

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 object is always under the light irradiation. Becquerel'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

{Excitation of electrode
{Excitation of solution

(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 TiO₂ (titanium dioxide) electrophotography at the laboratory next door, Dr. Fujishima attempted to test titanium dioxide (TiO₂). He constructed a cell with a single crystal rutile *n*-TiO₂ 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 regarded 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.