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Plasmon-Induced Water Splitting under Visible Light Irradiation using Gold Nanostructured Strontium Titanate Single Crystal Substrate

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using Gold Nanostructured Strontium Titanate Single Crystal
Substrate

Thesis by

Yuqing Zhong

In Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy

RESEARCH INSTITUTE FOR ELECTRONIC SCIENCE
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TO
MY PAPARENTS
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Thesis Abstract

As a potential solution to the energy crisis, H₂ production from water via solar irradiation has attracted global attention over the last few decades, because the chemical energy in H₂ can be stored for long periods. Numerous attempts have been made since the photoelectrochemical (PEC) water splitting based on an n-type TiO₂ photoanode was discovered. However, because of the wide band gap of the semiconductor materials adopted, only UV light can be used to directly drive the water splitting reaction. The UV irradiation merely accounts for 5% of the solar spectrum. Visible and infrared light, which take the major part, are still underutilized. Therefore, it is of significance to extend the light-energy conversion to longer wavelengths, especially to the visible and infrared regions. Common materials used for water splitting are particulate. They are undesired because extra energy is required to separate H₂ and O₂, which evolved in the same reaction chamber. In addition, an external electric bias is necessary in PEC water splitting. To overcome these problems, a plasmon-induced water splitting system under visible light irradiation using gold nanostructured strontium titanate (SrTiO₃) single crystal is presented in this study. Gold nanoparticles (Au-NPs) with particle size of several tens of nanometer were employed for SrTiO₃ surface decoration, which enhanced the SrTiO₃ photorespons in visible wavelength region due to the localized surface plasmon resonance. It is proposed that the simultaneous evolution of H₂ and O₂ can be realized without an electric wire connecting the anode and the cathode and with space conserved for light irradiation on the anode side through the use of two sides of the same semiconductor substrate.

In order to fabricate Au-NPs, a 3-nm Au thin film was sputtered on SrTiO₃ surface and annealed in nitrogen atmosphere at 800°C. After annealing, the gold films transformed to a discontinuous nanoparticle structure. The Au-NPs exhibited characteristic plasmon resonance band with a peak at ca. 630 nm. Numerical simulation shows that the electromagnetic field intensity is greatly enhanced around the interface between gold and SrTiO₃ substrate. The stoichiometric evolution of H₂ and O₂ was clearly
demonstrated. The efficiency action spectrum closely corresponds to the plasmon resonance spectrum, indicating that the plasmon-induced charge separation at the Au/SrTiO$_3$ interface promotes water oxidation and the subsequent reduction of a proton on the backside of the SrTiO$_3$ substrate. The photo energy derived from visible light irradiation is successfully converted to chemical energy, which is stored as the form of H$_2$ gas. As a substitution of the conventional external electric bias, the chemical bias used to promote water splitting is significantly reduced to 0.23 V by plasmonic effects (Chapter 2).

The co-catalyst effect on hydrogen evolution in the plasmon-induced water splitting is discussed in detail. A Pt board was stick on the SrTiO$_3$ substrate via In-Ga alloy to obtain ohmic contact. The water spitting yield with this SrTiO$_3$/Pt composite substrate was remarkably enhanced. Subsequently, the Pt board was decorated with a noble metal or metal oxide as a co-catalyst for H$_2$ evolution. Enhanced evolution of H$_2$ and O$_2$ with stoichiometric ratio was demonstrated with all kinds of co-catalysts. Rhodium thin layer exhibited relatively high performance as a 3-fold increment compared with the absence of any co-catalyst. The separate evolution of H$_2$ and O$_2$ was successfully realized, so as to suppress the undesirable reverse reactions of water splitting. A rational evaluation method of the co-catalyst is thus developed based on the elimination Schottky barrier (Chapter 3).

A facile plasmon-enhanced water splitting system using gold nanostructured semiconductor heterojunction is described. With a larger potential gradient in the energy band, the electron transfer can be facilitated by using semiconductors with different band positions. The substrate composed of single crystal SrTiO$_3$ with the rutile TiO$_2$ thin film heterojunction exhibited enhanced water spitting activity compared with the absence of TiO$_2$ thin film because the back electron transfer reaction might be prevented due to the synergistic effect. The effect on the H$_2$ evolution efficiency of the thickness of the Pt co-catalyst film was also explored (Chapter 4).

Herein, the plasmon-enhanced water splitting was demonstrated in visible wavelength with gold nanoparticles loaded SrTiO$_3$. The H$_2$ and O$_2$ generation efficiency is
highly dependent on the pH values of the solution environments. It is expected that the plasmon resonant wavelength of Au nanostructures can be tuned by simply changing their shape and/or size to cover a large part of the solar spectrum. It indicates the possibility of constructing an artificial photosynthesis system with low energy consumption. The results of these studies warrant future research to evaluate the mechanism of plasmon-enhanced water splitting and provide a facility approach for further design of the plasmon-enhanced solar energy conversion devices.

**Keywords:** electrochemistry, artificial photosynthesis, strontium titanate (SrTiO₃), localized surface plasmons, photochemistry, water splitting, nanostructures.
Chapter 1

Introduction

1.1 Background and Motivation

The dramatic increase of the world population in the last century raises the question of how long the resources of our planet will last. The world population has been estimated to be 7.209 billion by December 6th, 2014 and it is expected to increase even more rapidly according to the World Population Report of the United Nations Population Fund.\[1\]

At the same time the world energy consumption, mostly based on fossil fuels such as oil, coal and gas is also increasing.\[2\] These resources are created by a very slow geological process and their quantity is therefore limited. As a finite resource, it is reasonable to be expected to reach a limitation and decline in the production afterwards.

The oil and natural gas have been predicted to last for a number of decades by several estimations, while the coal could last up to a few hundred years, although there is no agreement on the exact numbers. Most of these analyses are based on conventional oil storage, but the numbers will be different if new oil resources can be found and extracted. Currently, oil companies are investing in unconventional oil, extracted it with techniques different from the traditional oil well method and from places that can not be reached with the present technology. This oil is definitely more expensive than the conventional one. The world economy will be seriously damaged if the production of oil starts to decrease rapidly. Therefore an effective solution of this problem by means of the introduction of new technologies must be activated well ahead of schedule since the time scale for introducing new technologies to our society could be very long.

The use of fossil fuels is also relevant to a number of other issues. For instance, when fossil fuels are consumed and burnt, CO\textsubscript{2} is emitted into the atmosphere. This gas will remain in the atmosphere for many years because it can not be fixed by nature rapidly. The
carbon cycle will be broken consequently. Human activities have been confirmed to give rise to the increase of the CO$_2$ concentration in the atmosphere. The CO$_2$ is supposed to bring about some environmental problems because it is a green house gas. The average temperature in the globe will be increased along with the CO$_2$ amount in the atmosphere. The warming of our planet will probably result in the melting of the arctic ice and glaciers and finally changes of climate with negative influence of all the life forms. Actually, the global temperature has already been observed increasing recently. The solution for the decrease of the CO$_2$ production needs to be mastered as quickly as possible.\[^3\]

![Figure 1.1 Total World Energy Consumption by Source 2013](image)

So far, there has been some CO$_2$ sequestration method proposed by several researchers. However, these solutions all involve capturing and trapping the emitted CO$_2$ underground. Therefore, they are not feasible solutions for long term since they cannot close the carbon cycle, but merely a postponement of the situation as a result.

When we pursuit a civilized society with the energy sources that are especially sustainable and renewable to substitute the fossil fuels, the solution has eventually been the sun that always seen shining in the sky over our heads. As a yellow dwarf star, the sun has a diameter of about 109 times compared with the one of the earth. The nuclear fusion of hydrogen into helium takes place in the sun and thus produces energy. This kind of energy diffuses into the surrounding outer space as the form of kinetic energy of light radiation or particles after generated in the core of the sun. It can be considered as a source
of energy that will never exhaust on human time scale, because the sun is supposed to keep shining for billions more years.

In Figure 1.2, the solar irradiance is plotted as a function of wavelength for standard condition (air mass 1.5, i.e., AM 1.5). The average flux of solar irradiation reaching the earth surface is 174.7 W/m² taking the scattering and absorption by the atmosphere and the clouds into consideration. The tremendous potential of the solar energy is obvious because the human average power consumption worldwide is about 15 TW every year. If we could build a photoelectric conversion device with a solar energy conversion efficiency of 10%, only 0.2% of the earth surface area needs to be covered with such kind of devices in order to obtain the energy of 15 TW as mentioned.

Nevertheless, the solar irradiation is not a source of energy that is constantly available. Because the day and night alters and it also highly dependent on the weather conditions, such as sunny and cloudy day, etc. Hence, this kind of energy has to be stored as a readily useable form. Whereas for the purpose of making large amount of energy stored, electricity has never been an ideal choice. Superior performance could be obtained by chemical energy with a higher energy density. In such scenario, the energy is stored in chemical bonds and could be released whenever necessary by a simple chemical reaction, combustion in the case of fossil fuels for instance.

![solar spectrum AM 1.5](image)

**Figure 1.2** The radiation energy in solar spectrum as a function of wavelength.
1.2 Origin of Photoelectrochemical (PEC) Water Splitting

Innovations in both science and technology are inspired by the increasing demand for renewable energy. Being considered as one of the most potential clean energy carriers, hydrogen possesses the unique characters. It has a very high energy density. The enthalpy of combustion is 286 kJ/mol. And since the only product after the burning of hydrogen is water, without any other pollutant or green house gas, it is environmental friendly. Furthermore, hydrogen also has some important industrial applications, e.g., fuel cell industry and industrial ammonia synthesis. Up until now, the production of hydrogen is mainly by means of biomass or fossil fuels reforming reactions.\(^{[4]}\) The commercial hydrogen gas is produced by the steam reforming of natural gas (methane) in industry.

\[
\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow 4\text{H}_2 + \text{CO}_2 \quad \Delta G^0 = 131 \text{ kJ mol}^{-1}
\]  

(1-1)

If we take energy and environmental issues into consideration, the present technique is defective and even unacceptable. Firstly, very high temperature (700-1000°C) is necessary during this process since it is an intensive endothermic reaction. Secondly, this reaction has to consume the non-renewable fossil fuels and there is green house gas \(\text{CO}_2\) emission as a byproduct in the process. These drawbacks during the industrial production process hinder the extensive application of \(\text{H}_2\). As a consequence, the production of \(\text{H}_2\) via environmental-friendly and renewable methods has been come an urgent issue.

Water is a perfect source of hydrogen from the view point of saving fossil fuels and to avoid the undesired \(\text{CO}_2\) emissions. However, external energy driving force, e.g., electrical power, is needed in order to split water into \(\text{H}_2\) and \(\text{O}_2\). The process is a general knowledge as the electrolysis of water.

\[
\text{H}_2\text{O}(g) \rightarrow \frac{1}{2}\text{O}_2(g) + \text{H}_2(g) \quad \Delta H^0 = 241.8 \text{ kJ mol}^{-1}
\]  

(1-2)

An inexpensive and clean energy substitution that is capable to supply the power for our planet could be expected as the form of \(\text{H}_2\) if we can make use of a renewable source, such as solar energy, as the energy input.\(^{[5]}\) Some hydrogen production methods from
water using solar light have been proposed. One of them is electrolysis of water by a solar cell. Besides, promising strategies have also been provided through photocatalytic or (PEC) water splitting to achieve this purpose.\textsuperscript{[6-8]}

Honda and Fujishima demonstrated the photoelectrochemical water splitting for the first time under ultraviolet (UV) irradiation using n-type single-crystal TiO\textsubscript{2} photoelectrode in 1972.\textsuperscript{[9,10]}

Under UV irradiation, electrons and holes are generated in TiO\textsubscript{2}, as shown in Figure 1.3. With some external electric bias, water can be reduced by the photo-induced electrons to generate H\textsubscript{2} on the Pt counter electrode. On the other hand, O\textsubscript{2} will be formed on the TiO\textsubscript{2} photoelectrode via the water oxidation by the remained holes. During this reaction course, the UV light harvesting and the electron generation for water reduction are through the agency of the TiO\textsubscript{2} semiconductor. It plays a key role in the conversion of the irradiation energy into the chemical energy, which is stored in H\textsubscript{2}, by splitting the water molecules. This kind of functional semiconductor is thus commonly referred to as photocatalyst in this research field. In the last few decades, a great deal of research on the photocatalytic water splitting based on the semiconductor materials have been proceed after the pioneer work of Honda and Fujishima.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{The sketch map of Honda-Fujishima effect-water splitting using a TiO\textsubscript{2} photoelectrode.}
\end{figure}
Among the various kinds of semiconductors, only a few of them are capable of performing the photocatalytic water splitting reaction. As is known to all, there is a band gap separating the conduction band (CB) and the valance band (VB) in semiconductors. The electrons can be excited from CB to VB and leaving holes in the VB if the semiconductor is irradiated by an incident light with the energy larger than its band gap. Then H₂ and O₂ will be subsequently formed through the water reduction by the electrons and the water oxidation by the holes respectively to complete the overall water splitting.

Theoretically, in order to ensure the water splitting reactions to carry out normally, there are three key issues. For the thermodynamically aware, the electrons and holes generated by the incident light excitation should have the appropriate redox potentials so as to perform the reduction and the oxidation reactions of the water molecules. In other words, the bottom position of the conduction band needs to be more negative than the redox potential of H⁺/H₂ (0 V vs. NHE), and meanwhile the top position of the valence band needs to be more positive than the redox potential of O₂/H₂O (1.23 V vs. NHE), as shown in Figure 1.4. As a consequence, only the semiconductors with a band gap larger than 1.23 eV and with proper positions of CB and VB are candidates for water splitting.

Figure 1.4 Fundamental steps for water splitting reaction by solid-state photocatalysts.

Based on the above mentioned analysis, it seems that the ideal options of the materials for water splitting are semiconductors with relatively large band gaps. To date, a lot of
such semiconductors have been investigated for PEC water splitting, such as TiO$_2$,$^{[11]}$ ZrO$_2$, ZrO$_2$, $^{[12]}$ K$_4$Nb$_6$O$_{17}$, $^{[13, 14]}$ et al. Nevertheless, a severe drawback of the large band gap semiconductors is that they can only absorb the UV light. Whereas taking the efficiency issue into consideration, the energy composition of the solar spectrum (AM 1.5) is constituted by ca. 2% ultraviolet light, 47% visible light (corresponding to the wavelength region from 380 nm to 780 nm) and 51% infrared light. A major part of the solar energy will thus be wasted if we use the large band gap semiconductors for water splitting. Therefore, many new types of photocatalysts that respond to visible light are currently under investigation. Besides these basic requirements and efficiency problems, the stability of the semiconductor materials in aqueous solutions under irradiation of light is another important issue. Due to their appropriate energy band positions, several chalcogenide semiconductors have been considered as suitable photocatalysts for water splitting that respond to visible light irradiation. Even though some of these chalcogenide semiconductors, CdS for example,$^{[15, 16]}$ is capable of splitting water very efficiently under visible light irradiation,$^{[17]}$ the CdS itself will also be oxidized by the photogenerated holes during the water splitting reaction process. A dramatic decrease of the water splitting efficiency is inevitable as the result of the decomposition of the catalytic material CdS. Therefore, for most chalcogenide photocatalysts, this is a critical defect. At present, a great challenge still remains for the development of semiconductors materials that are stable and feasible for photoelectrochemically splitting water very efficiently under the solar irradiation.
1.3 PEC Water Splitting over Semiconductor Photocatalysts

1.3.1 Basic Principles of PEC Water Splitting

Only the deep ultraviolet light with a wavelength shorter than 190nm can be used to split water directly, since the visible light cannot be absorbed.\[^{18}\] As mentioned in the former section, at least 1.23 V bias is required to promote the electrolysis of water. The bias voltage at this amount is corresponding to an irradiation light wavelength of about 1000 nm. Therefore, the utilization of the visible region of the solar spectrum for water splitting could be expected theoretically, in condition that the irradiation is used very effectively. The original work of H₂ generation from water splitting was done by Honda and Fujishima in 1970s. As shown in Figure 1.5, the typical PEC water splitting cell they have used is composed of a photoanode of n type TiO₂ semiconductor and a Pt counter electrode.

![Figure 1.5 Photoelectrochemical water splitting cell based on n type semiconductor TiO₂ photoelectrode.\[^{19}\]](image)

The surface region of the TiO₂ photoelectrode is charged, as the result of the charge transfer at the interface between the electrolyte and TiO₂, since they contact. The charges move from the TiO₂ to the electrolyte, a surface charge area is thus formed and the energy
band of the TiO$_2$ bends upwards, as depicted in the figure. The potential barrier resulted by this energy band bending is referred to as Helmholtz barrier. The property of the semiconductor and the characteristic of the aqueous electrolyte both affect this barrier. At the interface between the electrolyte and semiconductor, this Helmholtz barrier could drive the separation between electrons and holes. Furthermore, the transportation of chargers at the bending band region would also be facilitated. Electron and hole pairs will be generated in the TiO$_2$ when it is irradiated by light with an energy larger than its bandgap value. The electrons excited by light irradiation will transfer to the counter electrode and generate H$_2$ evolution by reducing water, whereas the holes will remain at the TiO$_2$ surface and generate O$_2$ evolution via water oxidation.$^{[20, 21]}$ The reactions on the two electrodes can be described by equations as follow:

\[
\text{Photanode: } \quad \text{H}_2\text{O} + 2h^+ \rightarrow 2\text{H}^+ + 1/2\text{O}_2 \quad E_{\text{ox}}^0 = -1.23 \text{ V} \quad (1-3)
\]
\[
\text{Cathode: } \quad 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \quad E_{\text{red}}^0 = 0 \text{ V} \quad (1-4)
\]

In principle, to drive the solar water splitting, a minimum amount bias voltage of 1.23V is generally required between the two electrodes. The bandgap of the semiconductors used in the water splitting reaction is usually larger than 1.23V accordingly. Nevertheless, the essential conditions for a water splitting system to function stably include but are not limited to a suitable bandgap value. An external electric bias is necessary to drive the water splitting reaction in many situations, even using a semiconductor with a bandgap larger than 1.23 eV, such as Fe$_2$O$_3$ and WO$_3$. Actually, the external bias needed is highly dependent on the energy band structure of the semiconductors.

There are three major steps in a typical photocatalytic reaction, as shown in figure 1.6. They all have strong impact on the photocatalytic capability of a photocatalyst.
Figure 1.6 Processes involved in photocatalytic overall water splitting on a heterogeneous photocatalyst.

(i) Electron hole pairs generation in photocatalysts by means of photon absorption. If the incident irradiation has an energy larger than that of the semiconductor bandgap, the photons from the incident light can be absorbed and electron hole pairs will be generated consequently. The electrons will transfer to the conduction band of the semiconductor after the excitation by the incident photons. On the other hand, the holes will remain at the valence band. The electrons and holes will reduce and oxidize water molecules to form H₂ and O₂ generation respectively to accomplish the overall water splitting.

(ii) The separation and migration of the electron hole pairs generated by photoexcitation. Generally, before the electron hole pairs participate in the photocatalytic reactions, they need to separate and transfer to the reaction sites on the photocatalysts surface. During this process, the crystal structure, crystallinity and the particle size of the semiconductor material show a great influence. Defects often function as a charge trap and also a recombination center for the electrons and holes generated by photoexcitation. Therefore, they are undesired in the semiconductor used as a photocatalytic material since
the activity will sure be ruined. The photocatalyst with relatively higher crystallinity takes advantage for charge separation and migration in this respect since the number of defects would be smaller. The photocatalyst particle size should be small in order to obtain higher efficiency. The reason is that the surface area and the number of the reactive sites are larger for smaller particles. Furthermore, the distance that an electron or a hole has to transfer to the surface reaction sites is shorter so as to reduce the recombinations.

(iii) The chemical reactions on the semiconductor surface. This step is influenced by the active sites and the area of the surface. A large part of the electrons and holes generated in the above steps will be lost in the recombination instead of participate in the water splitting, in spite of the fact that they possess enough potentials thermodynamically for the reaction. To address this issue, many kinds of co-catalysts, such as Pt,[22] Pd,[23] Ru,[24] NiO,[25] RuO₂,[26] and Cr/Rh oxides,[27] are decorated on the surface of photocatalysts. The function of these co-catalysts is generally considered to be as the active sites, where the photocatalytic reactions take place. Except for the formation of the active sites on the semiconductor surface, increasing the surface area of photocatalysts, e.g. fabrication of some nanostructures on the photocatalysts, is another effective method to enhance the photocatalytic activity.

These three steps are all essential for photocatalytic water splitting reaction. Hence, an ideal photocatalyst should possess suitable energy band structure, bulk properties and surface characters. Until now, the photocatalytic water splitting research still remains in the laboratory level. This means that some mechanisms are not yet clearly understood. And visible light driven photocatalysts with acceptable efficiency have not been developed. A lot of efforts have been made to explore new type of photocatalysts and to functionalize or modify photocatalysts that already exist.

1.3.2 Common Materials for PEC Water Splitting

Some essential requirements have to be fulfilled in the semiconductor materials used for the water splitting reaction so as to obtain a considerable efficiency. Generally, the
semiconductors should have conduction band and valence band straddling the redox potentials of $E^0(\text{H}^+/\text{H}_2)$ and $E^0(\text{O}_2/\text{H}_2\text{O})$.\cite{28} By this means, the water splitting reaction can be promoted by the photogenerated electrons and holes with enough electrochemical potential in the absence of any external bias. Moreover, the semiconductors should be capable of absorbing solar irradiation efficiently and also stable for a long term during the water splitting process. The absorption ability for solar irradiance is affected by the semiconductor bandgap. It greatly influences the solar to hydrogen conversion efficiency.

The solar energy spectrum on the basis of irradiation energy and photon numbers is shown in Figure 1.7. The UV irradiation only takes a quite small part of the whole solar spectrum as can be seen in the figure.

![SOLAR ENERGY SPECTRUM](image)

**Figure 1.7** Number of photons in solar spectrum, versus photon energy. The optical band gaps of common metal oxide photocatalysts are indicated for comparison.\cite{29}

The minimum bandgap for a semiconductor used in PEC water splitting is 1.23 eV in theory. However, because of the energy loss in the PEC water splitting process, the photons that could be utilized practically, usually have energy larger than 1.23 eV. And the solar to hydrogen conversion efficiency is still much smaller than we expected. There are several reasons that can induce this energy loss, such as the polarization within the
PEC, the recombination between electrons and holes, and the potential loss caused by the resistance of electrodes and contact. The energy loss has been estimated to be about 0.8 eV. The practical energy limit of the photons feasible for PEC water splitting is thus determined to be about 2.0 eV. The great effort that has been devoted into the research of visible light respond PEC water splitting is also based on this concern.

Many researchers have focused on the investigation of new type semiconductor materials with preferable performance for PEC water splitting ever since the innovative work with a TiO$_2$ photoelectrode succeeded. So far, numerous materials have been developed for the PEC water splitting, including metal oxides such as TiO$_2$, Fe$_2$O$_3$, ZnO, Nb$_2$O$_5$, BiVO$_4$, ZrO$_2$, WO$_3$, metal nitrides such as Ta$_3$N$_5$, metal phosphides such as GaP, metal titanate such as SrTiO$_3$, BaTiO$_3$, metal tantalate such as KTaO$_3$, and metal oxynitrides such as TaON. These materials are all used as photoelectrodes. They can be classified as either photoanodes or photocathodes according to the different reactions occur on their surfaces. As described in the former section, there are three main steps in the PEC water splitting: solar irradiation absorption, charge separation and migration, and surface chemical reactions. The intrinsic properties of the catalytic materials, e.g. energy band structure, bandgap value, crystallinity, electronic conductivity, and particle morphology, have a significant influence on these processes.

The energy band structures of typical catalytic semiconductor materials and their corresponding bandgap values are shown in Figure 1. The normal hydrogen electrode (NHE) at pH=0 and vacuum energy level are both employed. For metal oxides, only the ones with bandgaps large enough, such as SrTiO$_3$, ZrO$_2$ and ZnO, can straddle the both redox potentials of water. However, the light harvesting ability will be limited if the bandgap is too large. And the PEC water splitting efficiency will also be seriously affected. Whereas in the case of metal oxides with relatively small bandgap, such as WO$_3$ and Fe$_2$O$_3$, external bias is necessary to promote the water splitting reaction since the conduction band position is not more negative than the reduction potential of water. Furthermore, the Fe$_2$O$_3$ has a very poor electrical conductivity, the recombination between
electrons and holes is thus severe because of its limited carrier diffusion length. CdSe and CdS seem to have both the suitable CB and VB positions and small bandgap values. However, they are not stable during the water splitting process. They can be readily oxidized to metal oxides and the ideal energy band structure would no longer exist.\textsuperscript{\textcolor{red}{[85, 86]}}

\textbf{Figure 1.8} The bandgap and band structure potentials of typical semiconductors relative to the redox potential of water; the potentials are versus normal hydrogen electrode (NHE) at pH=0 and vacuum potential.\textsuperscript{\textcolor{red}{[84]}}

For metal nitrides and metal oxynitrides, in despite of that the band structure and electronic property of catalytic materials can be modified by the incorporation of nitrogen, the nitride materials will finally lose their activity upon the irradiation because of photodecomposition. A considerable percentage of the solar irradiation can be absorbed by silicon, because its bandgap is quite small (1.1 eV). However, silicon has a valence band that is not more positive than the water oxidation potential. An external bias is thus inevitable. It can be supplied by making hybrid devices, e.g., a hybrid system of PEC device and dye sensitized solar cell.\textsuperscript{\textcolor{red}{[87-90]}} Nevertheless, because of the large surface overpotentials and surface oxidation, silicon is also unstable under irradiation.\textsuperscript{\textcolor{red}{[91]}} The solutions of the issues in catalytic semiconductors about light harvesting, energy band structures, electronic property, and chemical durability, have been systematically
investigated. Some strategies have been proposed such as nanostructure decoration and chemical modification, e.g., element doping, design of semiconductor surface heterojunction, and co-catalyst modification.

1.3.3 Development of Visible Light Driven Water Splitting

With the purpose of water splitting in the absence of any external bias, semiconductor materials with flat band potential more negative than the $\text{H}^+/\text{H}_2$ potential, such as SrTiO$_3$ or KTaO$_3$, are preferred. However, as shown in Figure 1.9, these materials are usually unable to absorb visible light because of their large bandgaps. The solar energy conversion efficiency is very low as a result.

![Diagram of water splitting](image)

**Figure 1.9** Photoelectrolysis of water using a SrTiO$_3$ photoanode. Due to the position of conduction and valence band edges hydrogen and oxygen are evolved without need of external bias.

So far, visible light driven photocatalytic materials have been investigated extensively. For UV respond metal oxide photocatalysts, as can be seen in Figure 1.8, the bottoms of
the conduction bands are slightly more negative than 0 V, whereas the tops of the valence bands are more positive than 3 V (vs. NHE at pH 0). As a consequence, visible light can not be absorbed due to the large bandgap. However, these metal oxide photocatalysts are capable of oxidizing water since there is a considerable difference between the top of the valence band and the oxidation potential of water (1.23 V vs. NHE). Hence, it would be of significance if we can maintain the conduction band position and meanwhile improve the band structure. Figure 1.10 shows the main techniques to utilize visible light by a metal oxide with a large bandgap. They are summarized accordingly as follows.

![Figure 1.10 Primary approaches of energy band engineering for a metal oxide to obtain the visible light response.](image)

(i) Doping with transition-metal ions. One of the most common used methods for the crystal structure modification of a metal oxide is to dope it with some other elements. In general, the dopant will substitute a lattice point of the crystalline host material. Consequently, it forms a donor or acceptor level in the forbidden band of the semiconductor by the dopant which is a transition-metal ion. These doping levels functions as a visible absorption center. Unfortunately, the dopant usually serves as discrete energy levels instead of an energy band. The efficient transfer of the electrons and holes will be seriously affected as the result. Furthermore, when we dope the host metal oxide with another element, the charge balance is destroyed in many circumstances.
Vacancies that function as recombination centers can be readily generated. Therefore, the doping method is not an ideal solution for the metal oxide material used as visible light driven photocatalyst to some extent.

(ii) Valence band control using the p orbitals of an anion or the s orbitals of metal ion. In despite of some successful examples about the above mentioned doping method, the adverse effect of the defects working as recombination centers is still serious. Moreover, the discrete doping levels formed by the dopants hinder the carrier transfer. In contrast, it would be preferable for the metal oxide to have a continuous valence band formed by atomic orbitals of the constituent elements. A lot of researchers have reported this kind of special photocatalysts with a valence band-control.\[95\]

![Figure 1.11](image)

**Figure 1.11** Basic principle of visible light driven water splitting based on spectral sensitization depicted by energy band alignment

(iii) Spectral sensitization. In the early 1970s, H. Gerischer demonstrated the spectral sensitization of semiconductor particles with large bandgap.\[96\] Since then, in order to realize the H\textsubscript{2} generation by visible light driven water splitting, a great effort has been made to the development of this strategy.\[97-104\] The main process of the spectral sensitized water splitting is shown in Figure 1.11. Organic dyes and inorganic semiconductors with a narrow bandgap can be employed as sensitizers. Their bandgap should be small enough to
absorb the visible light. In addition, their excited-state potential needs to be higher than the conduction band of the metal oxide to facilitated electron injection. The electrons injected are involved in the water reduction to generate H₂ at a co-catalyst such as Pt. While the sensitizers are compensate with electrons from donor molecules. Water is the ultimate electron donor in a system without the sacrifice reagent. However, sacrificial reagent such as alcohols, organic acids, and hydrocarbons, are commonly used to avoid the side reactions such as H₂-O₂ recombination. In this situation, the electron transfer from the sensitizer to co-catalyst, e.g. Pt, is mediated by the semiconductor. There is a competition between the water reduction and the electron back transfer to the oxidized sensitizer. Therefore, the H₂ evolution activity is highly dependent on the semiconductor material, the sensitizer and the co-catalyst in this system.\textsuperscript{105-115} To date, a number of visible light driven photosynthesis systems have achieved apparent quantum efficiency as high as several tens of percent for H₂ generation from water using spectral sensitizers with suitable electron donor.

Figure 1.12 Overview of water splitting on Z-scheme photocatalysis system with an iodate (IO₃⁻) and iodide (I⁻) ion redox couple.\textsuperscript{28}
Another main approach for achieving visible light driven water splitting is to apply a two-step photoexcitation process using two different photocatalysts, as depicted in Figure 1.12. This strategy is known as the Z-scheme water splitting. It was inspired by natural photosynthesis through which the green plants convert solar energy into chemical energy. In such a two-step system, the water splitting process is divided into two stages: one for H₂ generation and the other for O₂ generation. A solution containing the shuttle redox couple (Red/Ox in the figure) will connect them. At the H₂ evolution photocatalyst, H₂ evolves via water reduction by the photoexcited electrons, while the holes in its valence band oxidize the reductant (Red) to oxidant (Ox). The oxidant is subsequently reduced back to the reductant by photoexcited electrons generated at the O₂ evolution photocatalyst, where the holes oxidize water to evolve O₂. The energy requirement for photocatalysis is substantially reduced by this system. The utilization of visible irradiance for water splitting has thus become more efficient. This means that the semiconductor with the capability of either reducing or oxidizing water can be used in overall water splitting. For instance, some visible light active oxides such as SnO₂ can be used as O₂ evolution photocatalysts in condition that they can reduce certain oxidant to a reductant. Similarly, non-oxide photocatalysts such as sulfides, oxynitrides and dyes, can be used as H₂ evolution photocatalysts in condition that they can oxidize certain reductant to an oxidant. Therefore, many kinds of semiconductor materials can be utilized in the Z-scheme water splitting despite that they are unqualified in one-step system. Furthermore, separate evolution of H₂ and O₂ can be realized in Z-scheme system via a separator by which only the redox mediators can be transferred. It is theoretically impossible to obtain separate generation of H₂ and O₂ in a conventional one-step system because H₂ and O₂ are simultaneously evolved at small semiconductor particles. However, there is a critical drawback of the Z-scheme systems that the number of photons required in a two-step photoexcitation system is twice that for a one-step system to achieve overall water splitting.
1.3.4 Plasmon-enhanced Water Splitting

Plasmon is a collective oscillation of the free electron gas density in a conductive material, as shown in Figure 1.13. Light below the plasma frequency will be reflected since the electrons in the metal screen its electric field. Light above the plasma frequency will be transmitted since the electrons respond too slowly to screen it. Surface plasmons are coherent delocalized electron oscillations confined to the surfaces of conductive materials. The interaction between surface plasmons and light is very strong. If the real part of the dielectric function becomes zero, at the plasmon frequency, there will be a resonance in the absorption. Intense electric fields can be generated on the surface of the metal nanoparticles when they are irradiated by light at their plasmon frequency. The size, shape and material of the nanoparticle and its distance from other nanoparticles all have significant impact on the frequency of this resonance.\textsuperscript{[125-128]} For instance, if we fabricate the silver nanoparticle to a size small enough, its plasmon resonance can be shifted from the UV region into the visible range. Similarly, the regulation of the gold plasmon resonance from the visible region to the infrared region is also possible via the nanoparticle size miniaturization.

![Figure 1.13](image.png)

**Figure 1.13** Schematic of plasmon oscillation for a sphere, showing the displacement of the conduction electron charge cloud relative to the nuclei.\textsuperscript{[129]}

Improved photocatalytic water splitting under visible irradiation has been demonstrated by a number of researchers via plasmonic metal nanoparticles deposition on the top of anatase TiO\textsubscript{2}. In such a scenario, the H\textsubscript{2} and O\textsubscript{2} generation is detected by gas chromatography with mass spectrometry, and the photocurrents are monitored via a
Thomann et al. have observed the enhanced photocurrent of water splitting using Au/Fe$_2$O$_3$ as the photocatalyst. The maximum enhancement was as high as 11-fold. An interesting phenomenon was also discovered that the position of the gold nanoparticles in the Fe$_2$O$_3$ film had a great impact on the photocurrent enhancement peak position and curve shape. Enhanced photocatalytic water splitting was also reported by Torimoto et al. using Au core-SiO$_2$ shell particles decorated with CdS nanoparticles. As shown in Figure 1.14, Liu et al. deposited Au nanoparticles on the top of catalytic TiO$_2$ as photoanode. They have demonstrated photocurrents through the water splitting reaction with the enhancement of 5-fold and 66-fold at the visible irradiation wavelength of 532 nm and 633 nm, respectively.

Figure 1.14 (a) Schematic diagram of the photoelectrochemical measurement setup. (b) Photocurrent of anodic TiO$_2$ with and without Au nanoparticles irradiated with $\lambda = 633$ nm light for 22 s.

Ingram et al. reported a visible light driven photocurrent using nitrogen-doped TiO$_2$ decorated by Ag nanocubes with a 10-fold enhancement compared with in the absence of Ag nanocubes. Duan et al. also observed enhancement of light absorption by Ag nanoparticles on CdS with a SiO$_2$ intermediate layer in between. This intermediate layer can be used to regulate the plasmon resonance peak effectively. Some researchers have focused on the investigation of the optimum weight percentage of Au nanoparticles in TiO$_2$ instead of their nanoparticle geometry. However, the optimum Au weight
percentage distinguished from each other in the case of photocatalytic semiconductor with different morphology. It can not lead to a profound comprehension of the physical mechanism of the water splitting enhancement. Despite of the considerable enhancement excited by the plasmon resonance, the overall solar to energy conversion efficiencies are still quite low especially in the visible wavelength region.

**Figure 1.15** Plasmon-assisted photocurrent generation and water oxidation from visible to near-infrared wavelength using a Au-nanorods/TiO2 Electrode.[137]

Nishijima et al. reported the plasmon-enhanced photocurrent generation and water oxidation by visible and near infrared light irradiation, as shown in Figure 1.15.[137-140] They fabricated gold nanorods array on the surface of TiO2 photoelectrode. Stoichiometric evolution of oxygen was demonstrated via water oxidation through the irradiation of this photocurrent generation system. The electrons are supplied by water molecules, since there is no electron donor except a potassium perchlorate aqueous solution, which was employed as an electrolyte solution. The plasmonic optical antenna effect of the gold nanorods promoted the stoichiometric evolution of oxygen and hydrogen peroxide via the four- or two-electron oxidation process of water molecules, respectively. After the electron transfer from gold to TiO2, it is speculated that the water oxidation recovered effectively
via the multiple holes generated by plasmon-induced charge excitation. This photoelectric conversion system as proposed is considered to be a promising approach for artificial photosynthesis using visible and near-infrared light.
1.4 Evaluation of PEC Water Splitting

To date, hundreds of materials have been investigated as photocatalystst, and thousands of corresponding applications have already been published in academic journals concerning the modification and improvement of the existing photocatalysts so as to enhance the photocatalytic activity. Thereupon, the evaluation of the capability of these photocatalysts is necessary to be within a unified standard for both theoretical research and practical application.

1.4.1 Stoichiometry of H₂ and O₂ Evolution

For a water splitting process without any sacrificial reagent employed, both H₂ and O₂ should be formed in a stoichiometric ratio, i.e., the amount of the H₂ generation should be twice that of the O₂ generation. Occasionally, the H₂ evolution can be observed while the O₂ evolution is undetectable. In this situation, the amount of H₂ evolution is usually very small even compared with the amount of the photocatalyst. It is thus not confirmed if such kind of reaction is a photocatalytic process and it is crucial to clarify that this is not a sacrificial reaction.

1.4.2 Time Course of H₂ and O₂ Evolution

In a typical water splitting reaction, the amounts of the H₂ and O₂ evolution should increase with the irradiation time. The amount of evolved H₂ and O₂ over per unit irradiation time is one of the most important indicators for the assessment of the photocatalytic activity. The long term stability of a photocatalyst is usually investigated by repeated experiments. After the water splitting reaction for a long time, there should be no or negligible decrease in the activity for a stable photocatalyst.

1.4.3 Turnover Number

In the research field of catalysis, turnover number (TON) is an important index for the
character of many catalytic materials. In photocatalysis, TON is also indispensable to evaluate a catalyst. The quantity of the \( \text{H}_2 \) and \( \text{O}_2 \) evolved should overwhelm that of the photocatalysts employed. Otherwise, the process could be a chemical reaction instead of a photocatalytic reaction. There still remains a possibility that the \( \text{H}_2 \) and \( \text{O}_2 \) evolution are generated from the chemical reactions between water and semiconductor materials, or from the self-decomposition of the semiconductors. None of these is an essentially catalytic process.

In general, turnover number is defined as the number of reacted molecules per active site.

\[
\text{TON} = \frac{\text{number of reacted molecule}}{\text{number of active sites}}
\]

(1-5)

Nevertheless, precise determination of the number of active sites on a photocatalyst surface is impossible in the case of heterogeneous photocatalysis. Hence, an alternative method is proposed for practical application. The number of photocatalyst molecules is employed in above equation instead of the number of active sites. The equation is thus modified as follows:

\[
\text{TON} = \frac{\text{number of reacted electrons}}{\text{number of molecules in a photocatalyst}}
\]

(1-6)

The number of reacted electrons can be calculated from the number of molecules of \( \text{H}_2 \) or \( \text{O}_2 \) gas evolution. Since the number of all the photocatalyst molecules is definitely larger than that of the active sites on a certain photocatalyst surface, the TON value calculated by the above equation is actually smaller than the real value. Sometimes the photocatalytic activity is normalized by the weight of the photocatalyst employed, e.g., mmol h\(^{-1}\) g\(^{-1}\). However, that is somewhat inaccurate since the photocatalytic activity tends to be saturated with the weight of photocatalyst if the amount of photocatalyst used is large enough for a certain experimental condition. The optimum quantity of certain photocatalyst needs to be determined for each experimental system individually. In this situation, the photocatalytic activity mainly depends on the photon absorption by the
photon catalyst unless the irradiation is too strong.

1.4.4 Quantum Yield

Since photocatalytic water splitting has become a worldwide concern, numerous photocatalysts have been investigated using different experimental apparatus with distinct parameters by different laboratories. Even for the same photocatalysts, the activities will show a considerable difference, such as the evolution time course of \( \text{H}_2 \) or \( \text{O}_2 \) derived from the measurements, if they are measured with different experimental setups or in different conditions. Therefore, such kinds of activities are unacceptable for comparison in order to evaluate the efficiencies of the photocatalysts.

At present, quantum yield is generally acknowledged as a standard for the evaluation of the efficiencies of various photocatalysts reported by different research groups. The definition of the quantum yield is depicted as the follow equation:

\[
\text{Quantum yield} = \frac{\text{number of reacted electrons}}{\text{number of absorbed photons}}
\]  

(1-7)

The influence of different light sources can be excluded by using this quantum yield value for the assessment. However, the number of photons absorbed by the photocatalysts is very difficult to measure in practical terms. Therefore, the evaluation of the performance of photocatalysts is commonly indicated with an extended term “external quantum yield” or “apparent quantum yield”, abbreviated to EQY or AQY respectively.\[^{[19]}\]

\[
\text{AQY \%} = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100
\]  

(1-8)

Spectroradiometer can be used for the measurement of the number of incident photons. Due to the light reflection and scattering of the solid semiconductors, the number of absorbed photons is definitely smaller than that of incident photons. Therefore, the AQY is usually lower than the real quantum yield.

It should be noted that the quantum yield discussed above is different from the solar energy conversion efficiency which is frequently used in the assessment of solar cells.
Solar energy conversion \( \% = \frac{\text{Output energy as } \text{H}_2}{\text{Energy of incident solar light}} \times 100 \) \hspace{1cm} (1-9)

Since the activities of most photocatalysts are too low to measure, there is only a few photocatalysts exhibiting passable solar energy conversion efficiency until now. However, for the end of solar hydrogen production, the photocatalytic water splitting should finally be evaluated in terms of the solar energy conversion efficiency.

1.4.5 Photoresponse

When a photocatalyst is irradiated by light with energy larger than its band gap, water splitting should occur. The action spectrum is very important for the investigation of the photoresponse, particularly for a photocatalyst that responds to visible light. During the measurement of the action spectrum, monochromatic light is generally obtained using band-path and interference filters. Even if a material is capable for visible light absorption, it does not always have the photocatalytic activity induced by the excitation of the visible light absorption. The onset wavelength can be determined when using cut-off filters to observe the photoresponse. In dark condition with constant stirring, water splitting on some metal oxides can proceed by mechanocatalysis instead of photocatalysis.\[^{141, 142}\]

Therefore, for the purpose of confirming the photocatalytic reaction and excluding the possibility of the mechanocatalytic water splitting, some control experiments such as in the absence of any photocatalyst or any irradiation should be performed.
1.5 Current Scenario and Challenges

Photocatalytic water splitting offers an attractive potential solution for the production of environmentally clean energy carriers obtained from renewable material sources and abundant solar energy.[143, 144] The design and synthesis of complex water splitting strategy, which functions at high apparent quantum yield and long term stability for H₂ and O₂ evolution, with low activation barrier and moderate overpotential, remain major challenges in this field. A key issue is to devise an apparatus that exhibits superior capabilities. It should be able to efficiently separate H₂ and O₂ evolution with a high rate and sustain consecutive gas generation for many rounds of photocatalytic cycles.

Numerous schemes have been established by many researchers. However, some severe problems still remain on despite of the progress made in recent years, including:

(1) Only the UV light of the solar spectrum is utilized, whereas the visible and infrared irradiations which take a major part of the solar spectrum are underutilized.

(2) An external electric bias is constantly required throughout the water splitting process, which increases complexity of the water splitting system.

(3) Additional energy consumption will be necessary for the separation of the evolved H₂ and O₂ gas after the water splitting process. For the purpose of ensure the security during the transportation and storage, the purification of the H₂ gas is inevitable.

(4) In the case of the water splitting reaction using particulate semiconductor materials, undesired backward reaction, such as H₂-O₂ recombination and/or O₂ photoreduction, would readily be involved due to the adjacent reaction sites for H₂ and O₂ evolution.

(5) For the conventional water splitting systems, there is a schottky barrier between the semiconductor material and the co-catalyst, hindering electron transfer. The water splitting activity is thus restricted.

(6) There is an absence of an effective evaluation method of the various kinds of co-catalysts. The most suitable H₂ evolution co-catalyst for particular water splitting reaction environment is also suspensive.
(7) The charge carrier migration in the semiconductor is not efficient enough. The recombination between electrons and holes drastically retards the water splitting reaction.

These issues hamper the exploitation in water splitting reaction system assemblies and photocatalytic devices for fuel generation. If these challenges can be met, PEC water splitting may emerge as an economically viable and truly renewable pathway towards the clean H₂ production.
1.6 Aim and outline of this thesis

All warning signs in regard to the energy crisis and global warming force us to consider about the solution to utilize energy which derives from natural resources. Therefore, the principal aim of this thesis is to make use of renewable energy such as solar energy and convert it into chemical energy stored in H₂ gas by PEC water splitting process. The body of thesis consists of six chapters including the present chapter 1. This chapter briefly describes the backgrounds of the study, literature review, mechanism of the water splitting reaction and the objectives of the study. Chapter 2 introduces the apparatus designed for hydrogen production using water splitting and experimental details about the quantitative determination of hydrogen and oxygen evolution. Chapter 3 reports the plasmon-assisted water splitting using two sides of the same SrTiO₃ single-crystal substrate. The properties of the gold nanoparticles deposited on the SrTiO₃ single-crystal substrates were characterized. The influence of irradiation wavelength and pH value combinations on H₂ and O₂ generation were summarized and analyzed. Chapter 4 is devoted to the co-catalyst effects on hydrogen evolution in the plasmon-induced water splitting system. Schottky barrier effect between the semiconductor and the co-catalyst was eliminated. An effective evaluation method of various co-catalysts was proposed. Chapter 5 presents the plasmon-enhanced water splitting utilizing heterojunction synergistic effect between SrTiO₃ and rutile TiO₂. Enhanced water splitting activity was ascribed to the larger potential gradient between the front and back side of the composite substrate due to the energy band position difference between SrTiO₃ and rutile TiO₂. At the end of the thesis, chapter 6 summarizes the results described in chapter 3-5. This chapter also describes how this project leads to a future perspective on water splitting systems for solar fuels generation. Several possibilities are proposed as the further extension and development of this work.
1.7 References


Herrmann, J.-M., Disdier, J. and Pichat, P., Effect of chromium doping on the electrical and catalytic


Chapter 2

Plasmon-Induced Water Splitting Using Two Sides of the Same SrTiO$_3$ Single-Crystal Substrate

2.1 Abstract

A plasmon-induced water splitting system that operates under visible light irradiation is successfully developed. This system is based on the utilization of both sides of the same SrTiO$_3$ single-crystal substrate. The most important feature of this system is that both sides of a strontium titanate single-crystal substrate are used without an electrochemical apparatus. The water splitting system contains two solution chambers to separate H$_2$ and O$_2$ evolution. To promote water splitting, a chemical bias was applied by the regulation of the pH values at the two chambers. The quantity of H$_2$ evolved from the surface of platinum, which was used as a reduction co-catalyst, was twice the quantity of O$_2$ evolved from an Au nanostructured surface. Thus, the stoichiometric evolution of H$_2$ and O$_2$ was successfully demonstrated. The hydrogen-evolution action spectrum closely corresponds to the plasmon resonance spectrum, indicating that the plasmon-induced charge separation at the Au/SrTiO$_3$ interface promotes water oxidation and the subsequent reduction of a proton on the backside of the SrTiO$_3$ substrate. It is further elucidated that the chemical bias is significantly reduced by plasmonic effects, which indicates the possibility of constructing an artificial photosynthesis system with low energy consumption. Plasmon-induced water splitting occurred even with a minimum chemical bias of 0.23 V due to the plasmonic effects based on the efficient oxidation of water and the use of platinum as a co-catalyst for reduction.
2.2 Introduction

To address the global energy issues, the development of a system that converts solar energy to not only electrical but also chemical energy that can be stored for long periods is critical.\(^1\)-\(^3\) Honda and Fujishima have developed photoelectrochemical water splitting systems that use a TiO\(_2\) photoelectrode irradiated by ultraviolet light.\(^4\),\(^5\) However, only approximately 5% of the solar irradiance observed on the Earth’s surface is composed of ultraviolet radiation (<400 nm), whereas visible light (400-800 nm) and infrared light (>800 nm) represent 50% and 45%, respectively. Therefore, the extension of light-energy conversion to longer wavelengths, especially to the visible and near-infrared regions, is important.\(^6\)-\(^8\) The conversion of visible light can be achieved by several methods, including the use of a Z-scheme electron transfer process,\(^9\),\(^10\) TiO\(_2\) with the addition of certain dopants,\(^11\)-\(^14\) and semiconductor nanoparticles with a bandgap wavelength in the visible region.\(^15\)-\(^18\) To date, semiconductor particles have been used to induce H\(_2\) and O\(_2\) evolution through the response of such photocatalysts to visible light.\(^19\),\(^20\) One of the disadvantages of the use of semiconductor particles in a photocatalytic water splitting system that requires energy to separate H\(_2\) from O\(_2\) is that H\(_2\) and O\(_2\) are evolved in the same reaction chamber.\(^21\)-\(^23\) Recently, the evolution of H\(_2\) and O\(_2\) in different reaction chambers has been studied using photoelectrodes fabricated by sintering semiconductor particles.\(^24\) Except for the Z-scheme reaction system, such systems do not require cathode irradiation because hydrogen evolution occurs via a dark reaction. Therefore, the optimization of a reaction cell design that can effectively utilize light for water splitting is expected. In this chapter, it is proposed that the simultaneous evolution of H\(_2\) and O\(_2\) can be realized without an electric wire connecting the anode and the cathode and with space conserved for light irradiation on the anode side through the use of two sides of the same semiconductor substrate. It is a plasmon-induced water splitting system that responds to visible light, which is based on gold nanoparticles (Au-NPs) loaded onto SrTiO\(_3\) single-crystal substrates. The successful separation of H\(_2\) and O\(_2\) evolution in different chambers using both sides of the same substrate is also demonstrated. The
plasmon-induced charge separation between Au-NPs and oxide semiconductor interfaces studied here can act as a co-catalyst in water oxidation, which is considered to be a bottleneck process in water splitting. Thus, this system is promising for artificial photosynthesis and is expected to be deployed in the future.
2.3 Experimental details

2.3.1 Niobium doped strontium titanate single crystals

N-type SrTiO$_3$ has been proven to be efficient anodes for photochemical water splitting under UV light irradiation. While the large band gaps of SrTiO$_3$ (3.2 eV) resulted in their low conversion efficiencies of solar energy, thus hindering their practical applications. For the effective usage of solar energy, many efforts have been made to develop the visible light responding photoanodes. Recently, the band gaps of n-TiO$_2$ were effectively reduced by replacing oxygen with nitrogen or carbon to elevate the potential at the top of the valence band.$^{[11, 25]}$

Our group has already successfully observed photocurrent generation and O$_2$ evolution with TiO$_2$ substrate under certain electric bias. Whereas for overall water splitting, H$_2$ evolution with accurate quantity is also very important. Furthermore, it is highly desired to realize the overall water splitting without any electric bias. The conduction band (CB) electrochemical potential of TiO$_2$ is 0 V vs reversible hydrogen

![Energy band structures of TiO$_2$ and SrTiO$_3$](image)
electrode (RHE), which is the same as the redox potential of the proton reduction. As a result, it would be quite difficult for the TiO$_2$ to reduce protons to generate H$_2$ without any electric bias. While as shown in Figure 2.1, the CB position of the strontium titanate (SrTiO$_3$) is -0.2 V vs RHE, more negative than the redox potential of the proton reduction, which makes it take advantage at the H$_2$ evolution. Therefore, the SrTiO$_3$ was chosen as the catalytic material in this study.

At room temperature, SrTiO$_3$ crystallizes in the ABO$_3$ cubic perovskite structure where A and B are cations. The lattice constant of SrTiO$_3$ is 0.3905 nm. Its crystal structure is shown in Figure 2.2. The Ti$^{4+}$ ions are sixfold coordinated by O$_2^-$ ions, whereas each of the Sr$^{2+}$ ions is surrounded by four TiO$_6$ octahedra. Therefore, each Sr$^{2+}$ ion is coordinated by 12 O$_2^-$ ions. Within the TiO$_6$ octahedra, while a hybridization of the O-2p states with the Ti-3d states leads to a pronounced covalent bonding, Sr$^{2+}$ and O$_2^-$ ions exhibit ionic bonding character.\[26\] Hence, SrTiO$_3$ has mixed ionic-covalent bonding properties. This nature of chemical bonding leads to a unique structure, which make it a model electronic material.

![Figure 2.2 Crystalline structures of SrTiO$_3$](image)

Figure 2.2 shows the transmittance spectra of the Nb-SrTiO$_3$ (0.05 wt% and 0.5 wt%)
single crystals. The transmittance spectra of these single crystals were measured by using an ultraviolet–visible Spectrometer (Shimadzu UV-3100, Japan). It is obvious that in the region of UV light absorption, the samples almost show the same absorption edge (about 3.2 eV), corresponding to the electronic excitation from the O 2p state to the Ti 3d state.\textsuperscript{27} In the region of the longer wavelength, the Nb-doped SrTiO\textsubscript{3} single crystals show strong absorption. This phenomenon should partly be ascribed to the optical absorption of free carriers in the semiconductor. With the larger concentration of carriers, Nb-SrTiO\textsubscript{3} (0.5 wt%) shows stronger optical absorption of free carriers in the region of long wavelength than Nb:SrTiO\textsubscript{3} (0.05 wt%). The main features of Figure 2.3 are strong visible light absorption around 514 nm (c.a. 2.4 eV) for Nb-SrTiO\textsubscript{3} (0.05 wt%) and Nb-SrTiO\textsubscript{3} (0.5 wt%) single crystals. The enlargement of the transmittance spectrum for Nb-SrTiO\textsubscript{3} (0.5 wt%) single crystal is shown in the Figure 2.3 (b). It means that there are intermediate states within the band gap of Nb-SrTiO\textsubscript{3} single crystals.

Taking these aspects into consideration, the SrTiO\textsubscript{3} single crystals doped with Nb by 0.05 wt% was chosen as the semiconductor photocatalytic material in this study.

![Figure 2.3](image.png)

**Figure 2.3** (a) The transmittance spectra of the semiconductor single-crystal Nb-SrTiO\textsubscript{3} with different doping percentages (0.05 wt% and 0.5 wt%). (b) An enlarged view of (a) in which the transmittance spectra of 0.5 wt% doped Nb-SrTiO\textsubscript{3} is present.
2.3.2 Preparation of Au-NPs on a SrTiO$_3$ substrate

Single-crystal strontium titanate (SrTiO$_3$, 0.05 wt% niobium doped, 10 × 10 × 0.5 mm$^3$, Furuuchi Chemical Co.) with a (110) surface was used as a semiconductor substrate for water splitting. The SrTiO$_3$ substrate as purchased was sequentially rinsed with acetone, methanol, and deionized water in an ultrasonic bath for 5 min and was dried under a flow of pure nitrogen. The substrate was subsequently exposed to ozone for 5 min by excimer lamp (PC-01-H, N-Cobo Co.) irradiation under an O$_2$ atmosphere in order to remove the organic matter stuck to the surface. A thin gold film (3 nm) was deposited onto the front side of the SrTiO$_3$ by helicon sputtering (MPS-4000, ULVAC Co.) at a deposition rate of 1 Å/s and was annealed at a temperature of 800°C for 1 h in a nitrogen atmosphere to form the Au-NPs onto the SrTiO$_3$ surface.$^{[28]}$ The Au-NPs on the SrTiO$_3$ surface were observed by field-emission scanning electron microscopy (FE-SEM, JSM-6700FT, JEOL). The maximum resolution attainable at an electron acceleration voltage of 15 kV was 1 nm. The extinction spectrum of the Au-NPs was monitored using a UV/vis spectrometer (UV-3100, Shimadzu Co.).

![Diagram of Au-NPs on SrTiO$_3$ substrate fabrication](image)

**Figure 2.4** The gold nanoparticles loaded SrTiO$_3$ substrate fabrication and platinum board decoration process.
2.3.3 Construction of the water splitting device

An In-Ga alloy (4:1 weight ratio) paste was applied to the backside of the Nb-SrTiO<sub>3</sub> substrate to form Ohmic contacts. Subsequently, a Pt board (10 × 10 × 0.2 mm<sup>3</sup>, 99.98%, Nilaco Corporation) was adhered to the backside of the substrate via Ag paste (D-550, Fujikura Kasei Co.). A schematic illustration of the water splitting system based on the Au-NP-loaded Nb-SrTiO<sub>3</sub> substrate is shown in Figure 2.5. The water splitting device contained sealed reaction cells with two solution compartments separated by the SrTiO<sub>3</sub> substrate. The Au-NP-loaded surface served as the anode on the front side of the photoelectrode, which was irradiated by visible light to induce O<sub>2</sub> evolution, whereas a Pt board served as the cathode for H<sub>2</sub> evolution on the backside. In the front chamber, O<sub>2</sub> evolution is expected to follow the plasmon-induced charge separation and the subsequent water oxidation. The evolution of H<sub>2</sub> is expected in the back chamber because of the reduction of protons by photogenerated electrons injected into the conduction band of Nb-SrTiO<sub>3</sub> at the Pt surface, which was used as a reduction co-catalyst.[29] To adjust the chemical bias between the H<sub>2</sub>- and O<sub>2</sub>-evolution chambers, the pH was regulated using arbitrary concentrations of hydrochloric acid (HCl) and potassium hydroxide (KOH) aqueous solutions. The volumes of H<sub>2</sub>- and O<sub>2</sub>-evolution chambers are 600 and 230 µL, respectively. To maintain the charge balance between the two chambers, a salt bridge with 2 wt% agar was used. The pH values of the solutions were examined using a pH meter (AS600, AS ONE Co).

Figure 2.5 A schematic illustration of the water splitting device using Au-NPs loaded Nb-SrTiO<sub>3</sub> photoelectrode.
In order to keep the charge and ion balance between the two reaction chambers, a conventional salt bridge was used. The 100 mL potassium chloride (KCl) aqueous solution, which contained 30 g KCl (nearly saturated condition), was dissolved by agar powder with 2 wt%.\textsuperscript{[30]} The solution was then injected into a colorimetric tube, and heated in water bath to keep the temperature steady at 95 °C, so as to prevent the solution from solidification. A silica capillary tube with an inner diameter of 0.2 mm was inserted into the agar solution afterwards. Due to the capillary effect, the agar solution successfully entered into the silica capillary tube.\textsuperscript{[31]} Subsequently, the tube was taken out of the agar solution. After the refrigeration of the agar solution in the tube to the room temperature, a salt bridge was acquired. The tips of the salt bridge were inserted into the two reaction chambers respectively during the water splitting process. During the water splitting process, protons transferred from the front side to the back side of the reaction system through this salt bridge in order to keep the charge balance between the two reaction chambers. The salt bridge has the same function as a proton exchange membrane, e.g. nafion film.\textsuperscript{[32, 33]}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{salt_bridge_setup.png}
\caption{The installation for the fabrication of the salt bridge and its assembly to the water splitting reaction cell.}
\end{figure}
2.3.4 Quantitative determination of hydrogen evolution

The amount of evolved H\textsubscript{2} was quantitatively determined by a gas chromatograph equipped with a thermal conductivity detector (GC-TCD 2014, Shimadzu Co.). The area counts of the peaks and the identity of the gas were analyzed from the calibrated carrier times. The HCl aqueous solution was bubbled with N\textsubscript{2} for 60 minutes before each experiment in order to remove the residual O\textsubscript{2} in the solution. N\textsubscript{2} gas was injected into the H\textsubscript{2} evolution side, as reference gases for the yield calculations. The GC-TCD was equipped with a 6.0-m packed column (Shincarbon ST 50/80, Shimadzu Co.), and the carrier gas was Ar with a flow rate of 30 mL/min. The gas evolved (10.0 μL) from the backside chamber was injected. The column and sample injection temperatures were 120°C and 200°C, respectively. The detector temperature was set to 200°C.

The calibration curve of H\textsubscript{2} and the reference gas N\textsubscript{2} is shown in the Figure 2.8. According to this calibration, the H\textsubscript{2} detection limit of our GC-TCD device is $5.6 \times 10^{-5}$ mol dm\textsuperscript{-3} or less. Since the volume of the sample injected into the GC-TCD is 10 μL, the H\textsubscript{2} detection limit of our GC-TCD device is estimated to be 0.56 nmol.

![Gas chromatogram](image)

**Figure 2.7** Gas chromatogram of typical sample extracted from the H\textsubscript{2} evolution side after the water splitting process.
2.3.5 Quantitative determination of oxygen evolution

The amount of evolved $O_2$ was quantitatively determined by gas chromatography-mass spectroscopy (GC-MS 2010-plus, Shimadzu Co.). The area counts of the peaks and the identity of the gas were analyzed from the calibrated carrier times. The KOH aqueous solution on the $O_2$ evolution side of the cell was labeled with $^{18}O$-water (17.4 atom % isotopic purity) in order to quantify the oxygen evolution. The KOH aqueous solution was bubbled with Ar for 60 minutes before each experiment in order to remove the residual $O_2$ in the solution. Ar gas was injected into the $O_2$ evolution side, as reference gas for the yield calculations. The GC-MS used to separate and determine the $O_2$ was equipped with an electron ionization (EI) source and a 30.0 m RT-Msieve 5A column (RESTEK); He at a flow rate of 42 mL/min was used as the carrier gas. The gas evolved (5.0 μL) from the front side of the photoelectrode was injected in the split mode, with a split ratio of 30, and the selected ion monitoring (SIM) mode was used for the detection of $O_2$. The column and sample injection temperatures were maintained at room temperature. The EI ionization source temperature was set to 200°C.

The mass-to-charge ratio ($m/z$) of 28, 32, 34, 36, and 40 were determined by the gas chromatography-mass spectrometry (GC-MS) spectra. A typical GC-MS chromatogram of
the sample from the water splitting device after visible light irradiation is shown in Figure 2.9. The (m/z) of 28, 32, 34, 36, and 40 are corresponding to $^{28}\text{N}_2$, $^{32}\text{O}_2$, $^{34}\text{O}_2$, $^{36}\text{O}_2$ & $^{36}\text{Ar}$, and $^{40}\text{Ar}$ gas chromatogram respectively. The area of gas chromatogram was used for the calculation of gas concentration.

The peak of the $^{36}\text{O}_2$ was submersed in that of the $^{36}\text{Ar}$, which was an isotope of the reference gas used for quantitative determination. Because it was difficult to distinguish these peaks from each other, the $^{36}\text{O}_2$ was not used to calculate the amount of $\text{O}_2$ gas evolution. In order to prevent the contamination from the air during the measurement, $^{32}\text{O}_2$ was not used in the calculation either. Thus, the $^{34}\text{O}_2$ gas chromatogram was used for quantitative determination of the oxygen evolution, which was then compared with the natural abundance ratio. The calibration curve of $^{34}\text{O}_2$ using $^{40}\text{Ar}$ as a reference gas is shown in Figure 2.10. According to this calibration, the $^{34}\text{O}_2$ detection limit of our GC-MS device is $6.0 \times 10^{-6}$ mol dm$^{-3}$ or less. Since the volume of the sample injected into the GC-MS is 5 µL, the $^{34}\text{O}_2$ detection limit of our GC-MS device is estimated to be 0.03 nmol.

The mass-to-charge ratio (m/z) of 34 was determined from the gas chromatography-mass spectrometry (GC-MS) spectra. The gas of m/z 34 is a kind of oxygen isotope gas, which contains one $^{16}\text{O}$ and one $^{18}\text{O}$ atom. The gas chromatogram intensity of the m/z of 34 increased with irradiation time.

![Figure 2.9](image)

**Figure 2.9** (a) A typical GC-MS chromatogram of the sample from the water splitting
device after the anode side chamber was irradiated with visible light. Intensity was normalized to m/z 40. (b) A zoomed-in view of the area in which argon and oxygen peaks are present.

![Figure 2.10](image)

**Figure 2.10** The calibration curve of $^{34}\text{O}_2$ using $^{40}\text{Ar}$ as a reference gas.
2.4 Results and discussion

2.4.1 Characterization of Au-NPs

A top view scanning electron microscope image of the Au-NPs on Nb-SrTiO₃ single crystal substrates was used for statistical analysis of the Au-NPs particle size distribution based on the usage of free software ImageJ (http://rsb.info.nih.gov/ij/). With prolonged annealing, the gold thin film grows in shape to give a more ordered structure as reported previously.[34] The scanning electron microscope image and Au-NPs particle size histograms distribution of Au-NPs/SrTiO₃ were shown in the Figure 2.11.

![Image](image.png)

**Figure 2.11** The scanning electron microscope top view image (a) and the particle size histograms distributions (b) of Au-NPs on Nb-SrTiO₃ photoelectrode after annealing at 800°C in a nitrogen atmosphere. The scale bars represent 100 nm.

The SEM images confirmed that the gold films transformed to a discontinuous nanoparticle structure after annealing at 800°C in a nitrogen atmosphere, and the interparticle spacing was comparable to the nanoparticle size. The diameter of the Au-NPs distributes nearly symmetrically with the average size at around 52 nm, and the standard deviation for the structural size was estimated to be 19 nm. The surface area coverage of gold nanoparticles is approximately 26 % on the SrTiO₃. Typical scanning transmission
electron microscope (STEM) images of Au-NPs cross-section and top view were shown in Figure 2.12. The shape of Au-NPs on SrTiO₃ was spherical segmental structure with average height of about 32.7 nm. The Au-NPs tightly contact with TiO₂ surface.

![Figure 2.12](image)

**Figure 2.12** The transmission electron microscope cross section view with different magnification (a), (b) and top view (c) images of Au-NPs on Nb-SrTiO₃ photoelectrode after annealing at 800°C in a nitrogen atmosphere. The scale bars represent 100 nm in all images.

Typical XPS spectra characterization of Au-NPs on SrTiO₃ substrate after annealing at 800°C in a nitrogen atmosphere is shown in Figure 2.13. The Au 4f₅/₂ and 4f₇/₂ peaks were centered at approximately 87.5 eV and 83.8 eV, which are in good accordance with the standard values reported.³⁵ The X-ray diffraction patterns of Au-NPs on SrTiO₃ after annealing at 800°C in a nitrogen atmosphere is shown in Figure 2.14. The peak that represents the gold (111) crystal facet was clearly observed, indicating the crystalline nature of the gold nanoparticles. Figure 2.15 shows the extinction spectrum of the Au-NPs on the Nb-SrTiO₃ substrate. A localized surface plasmon resonance (LSPR) band peaking at a wavelength of 630 nm is clearly observed.
Figure 2.13 Partial XPS spectra characterization of Au-NPs on SrTiO$_3$ after annealing at 800°C in a nitrogen atmosphere.

Figure 2.14 X-ray diffraction patterns of Au-NPs on SrTiO$_3$ after annealing at 800°C in a nitrogen atmosphere.
2.4.2 Numerical simulations of Au-NPs on SrTiO$_3$

The extraordinarily powerful localized electromagnetic field that generated by localized surface plasmon resonance may have a strong impact on the water splitting activity enhancement. Nevertheless, the experimental measurement of the localized electromagnetic field enhancement is very difficult. Therefore, the computational simulation of the near-field intensity enhanced by the gold nanoparticles is an efficient method to address this issue.

The finite difference time domain (FDTD) simulation is a numerical analysis technique which is used for modeling the computational electrodynamics. This method is one of the many categories of the general class of grid-based differential time-domain numerical modeling methods. As a versatile modeling technique, FDTD is used to solve Maxwell's equations and provide animated displays of the electromagnetic field movement through the model. An increasing number of researches are using FDTD technique to investigate optical properties of certain noble metal nanostructures in recent years because the electric field intensity pattern is readily available in real space and the algorithm is independent of the particular structure to be solved. Additionally, noble metal
nanostructures have drawn considerable attention because of the existence of surface plasmon resonance, which give rise to resonant effects and field enhancement leading to many interesting applications.

To obtain a more rigorous understanding of the mechanism of water splitting activity enhancement, the FDTD simulation method (Lumerical) was thus adopted to simulate the electric field intensity distribution of gold nanostructures on SrTiO$_3$ substrate under the LSPR excitation. These simulations are based on the transmission electron microscope (TEM) image of the Au nanoparticle and SrTiO$_3$ surface, as shown in Figure 2.12, which is used to define the spatial extent of the Au nanoparticle islands in our simulation. To calculate the field distribution, the following parameters were used: the refractive index of the SrTiO$_3$ substrate was set as 2.4, the optical constants for gold was taken from Johnson and Christy, and the mesh accuracy was set at 0.5 nm.

Maps of the near-field electromagnetic intensity distribution patterns localized around gold nanostructures on SrTiO$_3$ at the maximum wavelength of the extinction spectra were obtained from the FDTD simulation method in both the x-z and x-y planes, as shown in Figure 2.16. For field enhancement, hemispherical shaped gold nanostructures with diameters of 52 nm were used under periodic boundary conditions. In the x-z plane, the intensity detector is located at the sphere center of the gold nanostructure and overlaps the x axis. In the x-y plane, the detector is located at the interface between the gold nanostructure and the SrTiO$_3$ substrate. Notably, from the simulation, the electromagnetic field intensity is greatly enhanced around the common boundary between gold, SrTiO$_3$ substrate, and aqueous solutions, with the highest enhancement factor of nearly 500, compared with the incident electric field at the SrTiO$_3$ surface. This electromagnetic response is dominated by local hot spots. This means that the electron hole pair generation rate is 500 times that of the incident electromagnetic field. Thus, an increased amount of charge is induced locally in the SrTiO$_3$ because of the local field enhancement of the plasmonic gold nanoparticles. Such kind of highly localized electromagnetic field was supposed to play a key role for the electron excitation and the subsequent charge
separation. While there is no way to measure the electronhole pair generation rate in an isolated plasmonic hot spot, the present work measuring plasmon-enhanced water splitting provides perhaps the most direct measurement of this, since every two electrons produce one hydrogen molecule.

### Figure 2.16
FDTD simulation showing the electric field intensity distribution around the gold nanostructure in the x-z (a) and x-y (b) planes. The dashed rectangle represents the periphery of the gold nanostructure. The scale bar shows the enhancement factor.

#### 2.4.3 Influence of irradiation wavelength on $H_2$ and $O_2$ generation

Figure 2.17 (a) depicts the irradiation time dependence of $H_2$ and $O_2$ evolution in the backside and front-side chambers, respectively. Experimental about the quantitative determination of $H_2$ and $O_2$ evolution was described in the supporting information. The pH value was adjusted to 1 on the $H_2$-evolution side, whereas the pH value on the $O_2$-evolution side was adjusted to 13 (i.e., the chemical bias was equivalent to 710 mV). A xenon light spectrally filtered over the wavelength range of 450 nm to 850 nm was used to irradiate the Au-NPs and induce LSPR. Under the irradiation conditions, the evolution of $H_2$ and $O_2$ increased linearly with increasing irradiation time. As for the time dependence of $H_2$ and $O_2$ evolutions, linearity was maintained in irradiation time, and it was not a quantity of evolution to the extent that pH changes. Actually, it has been confirmed that
the pH value did not change before or after the irradiation. In a separate experiment, it has also been confirmed that neither H\textsubscript{2} nor O\textsubscript{2} was evolved from a Nb-SrTiO\textsubscript{3} substrate without Au-NPs under the same irradiation conditions. No production of H\textsubscript{2} or O\textsubscript{2} was observed in the absence of irradiation for an extended period (6 h), even when the Au-NP-loaded Nb-SrTiO\textsubscript{3} substrate was used. Figure 2.17 (a) shows that the quantity of H\textsubscript{2} evolved from the surface of Pt, which was used as a reduction co-catalyst, is twice the quantity of O\textsubscript{2} evolved from the Au nanostructured surface. Therefore, the stoichiometric evolution of H\textsubscript{2} and O\textsubscript{2} was clearly demonstrated in the water splitting system based on the Au-NP-loaded Nb-SrTiO\textsubscript{3} single-crystal substrate.

**Figure 2.17** (a) An irradiation time dependence of H\textsubscript{2} (red circle) and O\textsubscript{2} (blue circle) evolution obtained in back and front side chamber, respectively. (b) The action spectrum of apparent quantum efficiency with several wavelength regions using a histogram. The solid line indicates LSPR band already shown in Figure 2.15.

The histogram in Figure 2.17 (b) shows the action spectrum of apparent quantum efficiency (AQE). The pH conditions used were a pH of 1 for the H\textsubscript{2}-evolution side and a pH of 13 for the O\textsubscript{2}-evolution side. Sectionalized yields of the AQE dependent on the irradiation wavelength was measured with the increment as 100nm. In the 600 ± 50 nm, 700 ± 50 nm, and 800 ± 50 nm wavelength regions, the evolution efficiency (mol/h) of H\textsubscript{2} is in approximate agreement with the segmented integral area of the the LSPR band of the
extinction spectrum indicated by the solid line in Figure 2.17 (b), whereas the evolution efficiency of H₂ in the 500 ± 50 nm wavelength region is higher than that indicated by the spectrum of the Au-NPs on the Nb-SrTiO₃. This result indicates that H₂ and O₂ evolution was induced not only by LSPR excitation but also by the direct excitation of the interband transition from the d-bands to the sp-conduction band of gold in the 500 ± 50 nm wavelength region. Thus, the H₂-evolution efficiency in the shorter-wavelength region is higher than that in the longer-wavelength region. Notably, the water splitting is closely related to the LSPR excitation because the AQE is strongly dependent on the LSPR band.

In the present system, the number of active sites or molecules of the photocatalyst is impossible to be estimated. Therefore, turnover number is unavailable as an index to evaluate the performance in this study. In addition, since the UV irradiation was cut off in order to investigate the visible response, solar energy conversion efficiency is also unaccessible in this research.

2.4.4 Influence of pH value combinations on H₂ and O₂ generation

To further understand this system in detail, a pH-dependence experiment was performed to investigate the effect of the chemical bias on the water splitting. In the experiment, a xenon light spectrally filtered over the wavelength range of 550 nm to 650 nm with an intensity of 0.32 W/cm² was used for the LSPR excitation. Figure 2.18 (a) indicates the representative irradiation time dependence of H₂ and O₂ evolution at the pH combination of 1 and 13. The evolution of both H₂ and O₂ increases linearly with increasing irradiation time, and the quantity of H₂ evolved is twice that of O₂ evolved, which is analogous to the results in Figure 2.17 (a). Figure 2.18 (b) shows the pH dependence of the H₂ and O₂ evolution efficiency. The pH value on the O₂-evolution side was fixed at 13, as indicated by the blue background in Figure 2.18 (b), which is the condition that preferentially induces water oxidation. The evolution efficiency of H₂ is twice that of O₂ at the observed pH value. However, the evolution efficiency of both H₂ and O₂ gradually decreased with increasing pH value on the H₂-evolution side, and no
production of H$_2$ or O$_2$ was observed at a pH value of 4. Therefore, a chemical bias was required in the water splitting in this system of at least 0.59 V, which corresponds to the difference between pH 3 and pH 13. However, a pH value of 1 was fixed on the H$_2$-evolution side, as indicated by the red background in Figure 2.18 (b), which is the condition that preferentially induces H$_2$ evolution. Similarly, the evolution efficiency of H$_2$ was twice that of O$_2$ at the observed pH value. In contrast, the evolution efficiency of both H$_2$ and O$_2$ gradually decreased with decreasing pH value on the O$_2$-evolution side. However, the evolution of both H$_2$ and O$_2$ was still observed, even at a pH of 6.8 using a pure water. In addition, neither H$_2$ nor O$_2$ evolution was observed at a pH of 6. Therefore, in this system, a chemical bias was required in the water splitting of at least 0.34 V, which corresponds to the difference between pH 1 and pH 6.8. Therefore, the chemical bias required for the water splitting changes as the fixed pH value in the chamber changes.

When the pH value at the cathode was fixed to 1 and the pH at the anode was increased from 6.8 to 10, hydrogen was evolved due to the reduction of protons at the cathode, whereas oxygen was evolved due to the oxidation of water molecules via a four-electron reaction. Therefore, the water splitting reaction did not exhibit a significant pH dependence. When the pH at the anode was increased from 11 to 13.5, oxygen was evolved due to the oxidation of water molecules and OH$^-$ ions. The amount of evolved gases increased gradually as the pH was increased at the anode. Similarly, when the pH at the anode was fixed at 13 and the pH at the cathode was gradually increased from 1, the quantity of the evolved gases decreased because the proton concentration at the cathode decreased with increasing pH values. Neither gas was detectable at pH 4 on the cathode side. On the basis of these results, it is hypothesized that hydrogen evolution was the rate-limiting process of the present water splitting reaction. Because water splitting did not proceed when the pH at the anode was 6, the minimum chemical bias in this system was estimated to be 230 mV, which corresponds to the combination of pH 3 (cathode side) and pH 6.8 (anode side). Although water oxidation is the rate-limiting process in a typical water splitting system, it is concluded that the water splitting proceeded at a relatively low
chemical bias of 230 mV because the plasmon-induced charge separation efficiently oxidized the water.

**Figure 2.18** (a) An irradiation time dependence of H₂ (red circle) and O₂ (blue circle) evolution at the pH combination of 1 and 13 under the conditions that the xenon light spectrally filtered to the wavelength from 550 nm to 650 nm with an intensity of 0.32 W/cm² was irradiated. (b) The pH dependence of the H₂ (closed circle and square) and O₂ (open circle and square) evolution efficiency under the conditions that the pH value in the H₂ evolution side is fixed at 1 as plotted on red background and the pH value in the O₂ evolution side is fixed at 13 as plotted on blue background, respectively.

To further explore the limiting pH conditions for H₂ and O₂ evolution, the pH values on the H₂- and O₂-evolution sides were fixed at 3 and 6.8, respectively, which are the minimum acidic and alkaline conditions observed in the previous experiments to promote evolution of H₂ and O₂, respectively. The irradiation time dependence of H₂ and O₂ evolution is shown in Figure 2.19(a). The results confirm that the evolution of both H₂ and O₂ increased approximately linearly with increasing irradiation time and that the efficiency of H₂ evolution was twice that of O₂ evolution. The pH dependence is shown in Figure 2.19(b), which is summarized as being analogous to Figure 2.18(b). The evolution efficiency of both H₂ and O₂ gradually decreased with increasing pH on the H₂-evolution side, and no production of H₂ or O₂ was observed at pH 4. When the pH value was set to 4 on the H₂-evolution side, the water splitting did not proceed at either pH value on the
O₂-evolution side. This result indicates that the reaction rate of hydrogen evolution is the rate-determining process in water splitting. In addition, the absolute efficiency is significantly lower than the previous data because of the insufficient chemical bias applied to that system. In the case where the pH value on the H₂-evolution side was fixed, water splitting was induced, even at a pH combination of 3 and 6.8, which corresponds to a minimum chemical bias of 0.23 V in this plasmon-assisted water splitting system.³⁶ To the best of the authors’ knowledge, this chemical bias is the smallest value reported for a water splitting system driven by visible-light irradiation.

![Figure 2.19](image)

**Figure 2.19** (a) An irradiation time dependence of H₂ (red circle) and O₂ (blue circle) evolution at the pH combination of 3 and 6.8. (b) The pH dependence of the H₂ (closed circle and square) and O₂ (open circle and square) evolution efficiency under the conditions that the pH value in the H₂ evolution side is fixed at 3 as plotted on yellow background and the pH value in the O₂ evolution side is fixed at 6.8 as plotted on green background, respectively.

### 2.4.5 Mechanism for the plasmon-assisted water splitting reaction

The pH dependence experiments clearly demonstrated that the pH dependence of water splitting exhibits an asymmetrical response. The mechanism for water oxidation is considered to rely on the adsorption of OH⁻ onto the surface of SrTiO₃, close to the Au-NPs. In addition, the efficiency of O₂ evolution is strongly dependent on the
concentration of OH\(^-\), as defined by the pH value, because the adsorbed hydroxyl ions must be oxidized by multiple electron holes to evolve oxygen.\(^{[37]}\) However, under neutral conditions, such as pH 6.8, the surface concentration of OH\(^-\) is lower than that under alkaline conditions. Water molecules must dissociate to form adsorbed OH\(^-\) on the surface of SrTiO\(_3\), thereby resulting in the observation that the reaction rate of water oxidation is lower than that of OH\(^-\) oxidation. Notably, the effective water-splitting process proceeds under neutral conditions in the present system, which suggests that water molecules could be directly oxidized by the plasmon-induced water splitting system. Thus, the efficient oxidation of water and OH\(^-\) also requires highly concentrated electron holes at a local site because multiple electron transfer processes are required with two water molecules or four OH\(^-\) groups. The possibility exists that the LSPR generates multiple holes at the plasmonically enhanced optical near-field because of an efficient charge separation and that the multiple holes trapped at the surface states of SrTiO\(_3\) near the hot site might be stored at a local site of the SrTiO\(_3\). The stored multiple holes confined at a local site of the SrTiO\(_3\) may be able to accelerate the oxidation of water or OH\(^-\) and the subsequent evolution of oxygen.

Figure 2.20 A schematic diagram of the hot sites near the interface between the Nb-SrTiO\(_3\) substrate and the Au-NPs.

Figure 2.21 illustrates the energy diagram of the plasmon-induced water splitting system based on the Au-NP-loaded SrTiO\(_3\) photoelectrode at the pH combination of 3 and 6.8. It is hypothesized that the plasmon resonance is first induced by visible and
near-infrared light, and the enhanced optical near-field excites an electron from the gold nanoparticles or from the surface-state electron of the Nb-SrTiO₃. The excited electron is transferred to the conduction band of the Nb-SrTiO₃. The electron that arrived at the back of the substrate reduces a proton on the Pt surface and hydrogen is evolved from the cathode. Conversely, the hole left behind at the Au/SrTiO₃/water interface oxidizes water or OH⁻ via multi-electron transfer, and oxygen is evolved from the anode. Thus, plasmon-induced water splitting was clearly demonstrated, and the efficient water oxidation due to the plasmon effect reduced the chemical bias by 0.23 V.

**Figure 2.21** Energy diagram of the plasmon-induced water splitting system using Au-NPs loaded SrTiO₃ substrate at the pH combination of 3 and 6.8. The flat band potential of SrTiO₃ at pH 6.8 was estimated as -0.601 V vs. SHE because the potential of the conduction band of SrTiO₃ is known to be -0.2 V vs. SHE at pH 0. The difference in the potential of 0.401 V is due to pH difference.

The water oxidation appears to proceed efficiently because the hole does not remain in the Au-NPs. Moreover, multiple holes are trapped in the surface states of Nb-SrTiO₃ in a spatially selective nanospace near the Au-NPs/Nb-SrTiO₃/water interface, thus allowing for oxidization of the water molecules. Therefore, it can be concluded that the plasmon-induced charge separation behaves like a co-catalyst for oxygen evolution. It is
reasoned that the generated holes did not remain in the Au-NPs because the Fermi levels ($E_f$) of Nb-SrTiO$_3$ and Au coincide when the Au-NP contacts the surface of Nb-SrTiO$_3$. It is known that $E_f$ exists slightly below the conduction band energy of Nb-SrTiO$_3$. Because the generated holes might easily migrate to the $E_f$, the holes will lose the capability of oxidizing water in a thermodynamically favored manner because the potential difference between the flat band potential and $E_f$ is approximately 0.9 V when Au is in contact with TiO$_2$. The main characteristic of the water splitting system is that hydrogen and oxygen are produced separately and can be removed from the different electrolysis chambers. Additionally, only the Au-NP side needs to be irradiated, which reduces the area required for light irradiation because the reduction of the proton is a dark reaction.

2.4.6 Stability of the plasmon-assisted water splitting system

The water splitting experiment with a longer time irradiation was carefully performed to check its stability. The irradiation time dependence of $H_2$ and $O_2$ evolution with a pH combination of 3 and 6.8 is shown in Figure 2.22. The linear relationship of both $H_2$ and $O_2$ evolution was obviously observed even with an irradiation of 48 hours. Thus, a stable plasmon-assisted water splitting system was constructed.

![Figure 2.22](image)

**Figure 2.22** The irradiation time dependence of $H_2$ and $O_2$ evolution with a pH combination of 3 and 6.8. The data from 1 to 6 as an irradiation time was taken from Figure 2.18 (a).
2.5 Conclusions

In conclusion, a stable and simple plasmon-induced water splitting system without an external electrochemical apparatus was successfully developed by using two sides of the same SrTiO$_3$ single-crystal substrate. The reaction cell involved no electric bias. Instead, the pH value regulation is adopted. Namely, the electric potential has been successfully substituted with chemical potential in the photocatalytic water splitting reaction. The huge advantage using plasmonic Au nanostructures is stable over long time unlike molecular sensitizers and its plasmon resonant wavelength can be tuned by simply changing their shape and/or size to cover a large part of the solar spectrum. A stoichiometric evolution of H$_2$ and O$_2$ was simultaneously obtained from two separate solution chambers. The quantity of the evolved gases linearly increased with the irradiation time. Solar energy has been successfully converted into chemical energy and stored in the form of hydrogen gas. The separate evolution of H$_2$ and O$_2$ is expected to suppress the recombination of the two gases. Even the irradiation of the unprecedented long wavelength from 750 nm to 850 nm succeeded in water splitting. The mechanism for the water splitting device occurs through plasmon-induced charge separation at the Au-NP/SrTiO$_3$ interface, thereby promoting water oxidation and subsequent reduction of a proton on the backside of the SrTiO$_3$ substrate. The H$_2$ and O$_2$ generation efficiency is highly dependent on the pH values of the solution environments. The pH dependence experiments revealed that the chemical bias is substantially reduced by plasmonic effects up to 0.23 V because of efficient water oxidation. Although the apparent quantum efficiency is still low (4.4 × 10$^{-4}$ % at 600 nm), these results indicate the possibility of constructing an efficient artificial photosynthesis system that responds to visible and near-infrared light and does not need the chemical bias through the combination of an efficient co-catalyst for H$_2$ evolution on the backside of a SrTiO$_3$ substrate as well as understanding the detailed mechanism.
2.6 References


1909-1920.


Chapter 3

Co-catalyst Effects on Hydrogen Evolution in the Plasmon-Induced Water Splitting System

3.1 Abstract

Recently great progress has been achieved in the development of photoelectrochemical (PEC) water splitting. Especially, water splitting systems that respond to visible light have received considerable attention in the past decade. The water splitting systems that respond to visible light have been developed according to metal ion doping to semiconductor, Z-scheme process, and dye or plasmon sensitization. Although the progress in plasmon-induced water splitting system made in recent few years, the water splitting efficiency is still low. It is well known that loading proper co-catalysts on semiconductors (as light harvesters) can significantly enhance the activities of PEC water splitting reactions. Therefore, it is of significance to establish a system with rational design to precisely evaluate the capacity of different kinds of co-catalysts. A lot of studies were performed using n-type semiconductor particles system to elucidate co-catalyst effects so far. In these studies, however, it is difficult to evaluate only the catalytic activity of H₂ and O₂ evolutions as following reasons; 1) An electron injected into the conduction band of semiconductor is hard to transfer to the H₂ evolution co-catalyst because Schottky barrier can be readily formed when a metallic co-catalyst for H₂ evolution contacts the n-type semiconductor, hindering the performances of the co-catalyst from being comprehended. 2) There is a possibility that a reverse reaction of water splitting occurs and these co-catalysts also promote reduction of the evolved O₂. In order to tackle these factors, a facile plasmon-induced water splitting system using gold nanoparticles (Au-NPs) loaded strontium titanate (SrTiO₃) single crystal substrate was
developed. In this chapter, the co-catalyst effect on hydrogen evolution in the plasmon-induced water splitting was investigated. To eliminate the adverse effect of the Schottky barrier, a Pt board was stick on the hydrogen (H₂) evolution side of the SrTiO₃ substrate via In-Ga alloy to obtain ohmic contact between semiconductor and metal or metal oxide co-catalysts. The water spitting yield with this SrTiO₃/Pt composite substrate was remarkably enhanced as compared to that with the Pt thin film without In-Ga Alloy as H₂ evolution co-catalyst. The importance of the ohmic contact for the H₂ evolution in the plasmon-induced water splitting system was thus successfully demonstrated. Subsequently, the Pt board was decorated with a noble metal or their corresponding metal oxide as a co-catalyst for H₂ evolution. Enhanced evolution of H₂ and O₂ with stoichiometric ratio was obviously demonstrated with all kinds of co-catalysts. As the result, among the co-catalyst materials examined, rhodium thin layer with a thickness of 2 or 3 nm deposited on platinum board exhibited relatively high performance as a 3-fold increment compared with the absence of any metal or metal oxide co-catalyst thin layer for this application. Furthermore, the evolution of H₂ and O₂ were successfully separated according to using two sides of the same SrTiO₃ substrate. The separate evolution of H₂ and O₂ was supposed to suppress the undesirable reverse reactions of water splitting such as H₂–O₂ recombination and/or photoreduction of O₂.
3.2 Introduction

In order to realize a substitution for the fossil fuels, the development of clean, environmental friendly, and sustainable energy sources has drawn considerable attention by many researchers. Currently, it has become common sense that solar energy will play a key role in the development of new energy sources since it is abundant, clean and especially renewable. Hydrogen has attracted significant interest as a renewable energy carrier offering both high-energy capacity and minimal environmental impact. As a sustainable approach for new energy sources, photocatalytic hydrogen production utilizing solar energy is a promising strategy.\(^1\)

Photoelectric conversion and the photoelectrochemical water splitting has been of great interest since the early 1970s after the first demonstration using a titanium dioxide (TiO\(_2\)) photoelectrode under ultraviolet radiation by Fujishima and Honda.\(^2\) Nevertheless, one drawback of TiO\(_2\) is that it can only be excited by ultraviolet light, i.e., with wavelengths shorter than ca. 400 nm. Therefore, only a very small portion of solar radiation (3–5\%) can be utilized to drive such chemical reactions. Thus, extension of its absorption wavelength range to the visible region becomes an important issue. Numerous attempts have been made afterwards to extend the cutoff wavelength of the water splitting system. To date, utilization of visible light has been attained by doping,\(^3\) defect creation,\(^4\) and organic dye sensitization.\(^5\) Thereinto, plasmon-induced water splitting realized by noble metal nanoparticles decorated on catalytic semiconductor materials possesses unique advantages, as has been reported by some researchers.\(^6,7\) Previously, our research group successfully demonstrated plasmon-enhanced photocurrent generation and water oxidation through irradiation with visible and near-infrared light using a TiO\(_2\) single crystal photoelectrode loaded with Au-NPs.\(^8\)

The solar to chemical energy conversion efficiency is still low and far from practical application up until now, although many materials have been found to be capable of performing the water splitting reaction. The reason might be that there are three crucial steps for the water splitting reaction which is considered to be not yet efficient: solar light
harvesting, charge separation and transportation, and the catalytic reduction and oxidation reactions. Among these problems, in this chapter, the co-catalyst effects concerning with the multiple electron transfer process is discussed.

As a thermodynamically uphill reaction, water splitting requires the transfer of multiple electrons, making it one of the most challenging reactions in chemistry. It is well known that adequate co-catalysts loaded semiconductors significantly enhance the activities of the water splitting. For semiconductor-based PEC systems, loading oxidation and/or reduction co-catalysts can facilitate oxidation and reduction reactions by providing the active sites and reaction sites while suppressing the charge recombination and reverse reactions. The important roles of co-catalysts in PEC water splitting reactions have been under investigation for a long time. Domen et al. have reported multiple co-catalysts to enhance the water-splitting activity, including co-catalysts for the reduction of water to form H₂ such as Pt, Rh, and co-catalysts for the oxidation of water to form O₂ such as IrO₂, Mn₃O₄, RuO₂.⁹,¹⁰ Based on the former work, it is already known that the photocatalytic activity is highly dependent on the kind, size and morphology of the co-catalysts. Nevertheless, the intrinsic properties of many kinds of co-catalyst and their interaction mechanisms with catalytic semiconductor materials are still not so clear at the present time. Thus, it is of special significance to evaluate the capacity of various co-catalysts and to acquire an in-depth understanding of their function in the process of the PEC water splitting reactions. However, in most conventional photocatalyst architectures, it is difficult to evaluate co-catalyst effect for hydrogen (H₂) evolution correctly in the water splitting system using semiconductor particles as following reasons. As for H₂ evolution, it becomes problem that Schottky barrier formed by loading metal on the surface of semiconductor makes electron transfer rate from the conduction band of semiconductor to the metallic co-catalyst slow as result in increasing the possibility to induce the back electron transfer reaction. Namely, it is not understandable because not only co-catalyst effects but also Schottky barrier effect is included in the experimental results. In addition, it also becomes problem that a reverse reaction of water splitting such as H₂—O₂
recombination to form H$_2$O and photoreduction of O$_2$ simultaneously induced in the semiconductor particles system because the co-catalysts also promote the reduction of the evolved O$_2$. Therefore, the evaluation of co-catalyst effect for H$_2$ evolution might not be simple. In the previous chapter, a facile artificial photosynthesis system using the In/Ga alloy to eliminate the Schottky barrier was described.\cite{11} The evolution of H$_2$ and O$_2$ has been successfully separated according to using two sides of the same SrTiO$_3$ substrate which work as cathode and anode, respectively.

Liao et al. reported that cobalt oxide (CoO) nanoparticles can carry out overall water splitting with a solar-to-hydrogen efficiency of around 5\%.\cite{12} However, the H$_2$ and O$_2$ were evolved at the same site of the identical nanoparticle material. Hence, the undesired recombination between H$_2$ and O$_2$ was thus inevitable. Luo et al. described a low-cost water splitting cell combining a solution-processed perovskite tandem solar cell and a bifunctional earth-abundant catalyst with a solar-to-hydrogen efficiency of 12.3\%.\cite{13} Despite the exceptionally high efficiency, external electric bias was constantly required in the water splitting process.

Herein, it is proposed that the stoichiometric evolution of H$_2$ and O$_2$ can be realized by using two sides of the same semiconductor substrate without any external electric bias. Chemical potential was employed by adjusting the pH value difference between the two reaction chambers, in order to substitute the conventional electrical potential as a driving force to promote the water splitting reaction.

In this chapter, the plasmon-induced water splitting system that responds to visible light using Au-NPs loaded SrTiO$_3$ single crystal substrate is presented. Electron transfer from the semiconductor material to the cathode was facilitated by the Ohmic contact, which was formed by In/Ga alloy paste. Noble metal and metal oxide deposited on Pt board as H$_2$ evolution co-catalyst were characterized and the photocatalytic activity of which were evaluated. With the O$_2$ evolution side architecture remained the same (Au-NPs loaded SrTiO$_3$), both the evolution yields of H$_2$ and O$_2$ were improved by all kinds of co-catalysts deposited on the H$_2$ evolution side. In this chapter, the performance
of H$_2$ evolution was explored using noble metal such as Rhodium (Rh) and Ruthenium (Ru) or their metal oxide as a co-catalyst in the plasmon-induced water splitting system, among which the Rh showed the best enhancement as 3-fold. It is thus speculated that the co-catalysts accelerated the electron transfer and its reaction with protons to form H$_2$ evolution. The recombination of electrons and holes was reduced accordingly, resulted in enhanced yields of both H$_2$ and O$_2$ evolution. Furthermore, the evaluation of various kinds of co-catalysts with the effects of Schottky barrier excluded became realizable since the successfully formation of the ohmic contact between the semiconductor material and the H$_2$ evolution co-catalyst. Moreover, H$_2$ and O$_2$ evolutions were performed in different chambers with cathode and anode, respectively. Au-NPs side works as anode for O$_2$ evolution and Pt board with metal or metal oxide co-catalyst side works cathode for H$_2$ evolution. Therefore, O$_2$ and H$_2$ were evolved from the surface and the back of the same SrTiO$_3$ substrate according to separate the evolved H$_2$ and O$_2$ as the result. The separation of H$_2$ and O$_2$ evolution in different chambers was supposed to inhibit the backward reactions so as to enhance the water splitting efficiency. According to eliminate the Schottky barrier effect and avoid a reverse reaction of water splitting, it becomes possible to evaluate co-catalyst effects on H$_2$ evolution.
3.3 Experimental details

3.3.1 Preparation of noble metal and metal oxide co-catalyst

Pt thin film was sputtered on the back side of the SrTiO$_3$ using Super Fine Coater ESC-101 (ELIONIX, Japan) with a deposition rate of 0.2 Å/s. The Ru and Rh species thin films were deposited onto the Pt substrate (10 × 10 × 0.2 mm$^3$, 99.98%, Nilaco Corporation) by a co-sputtering system (ACS-4000-C3-HS, ULVAC Co.), and the distance from the target to the substrate was maintained at 150 mm. The targets were ruthenium and rhodium metal with a purity of 99.95%, respectively. For the Ru and Rh oxide thin film deposition, a mixture of Ar and O$_2$ flow was maintained during the sputtering process. Whereas for the metallic Ru and Rh fabrication, an Ar gas flow with a rate of 29 sccm was induced in the absence of O$_2$ flow. The deposition pressure was kept at 2.9×10$^{-1}$ Pa. The substrate was without intentional heating during the deposition processes. The Pt board with noble metal or metal oxide thin film on the surface was adhered to the backside of the Nb-SrTiO$_3$ substrate via Ag paste (D-550, Fujikura Kasei). The X-ray photoemission spectrum (XPS) characterization was performed by X-ray photoemission spectrometer (JPS-9200, JEOL, Japan). The center part with 3 mm × 3 mm area of the substrate surface was used for XPS characterization. The AlKa line was used as the X-ray source. The C 1s signal was used as an internal reference (284.6 eV). The cross sectional structure and the elemental distribution of the thin films on the Pt board were analyzed by using transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS) on JEOL JEM-ARM 200F with aberration correction.

3.3.2 Electrochemical measurements

Bare Pt board and Pt boards with 2 nm Ru or Rh thin film prepared by the sputtering process were used as the working electrodes. Ag paste (D-550, Fujikura Kasei) film was pasted on the back of the Pt substrate and connected to the electrochemical analyzer (ALS/CH Instruments 852C, ALS) with a lead wire. A platinum wire and a saturated
calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively. The electrochemical properties of the electrodes were measured in an aqueous solution of 0.05 M K₂SO₄ adjusted to pH 1 with H₂SO₄ with continuous N₂ bubbling.
3.4 Results and discussion

3.4.1 Elimination of the Schottky barrier effect

In this study, a 0.05 wt% niobium (Nb)-doped strontium titanate (Nb-SrTiO₃) single crystal with a bad gap of 3.2 eV was employed as a semiconductor photoelectrode for efficient water splitting. The water splitting system comprises two reaction chambers separated by the Au-NPs loaded Nb-SrTiO₃ substrate, as shown in Figure 3.1. In order to facilitate the water splitting reaction, a chemical bias was applied between the H₂- and O₂-evolution chambers. Specifically, the pH was regulated using hydrochloric acid (HCl) and potassium hydroxide (KOH) aqueous solutions with a concentration of both 0.1 M. Hence, the pH value in the front side chamber (O₂ evolution side) was regulated at 13 while that in the back side chamber (H₂ evolution side) was set at 1 with alkaline and acidic aqueous solutions, respectively. According to the Nernst equation, the relationship between the redox potential (U⁰) and the pH value at 25°C is given by:

\[ U^0 = U^0(pH = 0) - 0.059 \times pH \]  

Therefore, the chemical bias applied between the two chambers was estimated to be 0.71 V.[14]

![Figure 3.1 A schematic diagram illustrating the water splitting device using the Au-NP-loaded Nb-SrTiO₃ photoelectrode.](image-url)
A φ6 mm$^2$ area of the gold-nanostructured Nb-SrTiO$_3$ substrate was irradiated by a xenon lamp with a light intensity of 0.32 W/cm$^2$ and a wavelength spectrally filtered from 550 nm to 650 nm as a visible light source in this experiment. The incident photon flux was measured using spectroradiometer (MSR-7000N, Optoresearch Co.). Under the irradiation of visible light to Au-NPs, plasmon-induced charge separation between Au-NPs and Nb-SrTiO$_3$, and subsequent water oxidation are supposed to take place at the front side chamber, so as to promote the O$_2$ evolution. Whereas in the back side chamber, H$_2$ evolution is expected on account of the reduction of protons by photogenerated electrons injected into the conduction band of Nb-SrTiO$_3$ at Pt surface used as a cathode material. A conventional salt bridge with 2% of agar in weight ratio was employed to maintain the charge balance between these compartments. It was clearly confirmed that the pH value did not change before and after the irradiation in each experiment, the salt bridge was thus verified to be effective.

**Figure 3.2** A schematic illustration of the photoelectrode architecture for water splitting using a Pt board (a) and a Pt thin film (b) as the hydrogen evolution site, and the irradiation time dependence of H$_2$ (solid circles) and O$_2$ (open circles) evolution (c) by...
which respectively. The red and blue colors correspond to the Pt board and Pt thin film, respectively.

In order to demonstrate the effect of the Schottky barrier to the water splitting activity in the present system, substrates with different cathode structure were fabricated. Their architectures and the H₂ and O₂ evolution time dependence are shown in Figure 3.2 (a) and (b), respectively. For the contrastive structure, Pt thin film with a thickness of 1 nm was sputtered on the back side of the Nb-SrTiO₃ substrate, as a substitute for the Pt board.

From the separate experiment, it has been confirmed that water splitting efficiency was best with a Pt thickness of 1 nm when Pt thin film was deposited by sputtering directly on the SrTiO₃ substrate. The averaged thickness of Pt film was controlled by sputtering time and determined by an absolute calibration method. Therefore, the film might be discontinuous because the film thickness was set to less than a grain size of 2 nm in this Pt sputtering process.

The XPS spectra of the back side Nb-SrTiO₃ surface before and after Pt nanoparticles deposition are shown in Figure 3.3. Characterization of Pt nanoparticles was conducted by X-ray photoemission spectrum (XPS, JPC-9010MC, JEOL). The AlKα line was used as the X-ray source. The C 1s signal was used as an internal reference (284.6 eV).

Under the irradiated conditions, the evolution of H₂ and O₂ is linearly increased with an irradiation time by both kinds of the structures. Stoichiometric evolution of H₂ and O₂ (2:1) was observed in both cases. Note that the H₂ and O₂ evolution by the photoelectrode with Pt thin film are only half that of the one with Pt board stick on the Nb-SrTiO₃ via In/Ga alloy. Without Au-NPs decoration, it has been confirmed that neither H₂ nor O₂ was evolved from a Nb-SrTiO₃ substrate under the same irradiation conditions. No production of H₂ or O₂ was observed by either photoelectrode architecture in the absence of irradiation for up to 6 hours.
Figure 3.3 Partial XPS spectra of the Nb-SrTiO$_3$ loaded with Pt nanoparticles. A comparison of before and after the Pt nanoparticle deposition on the back side surface.

Figure 3.4 depicts the energy band alignment of the composite substrate structure. It is hypothesized that an excited electron is transferred to the conduction band of SrTiO$_3$ immediately following the inter- or intraband transition of the Au-NPs induced by the plasmonically enhanced optical near-field or by hot electron transfer, thus leaving an electron hole trapped at the surface states of the SrTiO$_3$ near the Au/SrTiO$_3$/water interface. The trapped holes can subsequently induce the oxidation of hydroxyl ion or water molecules efficiently via multi electron transfer.$^{[15]}$ There is a potential gradient between the two sides of the Nb-SrTiO$_3$ substrate because a chemical bias was applied by pH regulations. Under the influence of this potential gradient, the photogenerated electrons injected into the conduction band of SrTiO$_3$ transferred to the back side and subsequently induced the reduction of proton at the Pt surface. With the Pt nanoparticles on the back side of the Nb-SrTiO$_3$, there is an undesired Schottky barrier between the Nb-SrTiO$_3$ and Pt, which hindered the electrons from transferring to the cathode, resulting in the relatively lower H$_2$ and O$_2$ evolution efficiency. Whereas using In/Ga alloy to stick the Pt board with the Nb-SrTiO$_3$ substrate, an ohmic contact is very important for the H$_2$ evolution in the plasmon-induced water splitting system, so as to facilitate the electron transfer.
Figure 3.4 Energy band alignment of the plasmon-induced water splitting system with the Au-NPs loaded SrTiO$_3$ substrate using Pt nanoparticles (a) and a Pt board (b) as the hydrogen evolution site respectively. $U_{FB}$ and $U^0$ show the flat band potential of SrTiO$_3$ and the redox potentials versus SHE (standard hydrogen electrode), respectively. The symbols [−] and [+] indicate electrons and holes.
3.4.2 Characteristics of the Ru and Rh species thin film on Pt board

A water splitting system is commonly composed of a semiconductor material and co-catalysts for H\textsubscript{2} and O\textsubscript{2} evolution, respectively. The photocatalytic activity of the system is highly dependent on the co-catalysts and their properties. Hence, the evaluation of different co-catalysts becomes a very important issue.\textsuperscript{[16, 17]} Based on the as mentioned composite structure, the Schottky barrier between the co-catalyst and the semiconductor could be eliminated, giving out the possibility to verify the performance of various kinds of co-catalysts.

The ruthenium (Ru)\textsuperscript{[18, 19]} and rhodium (Rh)\textsuperscript{[20, 21]} species, which have been considered to be excellent co-catalysts for H\textsubscript{2} evolution, were employed in the present study. A thin film of these two metals with a thickness of 2 or 3 nm was deposited by sputtering on the Pt board and served as a co-catalyst for H\textsubscript{2} evolution. By precisely controlling the oxygen flow during the sputtering process, oxide of Ru and Rh species were also prepared, respectively. The cross sectional view of a transmission electron microscope (TEM) image of Rh thin film with a thickness of 3 nm deposited on the Pt board by sputtering is shown in Figure 3.5(a) and its corresponding energy dispersive X-ray spectrometry (EDS) image is shown in Figure 3.5(b). It was obviously confirmed that a continuous Rh thin film with a thickness of 3 nm was formed on the Pt board surface. On the other hand, the cross sectional view of TEM image of rhodium oxide with a thickness of 4 nm and its corresponding EDS image are shown in Figure 3.5(c) and 3.5(d), respectively. Although images of the film with a thickness of 4 nm were demonstrated here instead of 2 or 3 nm film for easier understanding by TEM observation, importantly, rougher surface is clearly observed in the case of rhodium oxide film as compared to the Rh film. The top view SEM images for Pt boards partially covered by these thin films are shown in Figure 3.6. Due to the difference in the conductivity, all the thin films show a relatively dark color compared with the bare Pt board.
Figure 3.5 Cross sectional view of transmission electron microscope images for (a) Rh, (c) RhOx, (e) Ru and (g) RuOx, and their corresponding energy dispersive X-ray spectrometry (EDS) images (b) Rh, (d) RhOx, (f) Ru and (h) RuOx thin films deposited on the Pt board by sputtering. The signal of Rh/Ru and Pt in the EDS images is indicated by green and blue colors, respectively. The scale bars represent 5 nm in the all images.
Figure 3.6 The scanning electron microscope images for (a) Ru, (b) RuO$_x$, (c) Rh, and (d) RhO$_x$ thin film deposited on the Pt board by compact sputtering. The scale bars represent 1 μm in the all images.

The XPS spectra of the metal and oxide of Ru and Rh are shown in Figure 3.7. Without O$_2$ flow during the sputtering process, the peak positions of the Ru species are at 461.3 and 483.5 eV for Ru $3p_{3/2}$ and $3p_{1/2}$, the peak positions of the Rh species are at 306.5 and 311.3 eV for Rh $3d_{5/2}$ and $3d_{3/2}$, which are all in good coincidence with the standard values of the metallic species.$^{[22]}$ Whereas with O$_2$ flow during the sputtering process, the as-deposited Ru and Rh species are clearly oxidized, but not as much as a RuO$_2$ or Rh$_2$O$_3$ bulk reference. (462.7 and 484.8 eV correspond to the Ru$^{4+}$ oxide RuO$_2$, 308.4 and 313.2 eV correspond to the Rh$^{3+}$ oxide Rh$_2$O$_3$). Accordingly, these oxides will be referred to as RuO$_x$ and RhO$_x$ hereafter, respectively. Figure 3.8 depicts the thickness dependence of partial XPS spectra for RuO$_x$ thin film deposited on the Pt board. With an increased RuO$_x$ thickness, the corresponding XPS peak area ratio between Ru 3p and Pt 4f increase almost linearly.
Figure 3.7 XPS spectra for (a) Ru 3p and (b) Rh 3d thin films sputtered with (red solid line) and without (black solid line) O\textsubscript{2} flow on the Pt board. The black and the red dashed lines indicate the standard metal and oxidation state peak positions of Ru and Rh, respectively.

Figure 3.8 (a) The thickness dependence of partial XPS spectra for RuO\textsubscript{x} thin film deposited on the Pt board, the black, red, blue and green lines indicate the RuO\textsubscript{x} thickness of 1, 2, 3 and 4 nm, respectively. (b) The corresponding XPS peak area ratio between Ru 3p and Pt 4f.
3.4.3 Water splitting performance using various H$_2$ evolution co-catalyst

Water splitting was conducted with all kinds of the co-catalysts and with a bare Pt board as a control experiment. The schematic illustration of the photoelectrode architecture is shown in Figure 3.9(a). Figure 3.9(b) depicts the irradiation time dependence of photocatalytic H$_2$ and O$_2$ evolution over 2 nm Rh on the Pt board. Stoichiometric evolution of H$_2$ and O$_2$ (2:1) was still observed in the case of Rh co-catalyst. This result indicated that noble metal deposited on Pt does not involve any side reactions and works well as a co-catalyst for H$_2$ evolution. Figure 3.9(b) also shows the result of recycling reactions to verify the stability of the water splitting system. Significantly, the reaction proceeded with no noticeable deactivation in the 4 rounds recycling reactions with an irradiation time sums up to more than 80 h, demonstrating the good stability of the present architecture. With the reaction time approached 6 hours, the photocatalytic activity tends to be saturated. The increase of pressure due to the evolved gas in the system seemed to suppress further evolution of H$_2$ and O$_2$. Hence, various kinds of noble metal and metal oxide were used as H$_2$ evolution co-catalyst for comparison and the corresponding rates of H$_2$ and O$_2$ evolution is shown in Figure 3.9(c). The evolution of both H$_2$ and O$_2$ is linearly increased with an irradiation time in all cases. The quantity of H$_2$ evolved from the surface of all kinds of reduction co-catalyst is twice that of O$_2$ evolved from the Au nanostructured surface. Therefore, stoichiometric evolution of H$_2$ and O$_2$ was obviously demonstrated by various co-catalysts.

Compared with the bare Pt board, the H$_2$ evolution rate has been enhanced by all co-catalysts to varying degrees. These co-catalysts are supposed to facilitate the electron transfer and its reaction with the protons in the acidic solution environment. The primary role of the noble-metal or metal oxide thin film on the Pt board is to offer active sites for H$_2$ evolution reaction.$^{[23]}$ Thus, all above-mentioned results indicate that the Au-NPs/Nb-SrTiO$_3$/In-Ga alloy/Pt/co-catalyst architecture is a promising candidate as photocatalysts. Similar tendency was also observed using co-catalyst film with a thickness of 3 nm.
Figure 3.9 (a) A schematic illustration of the photoelectrode architecture for the overall water splitting using a Pt board decorated with various kinds of co-catalysts as the hydrogen evolution site. (b) The recycling irradiation time dependence of H₂ and O₂ evolution by the present water splitting system using Rh deposited on the Pt board as the H₂ evolution co-catalyst with a thickness of 2 nm. (c) A comparison for the rates of H₂ (pattern filled bars) and O₂ evolution (open bars) by the water splitting system using a Pt board decorated with various kinds of co-catalyst respectively.

The stability of the noble metal and metal oxide co-catalysts under visible light irradiation was confirmed using XPS. Each of the Pt boards with co-catalysts after 24 h light irradiation was collected and served for the measurements. Neither Ru 3p, Ru 3d, Rh 3p nor Rh 3d XPS spectra was changed after the irradiation by all kinds of the co-catalysts (Figure 3.10). Therefore, the present noble metal or metal oxide on the Pt board was quite stable under the present experimental conditions.
Figure 3.10 XPS spectra of Ru 3p and 3d for (a) Ru, (b) RuOₓ and Rh 3p and 3d for (c) Rh, (d) RhOₓ thin film on the Pt board before (black) and after (red) water splitting reaction for 24 h.

With the purpose of further confirming the function of the ohmic contact, as a comparison, a RuOₓ thin film with a thickness of 2 nm used as the H₂ evolution co-catalyst was deposited directly on the back side of the Nb-SrTiO₃ substrate in the absence of the In/Ga alloy and Pt board. The composite substrate structure and the corresponding time dependence of H₂ and O₂ evolution are shown in Figure 3.11. It was confirmed that the water splitting yield markedly declined without the In/Ga alloy and Pt board.
Figure 3.11 A schematic illustration of the photoelectrode architecture for water splitting using RuO\(_x\) thin film with a thickness of 2 nm deposited on the Pt board (a) and directly on the Nb-SrTiO\(_3\) substrate (b) as the hydrogen evolution site, and the irradiation time dependence of H\(_2\) (solid circles) and O\(_2\) (open circles) evolution (c) by which respectively. The red and blue colors correspond to with and without the Pt board, respectively.

As have been reported by many researchers, some noble metals and metal oxides deposited on a photocatalyst work as co-catalysts for H\(_2\) evolution even in this plasmon-induced water splitting. Ideally, the reaction occurring on such co-catalysts should be hydrogen evolution. In some cases, however, undesirable reverse reactions, such as H\(_2\)–O\(_2\) recombination to form H\(_2\)O and photoreduction of O\(_2\), occasionally take place on the surface of such co-catalysts, thereby hindering the forward reaction. To solve these problems, Maeda et al. reported that using Cr\(_2\)O\(_3\) shell, which is permeable to protons and hydrogen but not oxygen, photodeposited on noble-metals or metal oxides to prevent the reverse reactions.\(^{[24-26]}\) With the unique two chamber structure, the water splitting system
presented in this study is also capable to suppress the reverse reactions by the separate evolution of H₂ and O₂. Furthermore, certain metal oxides, RuO₂ for instance, can work as both a water reduction and oxidation site during the water-splitting reaction.\textsuperscript{[27, 28]} The separation of the H₂ evolution co-catalyst from O₂ evolution co-catalyst in two different chambers with different solution environment provides a new approach to investigate individual co-catalyst, excluding the influence from the other.

Cyclic voltammograms of the bare and Ru-, Rh-coated Pt electrodes obtained with continuous N₂ bubbling are shown in Figure 3.12. The currents indicating proton adsorption/desorption and hydrogen evolution were observed at from -0.2 to -0.1 V and -0.3 V, respectively, on all cases. For the Rh-coated Pt electrode, the current showed an enhanced slope compared with the bare Pt board when the voltage tends to -0.3V, indicating the H₂ evolution had been kinetically accelerated by the Rh decoration. However, the onset potential exhibited a negative shift with Rh thin film, revealing that it is thermodynamically adverse to the proton reduction. Whereas in the case of the Ru coating, on the contrary, the proton reduction and the H₂ evolution had an advantage thermodynamically, yet they suffered kinetically. Therefore, the higher yield of the H₂ evolution obtained by the Rh as a co-catalyst is presumably ascribed to the interplay between the above-mentioned two aspects. Furthermore, the work function of Rh (4.98 eV) is higher than that of Ru (4.71 eV). The electron transfer from Pt (with a work function of 5.65 eV) to the H₂ evolution co-catalyst might be thus preferable in case of Rh compared with Ru. The same tendency has been reported previously.\textsuperscript{[29]}
Figure 3.12 Cyclic voltammograms for bare and 2 nm Ru- and Rh-coated Pt electrodes in 0.05 M K$_2$SO$_4$ aqueous solution adjusted to pH 1 with H$_2$SO$_4$ under N$_2$ bubbling (scan rate, 50 mV/s).

The relatively higher yield of the H$_2$ evolution obtained by the Rh than the Ru as a co-catalyst is presumably ascribed to the difference of the free energy of hydrogen adsorption $\Delta G_H$. It was reported that this quantity is highly concerned with hydrogen evolution activity for a wide variety of metals and alloys. Actually, it is reported that the absolute value of $\Delta G_H$ of Rh is lower than that of Ru from DFT calculations. This means that the H$_2$ evolution is preferable in the case of Rh co-catalysts as compared to Ru one. As the result, rhodium thin layer with a thickness of 2 or 3 nm deposited on platinum board exhibited relatively high performance as a 3-fold increment compared with the absence of a metal or metal oxide co-catalyst thin layer. Furthermore, the co-catalyst effects for H$_2$ evolution in the plasmon-induced water splitting system have been successfully evaluated according to eliminate the Schottky barrier effect and separate two reaction chambers for hydrogen and oxygen evolutions to avoid a reverse reaction of water splitting.

3.4.4 Dependence of co-catalyst thickness on water splitting activity

Among all the co-catalysts examined, Rh showed the highest yield. Therefore, Rh was selected for the further investigation for the co-catalyst thickness dependence of the H$_2$ and O$_2$ evolution efficiency. As depicted in Figure 3.13, stoichiometric evolution of H$_2$ and O$_2$ was clearly observed with Rh co-catalyst by all thicknesses. With the increment of the Rh thickness, the rates of H$_2$ and O$_2$ evolution both increased up to 2 nm Rh thin film thickness, beyond 3 nm they leveled off markedly and remained almost constant. A 3-fold enhancement of the water splitting yield was obtained by the optimal Rh thickness, compared with the absence of any co-catalyst. The relatively low H$_2$ yield of the films with a small quantity of Rh depositions is due to insufficient sites present to trap electrons.
On the other hand, the decrease in activity at higher Rh loadings is probably related to excess coverage of the Rh nanoparticles deposited on the Pt board. Such excess loading can cause an inner-filter effect, contributing to a decrease in activity.\textsuperscript{[30]}

**Figure 3.13** The rate of $H_2$ and $O_2$ evolution by the present water splitting system using Rh thin film deposited on the Pt board as a $H_2$ evolution co-catalyst with different thickness.
3.5 Conclusions

In summary, a novel plasmon-induced water splitting system without an external electrochemical apparatus was successfully developed. Using semiconductor single crystal substrate to separate the two chambers for H₂ and O₂ evolution, the presented water splitting system features a stable and simple architectural design. The separation of the simultaneous evolution of H₂ and O₂ is supposed to suppress the recombination of the two gases. The mechanism for the water splitting device is considered by plasmon-induced charge separation at Au-NPs/SrTiO₃ interface, thereby promoting water oxidation and subsequent reduction of proton at the SrTiO₃ backside. As a result of the field enhancement by the LSPR near the Au-NPs, photoresponse has been expanded to the visible region. In the present study, efforts have been focused on the co-catalyst effect on H₂ evolution in the plasmon-induced water splitting. A plasmon-induced water splitting with noble-metal or metal oxide as a co-catalyst for H₂ evolution without the Schottky barrier effect and a reverse reaction of water splitting was successfully developed. The Schottky barrier between the Pt cathode and the semiconductor material was successfully removed by employing the In/Ga alloy paste. Thereupon, the accessible evaluation of different kinds of co-catalysts would be possible due to the ohmic contact. With noble-metal or metal oxide decorated on the Pt board as a H₂ evolution co-catalyst, stoichiometric evolution of H₂ and O₂ was observed in all cases, the yields of water splitting has been enhanced to different levels. Among all the co-catalysts tested, metallic Rh gives the greatest improvement of the efficiency as 3-fold compared with the absence of any co-catalyst. The activity also shows a thickness dependence on the co-catalyst. In addition, the plasmon-induced water splitting system with a noble metal as a co-catalyst is highly stable with an irradiation time sums up to more than 80 h. It is of significance to understand and to evaluate the roles of co-catalysts in photocatalytic reactions. The present study has paved a new avenue of utilizing various co-catalysts in the design of new and efficient systems for plasmon-induced water splitting.
3.6 References


Chapter 4

Plasmon-Induced Water Splitting Utilizing Heterojunction

Synergistic Effect between SrTiO$_3$ and Rutile TiO$_2$

4.1 Abstract

A facile plasmon-enhanced water splitting system using gold nanostructured strontium titanate (SrTiO$_3$) single crystal photoelectrode with titanium dioxide (TiO$_2$) thin film heterojunction was developed. Simultaneous evolution of hydrogen (H$_2$) and oxygen (O$_2$) in stoichiometric ratio was successfully observed in separate reaction chambers under visible light irradiation. The substrate composed of single crystal SrTiO$_3$ with the rutile TiO$_2$ thin film heterojunction exhibited enhanced water splitting activity compared with the absence of TiO$_2$ thin film because the back electron transfer reaction might be prevented due to the synergistic effect. A thickness dependence of the Pt co-catalyst on the water splitting activity is also discussed.
4.2 Introduction

The human demand for energy is increasing dramatically in recent years, while the fossil fuel is diminishing and may exhaust in the next few decades. Moreover, we have long been puzzled by environment problems caused by the usage of fossil fuel, e.g. greenhouse gas emissions. Therefore, it is crucial to exploit a new energy source to replace the traditional one. Among all the novel energy considered and explored, solar energy draws much attention since it is clean, abundant, widespread, and inexhaustible. Because fuel cells can convert hydrogen to electrical energy with high efficiency, hydrogen serves as an important chemical energy storage material. The use of hydrogen has been restricted to industrial applications until now, it is currently being expanded for use as a new energy source.

The construction of a light-energy conversion system that uses sunlight for renewable energy with high efficiency is required for the realization of a low-carbon society. Artificial photosynthesis, which stores solar energy as a stable chemical and enables energy use when required, is an important subject. It has attracted attention as a method for storing useful chemical energy, as the form of hydrogen, without any environmental impact. Because the required components for hydrogen generation are only water and sunlight, these energy storage products can be generated using reactants that are virtually infinitely available on Earth. The construction of an artificial photosynthesis system that is sensitive to light energy from ultraviolet to near-infrared wavelengths is indispensable for enhancing the solar energy conversion efficiency of artificial photosynthesis.

H₂ evolution via a photoelectrochemical water splitting using solar light irradiation has been extensively studied ever since the pioneering investigation of Honda and Fujishima in 1971.¹,² Since then, water splitting systems that respond to visible light have been developed according to doping the semiconductor materials with metal ion,³,⁴ utilizing a Z-scheme process with a combination of two kinds of visible wavelength semiconductors via redox mediator,⁵ and using dye or plasmon sensitization.⁶
A plasmon-assisted water splitting system using two sides of the same SrTiO$_3$ single crystal substrate with Au-NPs on the front side and a platinum (Pt) board with ohmic contact on the back side was successfully demonstrated in the previous chapter. In this system, it is considered that an excited electron is transferred to the conduction band of SrTiO$_3$ following the inter- or intraband transition of the Au-NPs induced by the plasmonically enhanced optical near-field. Thus the electron migrates to the back side of the SrTiO$_3$ substrate and reduces protons on the Pt co-catalyst surface for H$_2$ evolution. On the other hand, a hole in the Au-NPs might be trapped on the surface state of the SrTiO$_3$ near the Au/SrTiO$_3$/water interface, and the trapped holes can subsequently induce the oxidation of hydroxyl ions or water molecules efficiently via multi electron transfer for O$_2$ evolution.$^7$

On despite of the progress made in recent few years, the relatively low efficiency still hinders the application of the plasmon-assisted water splitting system. One of the conventional problems lies in the rapid recombination between electron and hole after the charge separation. The unidirectional transportation of electrons utilizing two types of semiconductors with different conduction band energies is thus preferable for use in photoelectrochemical water splitting systems so as to prevent the backward electron transfer.

It is known that a mixture of anatase/rutile TiO$_2$ materials have been reported to exhibit advanced performance for photocatalytic reactions.$^{[8-11]}$ It is considered that the mechanism was ascribed to the different energy band structures between anatase and rutile TiO$_2$. It is commonly known that SrTiO$_3$ shares similar energy band structure with anatase TiO$_2$.$^{[12]}$ Hence, it is of significance to elucidate the synergistic effect of the combination of SrTiO$_3$ and rutile or anatase TiO$_2$ on the plasmon-induced water splitting system. In this chapter, an improvement of plasmon-enhanced water splitting using Au-NPs loaded SrTiO$_3$ single crystal photoelectrode with a TiO$_2$ thin film heterojunction is explored. The H$_2$ evolution co-catalyst thickness dependence of the water splitting yields is investigated. The role of semiconductor materials with different energy band structure is also discussed.
4.3 Experimental details

Single-crystal strontium titanate (SrTiO₃, 0.05wt% niobium doped, 10 × 10 × 0.5 mm³, Furuuchi Chemical Co.) with a (110) surface was used as a semiconductor substrate for water splitting in this study. A thin gold film with a thickness of 3 nm was deposited onto the front side of the SrTiO₃ by helicon sputtering (MPS-4000, ULVAC Co.) at a deposition rate of 1 Å/s. The substrate was subsequently annealed at a temperature of 800°C for 1 h in a nitrogen atmosphere. The thin film was transformed to discontinuous gold nanoparticles (Au-NPs) after annealing. On the other hand, as a H₂ evolution co-catalyst, a Pt thin film was subsequently sputtered by an ESC-101 Super Fine Coater (ELIONIX Co.) on the back side of the SrTiO₃ substrate.

4.3.1 Preparation and characterization of the TiO₂ thin film

Atomic layer deposition (ALD) is a method for depositing thin films conformally on substrates with uniform thickness. It is a self-limiting process in which the film thickness can be accurately controlled by reaction cycles. (Figure 4.1 shows a reaction cycle for a layer of TiO₂ growth.) The low deposition temperature and purging procedure make ALD advantageous in preventing substrates from other unnecessary side reactions. It is therefore very useful for growing oxides (e.g. TiO₂ and Al₂O₃), nitrides (e.g. TiN and TaN), and high-k dielectrics for electronic applications. This method was adopted to grow heterojunction nanomaterials and fabricate electronic devices.

Titanium dioxide thin films with different thicknesses were deposited onto the SrTiO₃ substrate using a commercial hot-wall flow-type ALD reactor (SUNALETM R series Atomic Layer Deposition reactors, Picosun, Espoo, Finland). The deposition procedure involved alternating exposure of TiCl₄ and deionized water vapor at a process temperature of 300 °C with N₂ as a precursor carrier and purge gas at a pressure of 1.6 kPa. The pulse and purge times for the precursors were 0.1 and 4 s, respectively. The deposition rate of TiO₂ on the SrTiO₃ substrate was estimated to be 0.41 Å per cycle. To
fabricate uniform, one sided deposition TiO$_2$ films, the SrTiO$_3$ substrate was tightly attached to a smooth cover glass, which was washed with deionized water in an ultrasonic bath for 5 min. The TiO$_2$ film thickness was estimated from the interference oscillations in the visible spectra using an optical spectroscopic reflectometer (F20, Filmetrics, U.S.A.) with a lower bound accuracy of ±2 nm, and the difference between film thicknesses is ±4 nm.

The reaction process is

1. (−OH) (s) + TiCl$_4$ (g) → (−O−)TiCl$_3$ (s) + HCl (g)  (adsorption)  (4-1)
2. (−O−)TiCl$_3$ (s) + 2H$_2$O (g) → (−O−)TiO(OH) (s) + 3HCl (g)  (reaction)  (4-2)

Figure 4.1 Reaction cycle for the growth of one layer of TiO$_2$ on the SrTiO$_3$ substrate by atomic layer deposition.

The X-ray diffraction spectra of the TiO$_2$ thin films were recorded with a RIGAKU RINT-2000/PC using Cu Kα radiation and a scanning speed of 2° (2θ)/min within the 2θ range from 20 to 80°. Characterization of the TiO$_2$ thin film was also conducted by X-ray photoemission spectrum (XPS, JPC-9010MC, JEOL). The AlKα line was used as the X-ray source. The C 1s signal was used as an internal reference (284.6 eV).
4.4 Results and discussion

4.4.1 Dependence of Pt co-catalyst thickness on water splitting activity

The plasmon-induced water splitting system was constructed as a sealed reaction cell with two chambers, which were separated by the SrTiO₃ substrate as shown in Figure 4.2.⁷, ¹³ The Au-NPs decorated surface was on the front side, which was irradiated by visible light, whereas the surface with Pt thin film was on the back side. The pH values for the front and back side chambers were adjusted to 13 and 1 using aqueous potassium hydroxide (KOH) and hydrochloric acid (HCl) solutions respectively. These two reactions were supposed to take place in the front and back side respectively:

\[ 4h^+ + 4OH^- \rightarrow O_2 + 2H_2O \]  \hspace{1cm} (4-3)

\[ 2e^- + 2H^+ \rightarrow H_2 \]  \hspace{1cm} (4-4)

The acidic and alkaline conditions were engaged as a chemical driving force to promote these two reactions.¹⁴-¹⁷ To maintain the charge balance between the two chambers, a conventional salt bridge with 2wt% agar was employed. The pH values for both chambers were confirmed to be unchanged before and after each irradiation experiment.

Figure 4.2 (a) A schematic illustration of a plasmon-induced water splitting system using an Au-NPs loaded SrTiO₃ substrate with a rutile TiO₂ layer.
As shown in Figure 4.3, plasmonically-enhanced optical near-field promotes a hot electron transfer from Au-NPs to the conduction band of SrTiO$_3$, and namely plasmon-induced charge separation is induced as the result.$^{[18, 19]}$ The Pt on the back side of the SrTiO$_3$ is supposed to act as an electron trap site and co-catalyst for the H$_2$ evolution. The holes remaining in the Au-NPs, which might be trapped in the surface states of SrTiO$_3$ near the Au/SrTiO$_3$/water interface, induce the oxidation of water molecules and hydroxyl ions to evolve O$_2$.\textsuperscript{[20, 21]}

According to the extinction spectrum of the Au-NPs on the SrTiO$_3$ substrate, which clearly show a localized surface plasmon resonance band. The samples were irradiated by a xenon light spectrally filtered over the wavelength range of 550 nm to 650 nm with an intensity of 0.32 W/cm$^2$.

![Figure 4.3](image)

**Figure 4.3** Energy band diagram of the plasmon-induced water splitting system using an Au-NPs loaded SrTiO$_3$ substrate with and without the rutile TiO$_2$ layer. The symbols $[-]$ and $[+]$ indicate electrons and holes, respectively.

First of all, the effect on the H$_2$ evolution efficiency of the thickness of the Pt co-catalyst film was explored in the plasmon-induced water splitting system. Samples
with different Pt thickness were fabricated, and their performance of the water splitting was evaluated.

In this experiment, the average thickness of the Pt film was controlled by sputtering time and was determined by an absolute calibration method. Therefore, there is a possibility that the film may become discontinuous if the film thickness was set to less than the grain size in Pt sputtering. Figure 4.4(a) depicts the irradiation time dependence of the \( \text{H}_2 \) and \( \text{O}_2 \) evolution by the water splitting system with a Pt thickness of 1 nm as a typical example. The evolution of both \( \text{H}_2 \) and \( \text{O}_2 \) increased almost linearly with the extended irradiation time. Furthermore, the amount of evolved \( \text{H}_2 \) was approximately twice that of the evolved \( \text{O}_2 \), demonstrating a stoichiometric ratio from successful overall water splitting in all Pt thickness cases. In a separate experiment, it was confirmed that neither \( \text{H}_2 \) nor \( \text{O}_2 \) was evolved from a \( \text{SrTiO}_3 \) substrate without Au-NPs under the same irradiation conditions. No production of \( \text{H}_2 \) or \( \text{O}_2 \) was observed in the absence of irradiation over an extended period as long as 6 h, even with the Au-NPs loaded on the \( \text{SrTiO}_3 \) substrates. The water splitting activity by various Pt co-catalyst loading amount, represented by the \( \text{H}_2 \) evolution rates, is summarized in Figure 4.4(b). The samples with Pt co-catalyst decoration all exhibited superior water splitting performance compared with that in the absence of any co-catalyst. The activity increased with Pt loading to a maximum at a thickness of 1 nm, above which the activity decreased. The relatively lower \( \text{H}_2 \) evolution efficiency with less Pt depositions is considered to be attributed to the lower density of Pt particle grains based on the insufficient sites for electron trapping because that the grain size in Pt sputtering is estimated to be \( \sim 2 \) nm using this apparatus, and a significantly thinner film is expected to be discontinuous. While on the other hand, with increased Pt depositions, the active surface sites and the surface area of the Pt will also decrease because the film gradually becomes continuous, and hence resulted in lower water splitting performance. The Pt thin film thickness was thus fixed as 1 nm in the following experiments.
Figure 4.4 (a) The irradiation time dependence of H₂ and O₂ evolution by the water splitting system with a Pt co-catalyst thickness of 1 nm. (b) The Pt co-catalyst thickness dependence of the H₂ evolution rate.

The function of the Pt co-catalyst is speculated to be twofold. Firstly, it is capable to trap the electrons transferred from the semiconductor substrate. The recombination between electrons and holes is thus retarded. Secondly, the following three reactions are supposed to take place in sequence during the H₂ evolution process at the back side chamber of the water splitting system:

Volmer reaction: \[ e^- + H^+ + Pt \rightarrow Pt-H \]  
Heyrovsky reaction: \[ e^- + H^+ + Pt-H \rightarrow H_2 + Pt \]  
Tafel reaction: \[ Pt-H + Pt-H \rightarrow H_2 + 2Pt \]

The Pt-H represents the hydrogen atoms adsorbed on the Pt surface. The Volmer reaction, the initial discharge of protons to give adsorbed hydrogen atom, is followed by combination of an adsorbed hydrogen atom with a proton in the solution and an electron to give H₂ (Heyrovsky reaction) or the combination of two adsorbed hydrogen atoms (Tafel reaction). Generally, with Pt as the cathode material, Tafel reaction would be the rate determining step on account of its very small overpotential for the H₂ evolution. Whereas in the present study, it has been demonstrated that the proton concentration greatly affects the H₂ evolution. Detailed investigation is currently in process.
The Pt thin film works as a catalyst providing reaction site for the electrons and protons to generate hydrogen radicals. Instead of diffusing into the solution, these hydrogen radicals adsorbed at the surface of the Pt co-catalyst. Subsequently, two hydrogen radicals combined and formed one hydrogen molecule evolution. Normally, the backward reaction of the hydrogen radical formation would also occur. However, the presence of the Pt functioned as a catalytic center effectively hindering this backward reaction.

4.4.2 Characteristics of the TiO₂ thin film

A TiO₂ thin film with a thickness of 300 nm was deposited on the back side of a SrTiO₃ substrate by atomic layer deposition (SUNALETM R series, Picosun Oy.) prior to the Pt decoration. The samples were subsequently annealed at different temperatures for 1 hour. The XRD investigation, as shown in Figure 4.5, indicates that the crystallographic phase of the TiO₂ thin film is anatase-type after annealing at 800°C, whereas it transformed to rutile-type by increasing the annealing temperature to 1000°C. ²³-²⁶

![X-ray diffraction patterns of bare SrTiO₃ (black line) and SrTiO₃ substrates with a TiO₂ thin film annealed at 800°C (red line) and 1000°C (blue line), respectively.](image)

**Figure 4.5** X-ray diffraction patterns of bare SrTiO₃ (black line) and SrTiO₃ substrates with a TiO₂ thin film annealed at 800°C (red line) and 1000°C (blue line), respectively.
Red letters and blue letters indicate facets derived from anatase and rutile TiO$_2$, respectively.

The surface element composition and chemical state of the sample were further confirmed by XPS results, and the corresponding experimental results are shown in Figure 4.6. The Ti 2p XPS spectrum of the TiO$_2$ thin film on the SrTiO$_3$ substrate shows two major peaks with binding energies at 464.9 eV and 459.1 eV, corresponding to Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$, respectively, which are the typical characteristic of a TiO$_2$ phase. The spectrum of O 1s of the TiO$_2$ thin film on the SrTiO$_3$ substrate is observed with a peak at binding energy located at 530.4 eV. This energy peak corresponds to the coordination of oxygen in Ti–O–Ti. Furthermore, the Sr 3d peaks were detected only on the surface of bare SrTiO$_3$ substrate in the absence of the TiO$_2$ deposition. Therefore, the thin film fabricated by atomic layer deposition on the SrTiO$_3$ substrate was thus confirmed to be TiO$_2$. 

![Graphs of Ti 2p, O 1s, and Sr 3d XPS spectra](image)
**Figure 4.6** XPS survey spectra of SrTiO$_3$ substrate with and without the TiO$_2$ thin film by atomic layer deposition: (a) Ti 2p, (b) O 1s, (c) Sr 3d.

### 4.4.3 Water splitting performance by TiO$_2$ with different crystalline phases

Figure 4.7(a) demonstrates the H$_2$ and O$_2$ evolution rates of water splitting systems with anatase or rutile TiO$_2$ layers were comparable to that without any TiO$_2$ layer between the SrTiO$_3$ substrate and the Pt co-catalyst. The activity was increased with rutile layer decoration. The enhancement of the water splitting activity using a rutile-TiO$_2$ layer is estimated to be 25%. This might be due to the conduction band of rutile, which is 0.2 eV lower than that of SrTiO$_3$. As illustrated in Figure 4.3, because of the pH difference, there is a potential gradient between the O$_2$ evolution and H$_2$ evolution sides of the substrate, under the influence of which the excited electrons are transferred from the Au-NPs to the Pt co-catalyst, so as to accomplish the water splitting reaction. With the lower conduction band position at the H$_2$ evolution side, the electron transfer is supposed to be further facilitated due to the greater conduction band slope as result in the prevention of back electron transfer, despite H$_2$ evolution being thermodynamically disfavored by the forming of the rutile TiO$_2$ layer.

On the other hand, in the case of the water splitting system with the TiO$_2$ as anatase-type, whose conduction band energy is almost same as that of SrTiO$_3$, the activity decreased compared to that without the TiO$_2$ layer. The reason is speculated to be that the recombination between electron and hole is aggravated in this anatase layer, on account of the inevitable formation of the lattice defects during the atomic layer deposition process. These defects could serve as a recombination center for electrons and holes.\textsuperscript{[27]} It is noteworthy that in all cases of the composite substrate architectures described above for water splitting, the front side where the oxidation reaction took place for O$_2$ evolution remained unchanged, i.e., Au-NPs/SrTiO$_3$. However, the activities varied remarkably, with H$_2$ and O$_2$ evolution maintaining a stoichiometric ratio, as the semiconductor material or
the morphology of the H₂ evolution co-catalyst changed. These aspects are thus considered to play a key role in the water splitting reaction.

In addition, the water splitting experiment using the present system with a pH combination of 9 and 1 in the front and back chambers was explored. The H₂ and O₂ evolution rates are shown in the following Figure 4.7(b). With a reduced chemical bias as compared to that with a pH combination of 13 and 1, the water splitting activities decreased in all cases with a stoichiometric ratio between H₂ and O₂ evolution maintained. However, the enhancement of the water spitting activity using a rutile-TiO₂ under layer with a pH combination of 9 and 1 is estimated to be 56 %, remarkably higher than that with a pH combination of 13 and 1 (25 %). This result supports the speculated mechanism that the rutile-TiO₂ under layer enhances a charge separation by forming larger energy band bending. Whereas the water spitting activity using the TiO₂ under layer as anatase-type with a lower chemical bias is further decreased compared with that without any TiO₂ layer between the SrTiO₃ substrate and the Pt co-catalyst.

**Figure 4.7** H₂ and O₂ evolution rates of water splitting systems with anatase or rutile layers compared with that without a TiO₂ layer. The pH value in the H₂ evolution side is fixed at 1. The pH value in the O₂ evolution side is fixed at 13 (a) and 9 (b) respectively. The pattern filled bars and open bars in the graph indicate the rate of H₂ and O₂ evolutions, respectively.
The lattice constant of the anatase TiO$_2$ is rather closer to that of the SrTiO$_3$ than the rutile TiO$_2$. In the case of the thin film deposition on the single crystal SrTiO$_3$ surface, it has been reported that the anatase TiO$_2$ is preferred to be formed as compared to the rutile TiO$_2$.\textsuperscript{[28]} The transition temperature of TiO$_2$ thin film from anatase to rutile phase is as high as 1000°C in this experiment, indicating the good stability of the anatase TiO$_2$ on SrTiO$_3$ compared with the rutile TiO$_2$. Thus, from the view point of the crystallinity, the water spitting activity of the system with an anatase TiO$_2$ under layer should be better than that with a rutile TiO$_2$ under layer. However, in despite of these considerations, the rutile TiO$_2$ under layer showed superior water spitting activity based on our experiment results. This enhanced water spitting activity is thus speculated to be ascribed to the enhanced charge separation by forming larger energy band bending with the rutile-TiO$_2$ under layer.
4.5 Conclusions

In summary, an almost stoichiometric evolution of H₂ and O₂ at separate sites have been successfully demonstrated by decorating noble metal nanoparticles and thin films on the two sides of the same single crystal SrTiO₃ substrate. The quantity of the evolved H₂ and O₂ increased linearly with the irradiation time. The activity of the water splitting was found to be highly dependent on the loading amount of the Pt, which was used as a H₂ evolution co-catalyst. The optimal thickness of the Pt thin film was determined to be 1 nm. The electron transfer from the oxidation reaction site to the reduction reaction site was facilitated by the synergistic effect of SrTiO₃ and rutile TiO₂, due to the difference between their energy band structures. The water splitting efficiency was thus enhanced to a certain degree.
4.6 References


Chapter 5

Summary and Future Perspectives

5.1 Summary

Energy is at the heart of most critical economic, environmental and developmental issues facing the world today. Clean, efficient, affordable and reliable energy services are indispensable for global prosperity. This thesis describes our efforts to develop a plasmon-assisted water splitting system under visible light irradiation using gold nanostructured strontium titanate single crystals so as to address the energy issues. This work defines a potential route for constructing efficient composite photoelectrodes comprising a semiconductor substrate, a nanostructured photo-sensitizer and a noble metal co-catalyst functioned for H₂ evolution.

A novel water splitting system using two sides of the same SrTiO₃ single crystal substrate was designed and fabricated. The experimental apparatus has two reaction chambers, separating the evolution of the H₂ and O₂. Numerical simulations indicated that a plasmonic near field enhancement was formed at the interface between the Au-NPs and the SrTiO₃ single crystal substrates. Under the influence of this near field enhancement, the optical absorption of the substrate was extended from UV light to visible light region with a peak at 600 nm. In this water splitting system, unlike the conventional ones, the reaction proceeded without any external electric bias. A chemical bias formed by aqueous solutions with different pH values between the front and back side of the composite photoelectrode was involved as a substitution. By analyzing the action spectrum, the water splitting yields were found to be in good consistent with the segmented integral area of the extinction spectrum of the Au-NPs. H₂ evolution from the water splitting is thus verified to be caused by the absorption of the visible light. The pH value dependence of the water splitting activity was
systematically investigated. It has been discovered that the efficient water oxidation due to the plasmon effect reduced the minimum chemical bias that capable of driving the visible-light response water splitting reaction to 0.23 V, which is the smallest value ever reported so far. In addition, the stability of this water splitting system was verified to be longer than 48 hours.

Based on the rational design of this reaction apparatus, the appropriate H₂ evolution co-catalyst was explored in order to further increase the water splitting activity. The schottky barrier was eliminated by using In/Ga alloy between the SrTiO₃ substrate and the Pt board. Various noble metal and metal oxide thin film were deposited on the Pt board as a H₂ evolution co-catalyst, among which the metallic Rh exhibited highest water splitting efficiency enhancement as 3 fold.

Besides the chemical bias regulation, semiconductor energy band engineering was also taken into account in this thesis. Specifically, TiO₂ thin films were deposited on the SrTiO₃ substrates as anatase and rutile crystal type by calcining in different temperatures. The composite substrate with a rutile TiO₂ under layer exhibited higher H₂ and O₂ evolution rates because of its conduction band position difference with that of the SrTiO₃. The electron transfer through the substrate was thus facilitated and the recombination between electrons and holes was hindered. Moreover, the size and shape of the Pt, which was used as a H₂ evolution co-catalyst, had a strong impact on the activity of the water splitting reaction. The optimal thickness of the Pt thin film was determined to be 1 nm.

In conclusion, it has been demonstrated in this thesis that a facile artificial photosynthesis reaction system utilizing solar irradiation was successfully developed. It is anticipated that the study presented here introduces new possibilities for efficient and stable water splitting catalytic systems for clean fuel generation leading towards a greener energy technology and sustainable future.
5.2 Future Perspectives

On the basis of the results obtained in present study, the plasmon-enhanced water splitting has been successfully demonstrated using solar light irradiation by Au-NPs loaded strontium titanate single crystal substrates. The innovative design of the water splitting system with only one substrate separating the H₂ and O₂ evolution sites features some unique properties. However, the performances of these composite photoelectrodes are still poor, and the active area for the solar light harvesting is restricted to a very small range in the current stage. The present reaction system is thus far away for large-scale production of water splitting. For the purpose of large-scale application, several aspects should be considered.

The future outlook of this thesis study can be extended to:
(1) The water splitting reaction mechanism and interaction of the loaded co-catalyst with the base semiconductor material is still not completely understood. A better knowledge of this system is of course very useful in designing active photocatalysis systems. Some attempts to investigate the mechanistic aspect on water splitting and the co-catalyst/semiconductor interface by means of kinetic analysis, spectroscopic and photoelectrochemical measurements, and computational approach have been reported so far. Specifically, understanding the interfacial property between a photocatalyst and the loaded cocatalyst would be the major challenge in this research field.

(2) The extinction properties of the Au-NPs have already found to be highly dependent on their size and shape. In the present study, visible irradiation with a wavelength at ca. 600 nm was employed as a light source according to the extinction spectrum. By varying the experimental conditions during the gold sputtering and annealing process or using electron beam lithography technique to fabricate gold nanostructure, an extended absorption to the longer wavelength (even in the infrared region) could be expected. Solar energy conversion efficiency will be greatly enhanced if we can make use of major part of the solar spectrum.

(3) In despite of the fact that the SrTiO₃ substrate adopted in this study was single
crystal type, defects are inevitable with such a thickness. Recombination between electrons and holes are likely to occur at these defects, the water splitting efficiency would be suffered as a result. Therefore, thinner substrates are considered to be better for avoiding losses due to electron trapping in the defect level. Furthermore, as a substitution of the single crystal substrate, semiconductor thin films are recommended to fabricate by atomic layer deposition or pulse laser deposition etc. so as to facilitate the electron transfer.

(4) A practical evaluation method of the capability of co-catalyst has been presented in this study. However, at the current status of the research, there are just a couple of noble metal and metal oxides examined. Having a lot more co-catalyst materials evaluated and finally constructing a co-catalyst library is of great guiding significance for the artificial photosynthesis system design.

(5) While making hydrogen from water is important, it is not the only future target. With the gold nanostructure as a light harvesting antenna, the present reaction system is capable of charge separation and electron transportation driven by visible irradiation. Multiple artificial photosynthesis reactions can be realized in the back side chamber of the system. For instance, CO₂ reduction into useful products and low carbon fuels like methanol and formic acid, ammonia production by nitrogen gas fixation, degradation of organic pollutants.

If these proposed goals are achieved, the present system could potentially be used in constructing efficient and robust artificial photosynthesis systems that respond, with lower chemical biases, to visible and near-infrared light.

The author believes that the present results are expected to give important information for this research fields. Finally, the author would like to expect this research field to be progressed more in the future.
List of Publications


   “Co-catalyst Effects on Hydrogen Evolution in a Plasmon-Induced Water Splitting System”

   “Plasmon-Enhanced Water Splitting Utilizing the Heterojunction Synergistic Effect between SrTiO$_3$ and Rutile-TiO$_2$”

4. K. Ueno, T. Oshikiri, X. Shi, **Y. Zhong**, H. Misawa
   “Plasmon-Induced Artificial Photosynthesis”
   Interface Focus, 2015, 5, DOI: 10.1098/rsfs.2014.0082.