

Dawn of the evolution of photoelectrochemistry

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Abstract

Photoelectrochemistry is a vigorous research area in chemistry that has drawn strong interest in recent years. In this field, numerous papers are being presented, and international symposiums are frequently held. This report reviews the origins of photoelectrochemistry and its progress to date.

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1. Scope of photoelectrochemistry

A number of authors has provided definitions of photoelectrochemistry in their review papers. Kuwana [1] defined it as:

- (a) Introduction of photo-excitation into the electrochemical system.
- (b) Formation of the excited state through the electrochemical process.

In my early report [2], it was defined as:

- (a) Reaction on the electrode in excited state:
 - a.1. Excitation of the electrode (metal or semiconductor).
 - a.2. Excitation of substances (adsorbed molecules, etc.) at the interface between the electrode and solution.
 - a.3. Excitation of reactive species in a solution.
- (b) Generation of electronically excited state by electrode reaction.
- (c) Combination of photochemical and electrode reactions.
- (d) Alternate generation of photochemical and electrode reaction.

This report discusses “introduction of photo-excitation into the electrochemical system” as described above. It is reviewed from the following three perspectives according to the region at which the electronically excited state generates when photo-irradiation is carried out on the electrochemical system.

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1.1. Light irradiation mode

electrode → water decomposition, photocatalysis

interfacial layer → dye sensitization

solution bulk → photogalvanic cell

The arrows indicate applications of each light irradiation mode. Fig. 1 is a diagram of the three modes.

2. Historical sketch

2.1. Becquerel effect

The French scientist Becquerel immersed two other metal electrodes such as platinum, gold, silver, brass, and silver coated with silver halogenide on the surface into acidic, neutral, and alkaline electrolytic solutions. Exposing one of the electrodes to sunlight, he found that electric current flows through the external circuit between two electrodes. The current was very small, with the pointer on the galvanometer only moving several degrees. Becquerel reported these results at Academy in Paris in 1839 [3]. Fig. 2 illustrates the Becquerel experiment. His study was considered the first paper on photoelectrochemistry, and this phenomenon is therefore known as Becquerel effect. Moreover, it is surprising that Becquerel found these historic results at merely 18 years of age.

Since his discovery, research on photoelectrochemistry has continued to advance, mainly in the area of electrochemistry, which is discussed later in this paper. In the 1950s, the

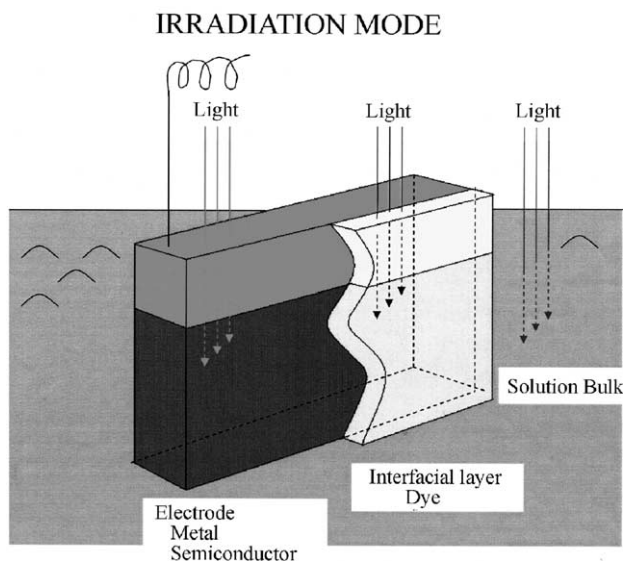
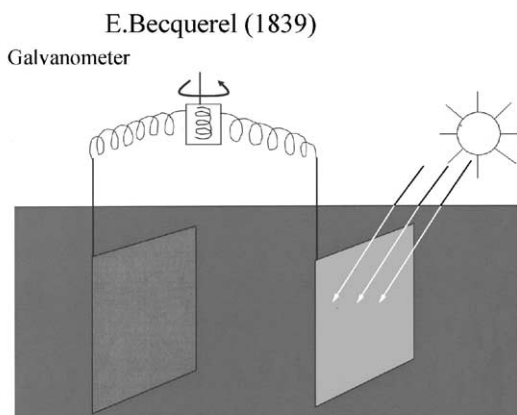


Fig. 1. Irradiation mode of the electrochemical system.

field of semiconductor materials progressed and was accompanied by brisk activity in the area of semiconductor electrochemistry as well. In parallel with such developments, we have thereafter witnessed a drastic escalation of studies on semiconductor photoelectrochemistry based on semiconductor photo-properties. This area presently stands as the most active academic arena in terms of both fundamental and applied research.

Though photoelectrochemistry continued to draw widespread interest from the 1950s to 1960s, no attempts were made to reexamine Becquerel's research from a quantitative perspective. The author thus carried out research on the immersion of two smooth platinum sheet electrodes in sulfuric acid solution, irradiating one of these electrodes with a high pressure mercury lamp, and measuring the photovoltaic effects as shown in Fig. 3 [4]. By only turning the light on and off, photovoltaic changes



Electrode: Pt, Au, Ag, Brass,
and Ag coated with AgI, AgBr, and AgCl
Solution: acid, neutral, basic

Fig. 2. Illustration of Becquerel's experiment (1839).

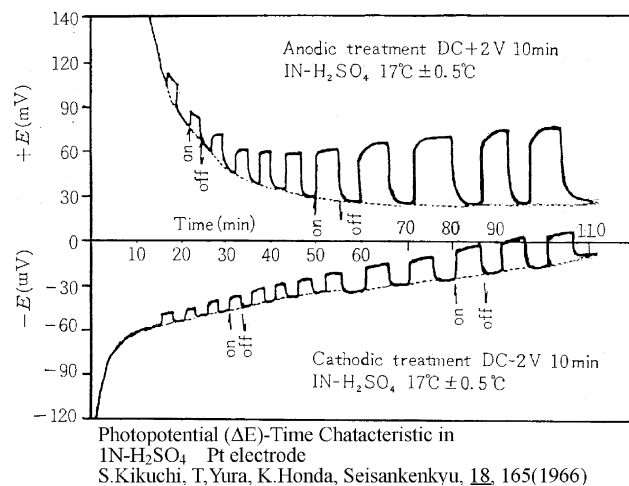


Fig. 3. Effect of light irradiation on Pt electrode.

of several 10 mV were easily observed, much more than expected.

2.2. Excitation of the solution

Since the end of the 19th century, studies have been conducted on successive photoelectrochemical reaction and electrochemical reaction, where electrolytic solution is irradiated as described in Fig. 1. This was called the Swensson–Becquerel effect. As shown below, the products of the photochemical reaction in the first cell return to their initial states through the conventional electrochemical back reactions in the first and second cells, generating the current. The system will serve for converting light energy to electrical energy.

The studies done by E. Rabinowitch using the thionine and Fe^{2+} system are well known [5]. Practical application has not been achieved, however, because reactants need to be completely recycled for light energy use.

2.2.1. Example of excitation of solution

Swensson–Becquerel effect, photogalvanic cell			
Photochemistry + electrochemistry			
Photochemistry	$A^* + D \xrightarrow{h\nu} A^- + D^+$	First cell	
Electrochemistry	$A^- \rightarrow A + e$		
Ground state electrochemistry	$D^+ + e \rightarrow D$	Second cell	
Goldmann		[14]	
Baur		[15]	
Iimori		[16]	
Rabinowitch		[17]	
Eisenberg and Silverman		[18]	

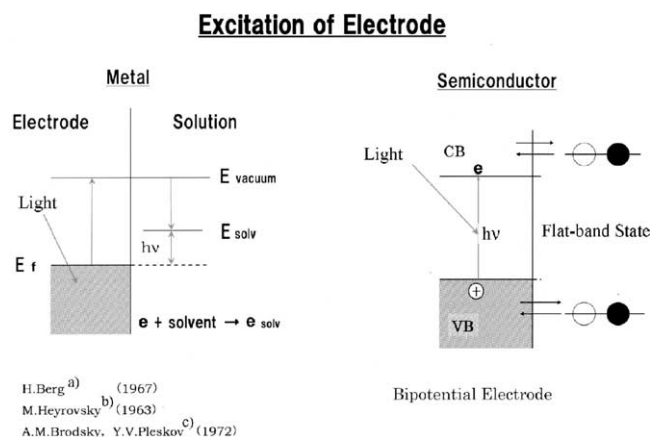


Fig. 4. Excitation of electrode: (a) [26]; (b) [27]; (c) [28].

2.3. Excitation of electrode

As both metal and semiconductor are generally used as electrodes, Fig. 4 shows the photo-process of these two kinds of electrodes.

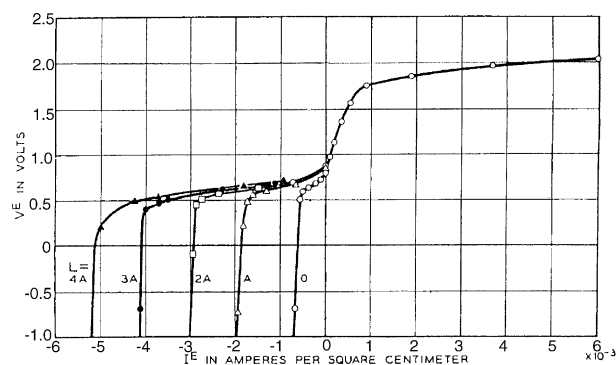
2.4. Metal electrode

The discharge of photoelectrons from metal is a commonly known physical phenomenon. Studies on photocurrent through light irradiation on electrodes immersed in electrolytic solution started to appear during approximately the 1960s, particularly in the area of polarography with dropping mercury electrodes. Several theories on its mechanism have been proposed. Today, it is understood through experiments that the difference between the work function E_f of electrode metal and solvation energy of electrons E_{solv} corresponds to the photoenergy required for generating photocurrent.

2.5. Semiconductor electrode

With the progress of semiconductor properties, semiconductors are now increasingly used as electrodes in the area of electrochemistry. Photoconduction is an important property of semiconductors. In 1955, the Nobel Prize winner for inventing semiconductor devices, Brattain and Garrett [6], reported the photoreaction properties of germanium electrodes. His work is considered to be pioneering research on semiconductor photoelectrochemistry and the origin of progress in this area.

Fig. 5 shows an example of photoresponse characteristics with the typical current–potential curve of n-Ge described in their report. When polarized to negative, typical rectification can be seen in the dark, however the current is found to increase proportionately to irradiation light intensity “L”. As shown on the right side of Fig. 4, electrons in the conduction band and positive holes in the valence band generated by light absorption cause charge transfer through the



Plot of V^p against I^p for n-type Ge in N/10 KOH, at different light intensities.
L = Intensity of light A = Unit of light intensity

Fig. 5. Current (I)–potential (V) curve of n-Ge as a function of light intensity [6].

interface to the chemical species in the solution at different potential levels corresponding to the bandwidth. Research on the theories and dynamics of semiconductor photoelectrode reaction is still actively carried out, and many reports are available.

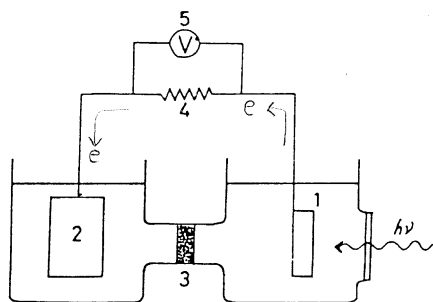
3. Appearance of TiO_2

After the studies on Ge by Brattain and coworkers, every typical monocrystalline semiconductor that was easily available as a single crystal in the 1960s was investigated in photoelectrochemical research. The following shows such semiconductors in the chronological order in which they were studied.

n-Ge	1955
n-Si	1958
n-CdS	1960
n-, p-GaAs	1965
n-ZnO	1966
p-NiO	1966
n-ZeSe	1967
n-, p-GaP	1968
n-SnO ₂	1968
n-KTaO ₃	1968

Semiconductor electrodes other than Ge and Si are oxide semiconductors, chalcogenide semiconductors, III–V semiconductors, etc. Most are of the n-type, with very few of the p-type variety. The author has also conducted studies using Ge, Si, CdS, ZnO, etc., where the use of single crystals was indispensable from scientific standpoint. Single crystals are, however, often expensive and difficult to obtain. Initially, a leading US manufacturer provides a supply of the ZnO single crystal free of charge, due to its being more expensive than diamonds.

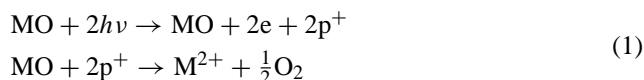
With the n-type semiconductor, an anode photocurrent proportional to the light intensity is generated as shown in



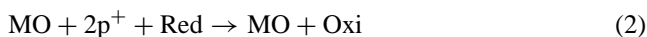
Electrochemical cell in which the TiO₂ electrode is connected with a platinum electrode. The surface area of the platinum black electrode used was approximately 30 cm².

Fig. 6. Cell for the decomposition of water with a TiO₂ photoanode [8].

Fig. 5. This reaction is expressed by the following formulas for oxide semiconductor (M²⁺O²⁻):



or



(1) is the dissolution reaction of the electrode semiconductor itself; in other words, the etching of the electrode. (2) is the oxidation reaction of reductant Red in the electrolytic solution to Oxi induced by photo-generated holes in the electrode. Here, reaction involving the generation of oxygen occurs when the water molecules become the donor. Mostly, reactions are competitive where (1) and (2) progress simultaneously. In this case, the etching of the electrode could not be avoided.

Around 1969, the laboratory at the Institute of Industrial Science, University of Tokyo, which was coincidentally next to the author's, was conducting studies on electrophotography using TiO₂ as the photoreceptor. A co-researcher of the author, Fujishima, obtained TiO₂ single crystal as a result of following the suggestion of T. Iida (currently professor at Saitama University), the researcher carrying out these studies; Fujishima used it as a photoelectrode, and found that only oxidation reaction of the chemical species in the solution occurs without any etching of electrodes [7]. Then, using platinum black as the counter electrode, we constructed a cell shown in Fig. 6, irradiated the light from a high pressure mercury lamp on the TiO₂, and found that oxygen is generated on TiO₂ by the decomposition of water due to anode reaction, and hydrogen is generated by cathode reaction of the Pt electrode. At the same time, electrons flow in the arrow direction through the external circuit, achieving electrochemical photolysis of water [8]. Fig. 7 shows the view of the cell. The generation of minute hydrogen bubbles can be observed on the platinum black electrode in the cathode compartment on the left.

Since presenting this study, the author has received numerous inquiries from researchers all over the world, many

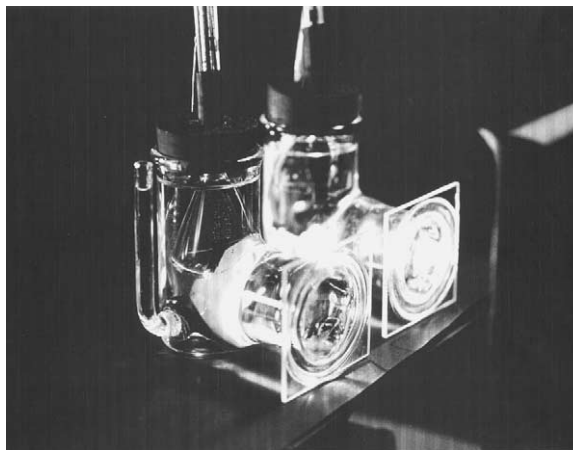


Fig. 7. View of the cell for the electrochemical photolysis of water; right compartment: TiO₂ photoanode, left compartment: Pt black cathode with the evolution of hydrogen.

of them asking how we were able to obtain TiO₂ single crystal.

Though this study was conducted from a purely academic perspective of photoelectrochemistry, because it was coincidentally carried out during the Oil Shock in 1973, it received widespread interest as a doorway to the use of solar energy. It was also greatly anticipated as a means of producing hydrogen fuel.

As mentioned earlier, the author has used expensive semiconductor single crystals in research, but in practical application, inexpensive materials are indispensable. For this reason, attempts to form oxide film (TiO₂) on the surface were made by heating titanium sheet metal available on the market using a gas burner. Water decomposition experiments by sunlight outdoors were conducted using this as a large photoanode for the first time [9]. Fig. 8 shows a photograph of the photoanode used at the time. The results confirmed that hydrogen can be produced by natural light without the need to supply external energy whatsoever.

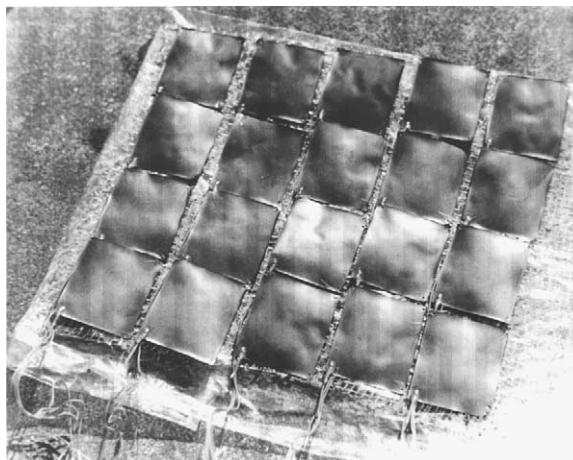


Fig. 8. View of TiO₂ photoanode formed by heating of Ti plate.

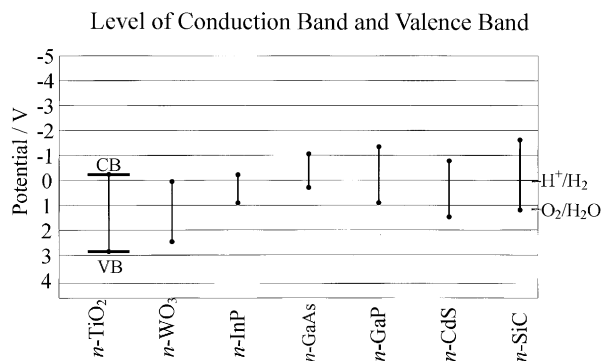


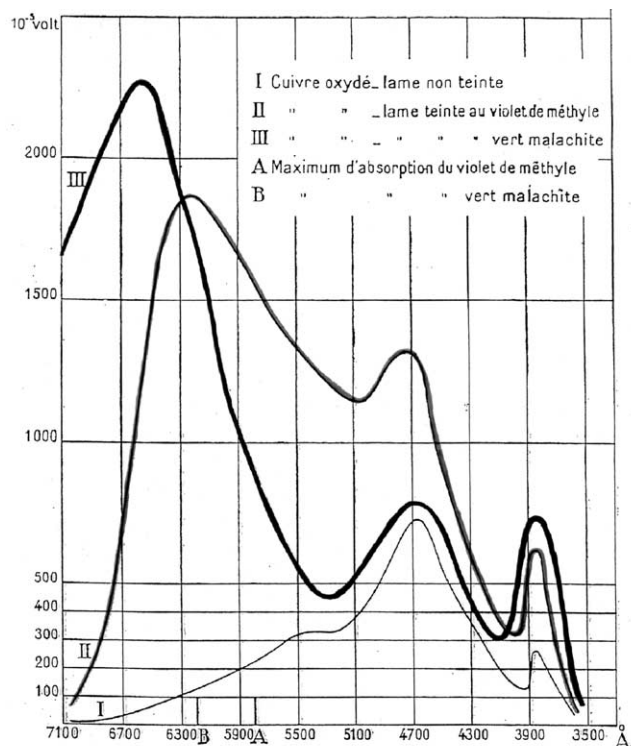
Fig. 9. Level of conduction band (CB) and valence band (VB) of n-type semiconductor electrodes.

In this way, the outstanding characteristics of TiO_2 as a photo-electrode can be attributed to its strong oxidation power. As a comparison, Fig. 9 shows a block graph of the positions of conduction band (CB) and valence band (VB) of the generally used n-type semiconductor. Lower position of the valence band is equivalent in meaning to stronger oxidation power. It shows that TiO_2 is the lowest. Since reports of titanium dioxide photoelectrode, many studies using new semiconductor materials, hybrid semiconductors, doped materials etc., have been presented. For details, refer to the respective literature.

4. Dye sensitization of photoelectrochemical process

Photoelectrochemical process always occurs after semiconductor electrodes absorb light with the wavelength of the intrinsic absorption band. Most semiconductors merely absorb part of the sunlight spectrum. In terms of effective use of sunlight, the working wavelength band of photoelectrode reaction should be expanded. In 1873, Vogel [10] already discovered dye sensitization by the use of silver halide photosensitive material. Since then, a massive amount of information on sensitizing dyes has accumulated. Interestingly, Becquerel was intrigued by this study, and has reported studies on photosensitization by chlorophyll [11], which means Becquerel had carried out pioneering research in both the photoelectrochemical and photographic areas.

Studies on dye sensitization in the arena of photoelectrochemistry date from the end of the 19th century for metal electrodes. Systematic studies have been reported since 1960, the year in which semiconductor electrodes made their debut. As historical references, Fig. 10 shows the sensitization curve by methyl violet and malachite green of copper oxide electrode [12], reported by Audubert in 1931. The degree of sensitization is indicated by the photopotential. Realization of sensitization in longer wavelength can be observed. Interestingly, Audubert predicted in his paper [12] that electrochemical photolysis of water would 1 day be achieved.



R. Audubert, "Les piles sensibles à l'action de la lumière", P.19 Hermann et Cie., (1931)

Fig. 10. Review of the photoelectrochemical dye sensitization work by Audubert.

Major studies on dye sensitization carried out on semiconductors after 1960 are listed in chronological order below:

ZnO	[19]	Hauffe and Range
	[20]	Gerischer and Tributsch
GaP, GaAs, Cu_2O	[21]	Tributsch and Gerischer
p-GaP	[22]	Memming and Tributsch
TiO_2	[23]	Fujishima et al.
CdS	[24]	Gerischer
	[25]	Fujishima et al.

The dyes used for the above dye sensitization are general types such as xanthene. However, most of these were not satisfactory in terms of sensitization efficiency and durability. In 1991, Grätzel and his group reported that the Ru bipyridyl complex has very high sensitization efficiency and stability [13]. Subsequently, solar cells with TiO_2 electrode using this dye as the sensitizer started to draw interest, and research is being carried out briskly in this area.

5. Concluding remarks

This report attempts to provide a historical outline of the progress of photoelectrochemistry. The information,

however, may not be complete due to the limited knowledge of the author. In recent years, other than the use of solar energy, progress is centering around environmental improvement and the generation of hydrogen by the complete decomposition of water by semiconductor photocatalyst; many reports and literature on these themes are available.

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