of Pt was made over SWNT film by the spattering method. The overall thickness of the Pt loaded SWNT film was about 15 μm. Hereafter, the film (c) is indicated as SWNTPt.

e. Methods

The EY-fixed TiO₂ and Fe₂O₃ films were used as a working electrodes and SWNT and / or Pt- based films were used as a counter electrode. The two electrodes were sandwiched and a mixture of KI (0.8 M) and I₂ (0.2 M) in water solvent was used as an electrolyte that was filled into a space between the two electrodes. The structure of the cell is schematically shown in Fig 1. A xenon lamp (Inotex 300-W LX-300F) with an IR cut-off filter was used as a light source (power 1 sun). For the measurement of the performance of solar cell, an I-V meter (Keithly 2400) was used. The I-V meter was connected to a computer with a Peccell
I-V curve analyzer (PECK2400-N). Mixture of KI (0.8 M) and I₂ (0.2 M) in water solvent was used as an electrolyte. The thin films were characterized by scanning electron microscope (SEM, Hitachi S-4100), X-ray diffraction (XRD) using an X-ray diffractometer (Rigaku) with Cu Kα radiation and absorption spectroscopy (Shimadzu, MPS-2000 spectrophotometer).

![Diagram of solar cell](image)

**Fig. 1** Structure of the solar cell based on SWNT film.

### 7.3. RESULTS AND DISCUSSION

**a. Characteristics of the films**

The UV-visible spectra for dye-fixed TiO₂ and Fe₂O₃ film are shown in Fig. 2. We can see that both the dye sensitized TiO₂ and Fe₂O₃ films have absorption edge in the visible range at around 580 nm. However, both the films show strong absorption also in the UV range.

![UV-visible spectra](image)

**Fig. 2:** UV-visible spectra of Fe₂O₃ thin film prepared by the laser ablation method.
**Fig. 3:** SEM images of (a) Fe$_2$O$_3$, (b) TiO$_2$ and (c) N-SWNT films.

Figs. 3 (a) and (b) show the SEM images of Fe$_2$O$_3$ and TiO$_2$ films, respectively, prepared by the laser ablation method. The particle sizes of TiO$_2$ on the film are almost homogenous, although some aggregated particles are found. In case of Fe$_2$O$_3$, a porous film is found with
particle sizes ranging from 90 to 120 nm. Fig 3 (c) shows the SEM image of N-SWNT film heated in low temperature (250 °C) under N₂ gas atmosphere. It is seen that the porous carbon nanotube film is composed of small amount of tubes and large amount of amorphous carbon. It was found from the SEM images of very thin SWNT films that poorly formed carbon nanotubes were burned out by heating under high temperature (>400 °C) in oxygen atmosphere.

The crystal structure of the Fe₂O₃ film and TiO₂ films were studied by XRD spectroscopy and the results are shown in Fig 4 and 5, respectively. From the XRD pattern of Fe₂O₃ powder and Fe₂O₃ film on ITO coated glass, it is seen that crystal structure of α-Fe₂O₃ is not destroyed by the laser ablation under the experimental conditions used. But it was found that a phase transformation occurs during the film preparation by laser ablation method from TiO₂ (P25) powder because of high temperature applied in the substrate [9] and the crystal structure of TiO₂ on the ITO glass is composed of about 40% anatase and 60% rutile forms.

![XRD pattern](image)

**Fig. 4:** XRD pattern of (a) α- Fe₂O₃ powder (b) an ITO glass (c) the Fe₂O₃ film prepared by the ablation method on ITO glass. The peaks of α- Fe₂O₃ are marked by the open circle and that of ITO are marked by the closed square.
Fig. 5: XRD pattern of TiO$_2$ film prepared by the ablation method on ITO glass.

b. Current-voltage characteristics

The characteristics of I-V curves of Fe$_2$O$_3$ and EY-fixed TiO$_2$-film solar cells using different counter electrodes are shown in Fig 6(a) and (b), respectively. It is seen from the two figures that open circuit voltage is higher for TiO$_2$ based solar cell but the closed circuit current is higher in case of Fe$_2$O$_3$ film solar cell. These differences arise from the different band positions, light absorption ability of the dye and semiconductor materials [10]. The efficiencies found from the both cells using different counter electrodes are shown in Table 1. The solar cells composed of SWNT films as counter electrodes had comparable conversion efficiency with Pt electrode. This comparable efficiencies SWNT electrode immures from it metallic nature [11] with extraordinary high electrical conductivity [12] and large surface area [13]. It can be concluded from this result that SWNT based counter electrode is feasible to use also in Fe$_2$O$_3$ film solar cells.

Suzuki et al. [7] that the electrochemical activity of carbon materials depends on the size, surface area and the resistance of the films. The sheet resistance of an electrode has an effect on the internal resistance of a solar cell and consequently, influences the fill factor of the cell and its conversion efficiency. The impurities (amorphous carbon, fullerene and other graphitic materials) present in the SWNT may induce increased resistance and cause
decrease in the efficiency of the solar cell. Previously, we have shown that the impurity has
negligible effect on the efficiency of TiO$_2$ and Fe$_2$O$_3$ based solar cells [14].

![Graph showing I-V curves for solar cell with (a) Fe$_2$O$_3$ and (b) EY-fixed TiO$_2$ films using
counter electrodes: O; SWNTPt-co, □; Pt, ▽; N-SWNT, ◇; O-SWNT. It was reported by

Applying high temperature during the preparation process of SWNT film, it was seen by
the SEM image that part of the nanotubes as well as amorphous carbon were burnt out. To
protect the burning of SWNT, lower temperature and N$_2$ gas atmosphere was used for other
SWNT films. As seen from Fig. 6 (a) and (b), this film gave comparatively higher
efficiency.

Most important noticeable result is seen in case of Pt loaded SWNT electrode. It has
comparatively higher efficiency than any other electrodes used in this experiment. As seen
from the Fig 3 (c), the SWNT film is not compact and large pore is present on it. Therefore, during the Pt spattering, the particle of Pt can deposited on the surface of SWNT and into the porous space and thus the surface area of the Pt is increased. Moreover, Pt itself acts as a light reflector at the same time and thus can remarkably improve the light absorption by the semiconductor surface [15]. This duel fact may be the main reason for the increased efficiency of the solar cell when Pt loaded SWNT film is used as counter electrode. However, as no surfactant was used for this film preparation, SWNT was weakly attached over ITO glass. Therefore, the prolong usage of this film was not possible. Alternative process of film preparation is under investigation.

**Table 1:** Efficiency and fill factors for EY-fixed TiO$_2$ and Fe$_2$O$_3$-film-based solar cell by using various counter electrodes.

<table>
<thead>
<tr>
<th>Type of CE</th>
<th>Efficiency (η) %</th>
</tr>
</thead>
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<tr>
<td></td>
<td>Fe$_2$O$_3$</td>
</tr>
<tr>
<td>SWNT-Pt</td>
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</tr>
<tr>
<td>Pt</td>
<td>0.12</td>
</tr>
<tr>
<td>N-SWNT</td>
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</tr>
<tr>
<td>O-SWNT</td>
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</table>

7.4 **CONCLUSION**

We have shown simple preparation method of TiO$_2$, Fe$_2$O$_3$ and SWNT films and the effect of Pt loading to SWNT on the I-V characteristics of solar cells. Although the efficiency of these solar cells was very poor for practical uses, it was found that Pt-loaded SWNT film gives comparatively better efficiency than that of Pt film only. If SWNT can be grown on a conducting substance and then coated with Pt, this film can be physically stable for prolong usage. Further studies are under investigation in our laboratory.
References

8.1 INTRODUCTION

Visible light-driven photocatalysts have received considerable attention because visible light (400 nm < λ < 800 nm) occupies the main part of solar light. Titanium dioxide (TiO$_2$) is well known as an efficient photocatalyst [1] and [2]. However, it is only activated under UV light because of its wide band gap. The development of the future generation of photocatalytic materials is important for the efficient use of solar light. Many works described the enhanced photocatalytic properties of TiO$_2$ by doping of nitrogen [3-5], sulfur [6] and carbon [7].

Recently, Suda et al. reported the preparation of N-doped TiO$_2$ films from TiN and TiO$_2$ by the laser ablation method [8, 9]. The laser ablation method has several advantages: e.g., highly purified thin films can be prepared because of its simple system and any materials from pure elements to multicomponent compounds can be used as a target [10-12].

For development of the study of N-doping in TiO$_2$ by the laser ablation method, we mainly studied the dependence of the N-doping on N$_2$ gas pressures. Here we propose the mechanism of N-doping by the laser ablation method on the basis of the results obtained. The decomposition of methylene blue and the hydrogen production using the N-doped TiO$_2$ films under visible light irradiation were also performed.

8.2 EXPERIMENTAL

TiO$_2$ targets were prepared by mixing 5.5 g of TiO$_2$ (Degussa P25) with 0.55 g of paraffin (10%) to prevent cracking. The mixed powder was pressed at 20 MPa for 1 h and
calcined at 400 °C for 6 h to form a TiO$_2$ pellet.

The pellet was introduced into the chamber and the experimental conditions were adjusted. A laser power of 2.8 J/(pulse cm$^2$) was used throughout the experiment. The wavelength of the laser (Nd-YAG Laser) was 532 nm. The distance between the substrate and the target was 3 cm. The substrate temperature was 600 °C. The laser irradiation time was 12 min. Irradiation of the target with a laser beam melted the target to form a plume. The plume was accumulated on the quartz substrate to form the TiO$_2$ thin film.

The prepared thin films were characterized by absorption spectroscopy (Shimadzu, MPS-2000 spectrophotometer), XRD (X-ray diffraction, Rigaku X-ray diffractometer, Cu Kα) and XPS (X-ray photoelectron spectroscopy, Shimadzu ESCA-1000).

The photocatalytic activity of the prepared thin films was evaluated by measuring the rate of decomposition of methylene blue and also the production of hydrogen in water-methanol mixture. For the decomposition of methylene blue, the thin film was fixed on a stand and dipped into a 50 cm$^3$ beaker containing $1 \times 10^{-5}$ mol/dm$^3$ methylene blue solution. This solution was irradiated under UV or visible light from the top of the beaker. A super-high-pressure mercury lamp (Ushio 500 W) was used as a UV light source with a UV-D33S filter. A xenon lamp (Ushio, 500 W) was also used as a visible light source with a L42 cut-off filter. The rate of decomposition of methylene blue was determined by measuring the change in absorbance of methylene blue during irradiation.

For the hydrogen production measurement, a Pt-loaded TiO$_2$ thin film (Pt/TiO$_2$) was prepared as follows. The TiO$_2$ thin film was stirred in an aqueous methanol solution (H$_2$O:MeOH = 1:1 by volume) containing a required amount of H$_2$PtCl$_6$ and irradiated by a Hg lamp. Photoreduction of H$_2$PtCl$_6$ to Pt particles took place, and Pt was deposited on the TiO$_2$ surface [13].

For hydrogen production, the thin film was dipped into a 10 cm$^3$ water-methanol mixture contained in a 40 cm$^3$ cylindrical flask. The top of the flask was sealed with a
silicone rubber septum. To remove oxygen gas, the suspended solution was bubbled with Ar gas (about 5 ml/min) for 1 h with stirring. Then photoirradiation was carried out under an Ar atmosphere of about 1 atm with stirring. The evolved gas was sampled through the silicone rubber septum by using a locking-type syringe at a constant time interval and the sampled gas was quantitatively analyzed by a gas chromatograph (detector; thermal conductivity detector (TCD), column packing; molecular sieve 5 Å, carrier gas; Ar). A super-high-pressure mercury lamp (Ushio 500 W) was used as a UV light source with a UV-D33S filter. A xenon lamp (Ushio, 500 W) was also used as a visible light source with an L42 cut-off filter.

8.3 RESULTS AND DISCUSSION

Fig 1 shows the absorption spectra of (a) the TiO$_2$ thin film prepared at 600 °C under O$_2$ gas of 133.3 Pa (1 Torr) and (b) the yellowish N-doped TiO$_2$ thin film prepared at 600 °C under N$_2$ gas of 133.3 Pa (1 Torr). The nitrogen substitutional doping of TiO$_2$ is thought to be a method for narrowing the band gap by changing the valence band structure without any change in the position of conduction band [14].

![Figure 1: Absorption spectra of (a) the white thin film and (b) the yellowish thin film under conditions of (a) O$_2$ 133.3 Pa (1 Torr) and (b) N$_2$ 133.3 Pa (1 Torr) (substrate temperature: 600 °C, distance between substrate and target: 3 cm, deposition time: 12 min, laser power: 2.8 J/(cm$^2$ pulse)).](image-url)
XRD spectra of the N-doped thin films indicate a decrease in the anatase phase with decreasing N\textsubscript{2} gas pressure as shown in Fig. 2. The intensity in the rutile phase in turn increases with decreasing N\textsubscript{2} gas pressure.

![XRD patterns of the thin films prepared under various nitrogen pressures](figure)

**Fig. 2:** XRD patterns of the thin films prepared under various nitrogen pressures ((a) 3.3 Pa, (b) 6.7 Pa, (c) 13 Pa, (d) 27 Pa, (e) 67 Pa, (f) 133 Pa, (g) 200 Pa, (h) 267 Pa). A and R denote anatase and rutile, respectively. For the other experimental conditions, see the figure caption of Fig. 1.

The relative amount of the N atom in the N-doped TiO\textsubscript{2} thin films was estimated on the basis of the XPS data using \(h/h_{\text{max}}\) ratios as shown in Fig. 3. Here, \(h\) is the height of the XPS peak of nitrogen in titanium dioxide lattice (the binding energy is ca. 397 eV) [8] and \(h_{\text{max}}\) is the maximum peak height of nitrogen under an N\textsubscript{2} pressure of 27 Pa. The heights of the XPS peaks of nitrogen in air, which are adsorbed on the titanium dioxide surface (the binding energy is ca. 406 eV) [8] were almost constant. The amount of the N atom in the N-doped TiO\textsubscript{2} thin film sharply increased with increasing N\textsubscript{2} gas pressure up to the N\textsubscript{2} pressure around 35 Pa and gradually decreased through the maximum.
Fig. 3: N$_2$ gas pressure-dependence of the relative amount of the doped N estimated from XPS data. For the other experimental conditions, see the figure caption of Fig. 1.

On the basis of the XRD (Fig. 2) and the XPS (Fig. 3) data, we propose a plausible mechanism of N-doping in the TiO$_2$ by the laser ablation. The crystal structural transition from rutile to anatase can be found at some pressures between 27 and 67 Pa as shown in Fig. 2. It is suggested that the N-doping is easy to occur near the critical point of the crystal transition, due to the instability of the crystal form. Furthermore, very recently it has been reported that molecular nitrogen (N$_2$) becomes monoatomic (N) under low pressures [15]. This report also can explain the reason why the N-doping is easy to occur in spite of the presence of triple bonds in the N$_2$ molecule. An N$_2$ molecule can split more easily under the low N$_2$ pressure than under the high N$_2$ pressure. In addition, the film turned yellow when the substrate temperature was higher than 500 °C. Therefore, it is suggested that the thermal energy originating from higher substrate temperatures is also needed for the N-doping. By taking into consideration the data in Fig. 2 and Fig. 3 and the temperature dependence of the N-doping, we propose that N-doping does not occur in the gas phase between the target and the substrate, but mainly on the quartz substrate.

Fig. 4 shows the SEM image of the N-doped TiO$_2$ thin film prepared by the laser ablation method (N$_2$ 1 Torr, 600 °C). From this image, we can see that the surface is rough. A large number of pores were also observed.
Fig. 4: The SEM image of the N-doped TiO$_2$ thin film (N$_2$: 133.8 Pa (1 Torr), substrate temperature: 600 °C, distance between substrate and target: 3 cm, deposition time: 12 min, laser power: 2.8 J/(pulse cm$^2$)).

Fig. 5 shows the dependence of the decomposition rate of methylene blue under visible light irradiation on the N$_2$ pressure corresponding to the relative amount of the N atom in the N-doped TiO$_2$ thin films. This kind of the reaction can be represented as follows:

$$-d[\text{MB}]/dt = k[\text{MB}]$$ .........................................................(1)

and after integration of Eq. (1)

$$\ln([\text{MB}]/[\text{MB}]_0) = -kt$$ .........................................................(2)

where $[\text{MB}]_0$ is the initial concentration of dye, $[\text{MB}]$ is the concentration of methylene blue after time $t$ of photocatalytic decomposition and $k$ is a rate constant related to the reaction properties of the solute. The rate constants $k$ for the pseudo first order reaction were obtained from the initial linear portion using Eq. (2).

The rate of decomposition of methylene blue increased with increasing N$_2$ pressure up to 200 Pa (see (g) in Fig. 2), above which the rate decreased as shown in Fig. 4. Though the relative amount of doped N increases under lower N$_2$ pressure, the photocatalytic activity decreases. This decrease is explained by the change in the crystal structure from anatase to rutile under lower N$_2$ pressures (Fig. 2).
Fig. 5: \( N_2 \) gas pressure-dependence of the rate constant of methylene blue decomposition under visible light. For the other experimental conditions, see Fig. 1.

The amount of hydrogen gas evolved under visible light irradiation was only one-500th of the amount of hydrogen gas evolved under UV light irradiation in spite of the usage of Pt-deposited N-doped TiO\(_2\) thin films. The bare N-doped TiO\(_2\) thin film generated no hydrogen gas under visible light irradiation. It can be concluded that the photocatalytic activity of the N-doped TiO\(_2\) thin films prepared by the laser ablation method is very small for the hydrogen production. This may be due to that the N-doped TiO\(_2\) thin films have some defects such as the oxygen defects which trap electrons necessary to reduce H\(^+\), resulting in low hydrogen production efficiency.

8.4 CONCLUSION

In the present work, the N-doped TiO\(_2\) thin films were fabricated by the laser ablation method and evaluated as a photocatalyst. We proposed the plausible mechanism of nitrogen doping by the laser ablation method. The elucidation of the mechanism will contribute to the development of more useful visible light-responsive photocatalyst thin films.
References

This thesis mainly comprises the experimental results and discussion on photocatalytic systems applied for H$_2$ production and solar cell. The search for the efficient conversion of solar energy into other useful forms arises from the increasing anxiety over the exhaustion of energy resources from fossil fuel and is also due to the pollution caused by the fossil fuel. Hydrogen and solar cell are the top most of the renewable energies to replace fossil fuel. Hydrogen is a very light and chemically reactive gas. When burned in an internal combustion engine, it produces almost zero exhaust and the only by-product is water. Solar cell can convert solar light directly to electrical energy.

**Chapter 1** gives a general introduction of the entire studies. Photoelectrochemical processes at artificial photosynthesis and semiconductors photocatalysts are the most important basics for all photocatalytic reactions. Photoelectrochemistry of semiconductor at semiconductor/liquid interface, or liquid junction, is the first concept of the semiconductor photocatalysis as described in this chapter. Moreover, the enhanced activity of photocatalysts by metal loading, dye sensitization, addition of sacrificial agent, and carbon salt has been discussed elaborately. Other research focused on the enhancement of photocatalysis by modification of TiO$_2$ by means of metal. Also the principles of solar cell, artificial photocatalyst, and structural feature of carbon nanomaterials are explained. Finally, the aim and objectives of this study is discussed.

**Chapter 2** shows the effect carbon nanotube on the photocatalytic activity of TiO$_2$ in terms of H$_2$ production from the mixture of water and alcohol. The drastic synergy effect
was found with an increase in the amount of H₂ gas by a factor of ca. 400 for single-walled carbon nanotubes (SWNT). The amount of hydrogen production using SWNT-TiO₂ is slightly lower than that of Pt-TiO₂. The difference is due to the presence of impurities in the SWNT. The dependence of the H₂ evolution on the content of carbon nanotubes and other carbon nanomaterials, concentration of various alcohols are discussed. Finally, a plausible reaction mechanism of H₂ evolution is presented.

Chapter 3 illustrates H₂ production from diacids and their decomposition over the mixture of TiO₂ and single walled carbon nanotubes. The highest hydrogen evolution rates from aqueous oxalic acid and fumaric acid were found to be 15.7 and 2.6 mol h⁻¹, respectively. In the absence of SWNTs, however, a negligible amount of hydrogen gas was observed. The content of SWNTs was changed from 1 to 20 wt% and the optimum hydrogen production was observed around 5 wt% for fumaric acid and 7 wt% for oxalic acid. The experiment was also performed to find the pH effect on the hydrogen production. The decomposition reaction was associated with the evolution of CO₂ gas. The influence of added inorganic anions on the hydrogen production was also studied.

Chapter 4 discusses the The spectroscopic studies carried out on chlorophyll (Chl) and cobalt(II)tetraphenylporphyrin (CoTPP) solubilized in poly(L-glutamate) (Poly(Glu))-decylammonium chloride (DeAC) as well as poly(L-glutamate, L-tyrosine) (Poly(Glu,Tyr))-DeAC complexes, in the presence of MV²⁺. Cooperative binding occurred between anionic polypeptides and cationic DeAC, leading to the formation of micelle-like hydrophobic clusters of DeAC. The fluorescence quenching of Chl as well as that of CoTPP by MV²⁺ indicates that electron transfer occurs in the polypeptide-surfactant complex. In the case of Poly(Glu,Tyr), the electron transfer is complicated by the presence of tyrosine residue. Well-dispersed, polypeptide-protected platinum colloid with an average size of 50
nm was formed in an aqueous solution of DeAC. Finally, hydrogen production was carried out in the presence of Chl or CoTPP in the Pt-loaded oly(Glu)-DeAC complex and MV$^{2+}$ as an electron acceptor and EDTA$^{2-}$ as a sacrificial electron donor. The rate of hydrogen production was dependent on the formation of the polypeptide.

**Chapter 5** describes the photocatalytic activity of a bilayer-thin film (GS/TiO$_2$) composed of GS and TiO$_2$, prepared by the liquid laser ablation method. The photocatalytic activities of the GS/TiO$_2$ particles were evaluated by measuring the rate constant for the decomposition of methylene blue in water and the photocatalytic hydrogen evolution in water-ethanol solutions. The clay portion of GS was found to enhance the photocatalytic activity by increasing the surface charge of TiO$_2$ and the number of protons around TiO$_2$ due to the ion exchange property of GS. This leads to the decomposition of methylene blue and also photoinduced hydrogen production.

**Chapter 6** discusses the effect of graphite silica (GS) on TiO$_2$ photocatalysis of photoinduced hydrogen production in water-methanol mixtures. Hydrogen production was drastically enhanced by GS in water-methanol mixtures. A synergy effect between the clay portion of GS and TiO$_2$ was proposed. The clay in GS has an ion-exchange property which leads to an increase in protons in the water-alcohol mixture leading to the increase in hydrogen production.

**Chapter 7** shows the application of single walled carbon nanotubes as a replacement for the Pt counter electrode in semiconductor based solar cell. Dye-fixed TiO$_2$ films and doubly layered Fe$_2$O$_3$ films were prepared and used in solar cells. For the both cells a single walled carbon nanotube (SWNT) film, prepared by simply pasting over ITO glass, was used as a counter electrode. A stable current (I)-Voltage (V) curve was found under UV-visible light
irradiation using KI+I$_2$ in water as an electrolyte. A comparison of I-V curves between Pt and SWNT films has been made. Under UV visible light irradiation almost similar results were found for both Pt and SWNT films. In the case of Fe$_2$O$_3$, the open circuit voltage was found to be low (about 90 mV) but the short circuit current was found to be comparatively high (about 0.75 mA cm$^2$) whereas those for the Eosin Y (EY)-fixed TiO$_2$ film with the SWNT film as a counter electrode, were found to be 350 mV and 0.27 mA cm$^2$, respectively.

Chapter 8 presents the N-doped TiO$_2$ thin films prepared by the laser ablation method under an N$_2$ gas atmosphere. The properties of the films such as color, the relative amount of N doped and the crystal structure strongly depended on substrate temperature and N$_2$ gas pressure. XPS data indicated that the amount of doped N unexpectedly increases with decreasing N$_2$ gas pressure in the range of ca. 40 – 270 Pa. We proposed that the N-doping occurred when N species and TiO$_2$ particles collide on the substrate. The decomposition of methylene blue using the N-doped TiO$_2$ thin film was also performed under visible light irradiation. Moreover we succeeded in enhancing the photocatalytic activity of the thin films under visible light by changing the distance between the target and the substrate.


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