Developing from Photoelectrochemistry to Photocatalytic Reactions

Electrochemistry is one of the major foundations of chemistry with a long history of research and development. It was 165 years ago when the concept of photo-effect was introduced into electrochemistry, during the time that Edmund Becquerel discovered the photovoltaic effect in 1839, while experimenting with electrolytic cells with two metal electrodes immersed in sulfuric acid to learn the effects when exposed to solar light.

Whenever we can see the object, that objectis always under the light irradiation. Becquere's study was ingenious in that he purposely studied the effects of photoirradiation, to which most researchers did not even give special attention. This is probably why he is known today as the father of photoelectrochemistry.

Studies thereafter continued in this area to gradually, but accumulate theories and facts. However, this subject never became an active field of chemistry. It was not until the late 19th century when sensitizing dye was discovered, that studies spun-off to focus on dye-sensitized cells, as the world moved into the early 20th century. In 1931, Rene Audubert, backed by his studies, predicted that electrochemical photolysis of water would eventually be possible. This is indeed an extremely ingenious foresight, considering the scientific standards of 70-plus years ago.

By the mid-20th century, the semiconductor was introduced as a device, but it was not until 1955, when W. H. Brattain and C. G. B. Garrett discovered the photoresponses on a solid-state Ge (germanium) electrode, that photoelectrochemistry became a global research topic, along with the developments in photochemistry.

In 1949, I started to study the characteristics of the oxidation reduction potential of chemicals to develop photographs under the supervision of Professor Shinichi Kikuchi, at The University of Tokyo.

With silver halide photography, exposed silver atoms are the catalyst for the silver halide silver cation to be reduced to a silver atom. The reduction level is then evaluated by oxidation reduction potential. I initially used silver electrodes to measure oxidation reduction potential. However, I conceived to use silver halide as an electrode instead of the silver electrode, thinking that silver halide would more closely resemble actual photographic development. Since development is a reaction of exposed silver halide particles, I thought it would be better to measure the electrode potential under irradiation with light. This was the first step of my research in photoelectrochemistry that started around 1960.

I tried also to reproduce Becquerel's experiment. I immersed two platinum electrodes in sulfuric acid to form a cell in which both electrodes were supposed to have nothing to do with light, then irradiated the cell with a high pressure mercury lamp. I was surprised to find that this generated roughly 50mV of electromotive force. All these findings were unbelievable and I simply couldn't understand why science in general remained uninterested in these phenomena.

Silver chloride electrodes tended to rapidly degrade, therefore, I had a hard time in reproducing the same results. I also studied the mechanism of sensitization of dye using a dropping mercury electrode polarography to learn its dynamics under light excitation.

However, this only further confirmed how difficult it was to try to study the behavior of excited molecules, back in those days.

Around this time, I could work in collaboration with Dr. Tadaaki Tani, who was studying the electron transfer interaction between excited molecules and semiconductors. Today, he is the world leading scientist in the photographic science. In those days, electrochemistry was an important area of applied chemistry. However, it still remained an area of ground state. There was practically no awareness of the importance of a light-excited state. For this reason, from around 1965, Dr. Tani and I worked together to define the concept of “electrochemistry at the excited state”. Slowly, we were able to come up with scientific classification of photoelectrochemistry.

Where,

Photoelectrochemistry =

(1) Electrode reaction at excited state

$$\begin{cases}\text{Excitation of electrode}\\ \text{Excitation of solution}\end{cases}$$

(2) Formation of excited molecule with electrode reactions

Our group studies started systematically under the above concept, however, we gradually came to focus on the photoelectrochemistry of semiconductor electrodes and reactions of electrodes with sensitizing dye.

It was in 1966 that I met Dr. Akira Fujishima, my co-Laureate of this 2004 Japan Prize. Since, then we have worked together through good times and bad as co-researchers for over 20 years.

Semiconductor photoelectrode studies starting with Ge (germanium), soon became a competitive area of research in Japan and abroad from the 1960’s, as represented with Si (silicon), ZnO (zinc oxide) and CdS (cadmium sulfide) semiconductors. In the course of these studies, on the suggestion of Dr. Takeaki Iida studying TiO_2 (titanium dioxide) electrophotography at the laboratory next door, Dr. Fujishima attempted to test titanium dioxide (TiO_2). He constructed a cell with a single crystal rutile *n*-TiO_2 as an anode and platinum black as a cathode. Oxygen was generated without any dissolution of the anode. In other words, we succeeded in electrochemical photolysis of water.

High energy is required to break the interatomic bond of water molecules and to split the molecules into oxygen and hydrogen. However, water solutions are already dissociated into ions, therefore, only require roughly 1/4th the energy to split. When we first reported this study in Nature in 1972, the world was confronted with an oil crisis, and this study was considered as a way to manufacture hydrogen as a clean fuel and use solar energy. This attention was unexpected, but a great pleasure since this study became headline news from both aspects of clean fuel alternatives and environmental-friendliness. When the paper was first submitted we debated whether to give it the title of “Electrochemical Photolysis” or “Photochemical Electrolysis”. Eventually we decided on the former – “Electrochemical Photolysis”. Reminiscing back on those days brings back good memories.

Now that we look back to the past, we find that hydrogen was invariably disliked during the industrial electrolysis process. This was because hydrogen was always generated prior to produce the target material through electrolysis. This wasted energy and thus, it became a major technological goal to find out the conditions that made it difficult to form hydrogen. In other words, we sought for electrode materials that yielded high hydrogen overvoltage. With the changes in times, today, we instead require materials with low hydrogen overvoltage.

Semiconductor photocatalysis can be explained in terms of a local cell mechanism with a joint anode and cathode of a cell. Light irradiation equally gives rise to anode and cathode reactions with the same equivalence. Therefore, semiconductor photocatalysis and semiconductor photoelectrode reactions are essentially the same in mechanism, and fundamental studies in both areas progressed in parallel.

In 1971, Dr. Tadashi Watanabe joined our group of the studies on semiconductor photocatalysis. Studies other than TiO_2 (titanium dioxide) took place on CdS (cadmium sulfide), ZnO (zinc oxide) and other semiconductor particle dispersion systems. Dr. Fujishima later switched to planar fixation of TiO_2 (titanium dioxide) particles and its sustainable reaction under low intensity photolumination. As a result, semiconductor photocatalysis was epochally applied to decompose and eliminate environmental pollutants by applying the strong oxidative power of TiO_2 (titanium dioxide).

Photocatalysis is a term that was proposed in 1915 for the homogeneous reaction system. Initially, the light itself was regardes as a kind of catalysis. Furthermore, by the 1970's, some debated that it was not appropriate to use the word "catalyst" for a reaction proceeding under the action of light. Today the term has become a title of many international conferences and is a scientifically established term. We believe this is a result of it showing major results as a promising environmental catalyst.

Photocatalysis for the Environment

What is the main purpose of a real scientist? I believe that the purpose is to create a very comfortable atmosphere for all people and to enhance their life to a greater extent. The scientist must contribute to a maximum extent to fulfill this purpose.

Recently, there have been several TV and newspaper reports about photocatalysis. We have recognized that this technology is becoming more and more popular recently. For example, if we visit an electrical appliance shop, we soon realize the appearance of several products based on photocatalysis. For example, indoor air-cleaning systems based on photocatalytic systems have become very familiar in the market. These air cleaners contain special filters made from photocatalytic materials, which remove contaminants, such as those that cause bad odors, and bacteria from the indoor air, when it flows through these photocatalytic filters. That is the reason why these photocatalytic products have become very popular.

What is photocatalysis? This is our main subject. Catalysis is a phenomenon in which the properties of the catalyst material remain the same before and after the chemical reaction; however, the reaction proceeds faster in the presence of the catalyst. If this catalytic reaction happens only under irradiation, then it is called photocatalysis. This is similar to the reactions in the photosynthetic process in plants. In the case of photosynthesis, the reaction between carbon dioxide and water is enhanced under solar light to produce starch and oxygen. This reaction does not occur outside the plant, even under intense light. The chlorophyll in the plant absorbs light and enhances the photosynthetic reaction to produce starch and oxygen. However, the chlorophyll does not undergo any chemical change in this reaction. So, chlorophyll acts as photocatalyst.

In the case of photocatalysis, titanium dioxide works as photocatalyst, similar to the chlorophyll in plant photosynthesis. Titanium dioxide is not a special material. It is widely used as a pigment in paint. However, photocatalytic reactions occurring in the paint under solar light are not desirable, because the organic binder is decomposed. In contrast, photocatalytic reactions are very important for self-cleaning applications, for example.

What is the origin of titanium dioxide photocatalysis? The study of reactions under light is the origin. About 40 years ago, when I was a graduate student, I used a titanium dioxide single crystal in the rutile form for my experiments. I cut the cylindrically shaped titanium dioxide single crystal to form a slice and heated it in a reducing hydrogen atmosphere to induce conductivity in order to use it as an electrode. I examined the electrochemical behavior of this electrode in an electrochemical cell under irradiation with a 500 W xenon lamp. I found the evolution of gas bubbles at the electrode under irradiation. The gas evolution stopped when the irradiation was stopped. I also observed the flow of current from the electrode only when the gas evolution was observed under light. As the electrolyte in my experiment was water, I assumed the gas evolved at the electrode to be oxygen, due to the photocatalytic oxidation of water. Even after a long exposure of the titanium dioxide electrodes in this experiment, the surfaces of the electrodes did not change at all. I also confirmed the absence of any change in the weight after the photocatalytic experiment.

The gas evolved in the above reaction was confirmed to be oxygen, which was produced from water but not from the titanium dioxide. We assumed that the reaction in our experiment was water electrolysis. However, the potential applied in our experiment was not positive enough for water electrolysis, but the reaction happened, due to the irradiation of the electrode. This means that water electrolysis is possible, even at a negative applied potential, if the titanium dioxide electrode is irradiated. We named this reaction "the photosensitized electrooxidation reaction."

By using this photoelectrochemical phenomenon, we constructed a wet-type solar cell by coupling a titanium dioxide anode with a platinum electrode, which acted as a cathode. The results obtained from this experiment were published in the journal 'Nature'. Under irradiation with a xenon lamp, the oxygen evolution reaction occurred at the titanium dioxide anode, while hydrogen evolution was observed at the platinum cathode. While this reaction was in progress, electrical current was generated through a resistor connected between the electrodes. This means that we can construct a wet type solar cell.

By using this wet type solar cell, we started to produce hydrogen, which is a clean energy source, under solar light. To produce a large volume of hydrogen, we used a large area titanium dioxide electrode by heating titanium metal sheets on a gas burner to produce an oxide layer of one micrometer thickness. We could produce about 7 liters of hydrogen by irradiating one square meter area of titanium dioxide layer electrode in our solar cell on a fine summer day. However, we found that the calculated energy conversion efficiency was only 0.4%. Although this value is very small, the material cost is also very low in this system. This is a very interesting subject.

However, the photocatalysis phenomenon, which evolved from this fundamental photoelectrochemical behavior, has become very popular in recent days. Originating from this concept, the antibacterial effect and the deodorizing effect have become popular in indoor air purification. Also, the decomposition of oily dirt on the surfaces of the lighting units of highway tunnels became possible. Photocatalysis is a very nice system to make a clean atmosphere. Recently, we have also found another unique property of titanium dioxide, namely superhydrophilicity. This technology has been applied to the side-view mirrors of automobiles. Now, even on rainy days, safe driving is assured, due to this superhydrophilic effect.

Photocatalysis has two unique properties. One is the strong photocatalytic oxidation power, and the other is superhydrophilicity. Therefore, titanium dioxide photocatalysis has two key components. One is titanium dioxide, and the second is irradiation. When titanium dioxide is irradiated, these two properties operate simultaneously. The first aspect of photocatalysis is the very strong oxidation power, which means that any chemical approaching the surface of titanium dioxide decomposes very easily under light. Any organic compounds at the surface decompose into carbon dioxide and water. However, in this case, the extent of the reaction is limited by the number of photons. Therefore, the temperature in this reaction does not increase as it does in the case of the combustion reaction. The photocatalytic reaction occurs at room temperature.

Another unique property of titanium dioxide is superhydrophilicity. Normally, the surface of titanium dioxide becomes fogged when water condenses on it. However, after irradiation, the water droplets on the surface do not keep their spherical shape but become flat on the surface, thereby forming a uniform film. If oil is already on the surface, the water falling on the irradiated surface penetrates under the oil and removes it easily. By using this behavior, we can achieve an anti-fogging glass with self-cleaning properties. This technology is already being applied to side-view mirrors of automobiles in order to have safe driving.

Just recently, photocatalysis has been applied in many fields. Deodorizing, antibacterial, antifogging, and self-cleaning effects have become very attractive. Also, the photocatalytic effect has been extended to water treatment and the corrosion protection of steel. Very recently, visible light-responsive photocatalysis is becoming an active research field. If we succeed in applying this behavior, photocatalysis can be applied in even wider fields.