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Kohei Uosaki and Hideaki Kita

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## Photoelectrochemical Characteristics of Semiconductor-Metal/SPE/Metal Cells

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## ABSTRACT

A solid polymer electrolyte (SPE) photoelectrochemical cell, semiconductor-metal/SPE/Pt, is proposed as a new device to convert solar energy to electrical and/or chemical energy. The photoelectrochemical characteristics of  $\text{TiO}_2$ -Pt/SPE and  $\text{TiO}_2$ -Au/SPE were studied as well as those of the whole cell systems  $\text{TiO}_2$ -Pt/SPE/Pt and  $\text{TiO}_2$ -Au/SPE/Pt. By above bandgap energy illumination of the  $\text{TiO}_2$ -metal side, negative photovoltage and anodic photocurrent were observed, as reported at  $\text{TiO}_2$  electrodes. In whole cell systems, *i.e.*,  $\text{TiO}_2$ -Pt/SPE/Pt and  $\text{TiO}_2$ -Au/SPE/Pt, the conversion of light to electricity was achieved without using electrolyte solution.

The conversion of solar energy to chemical and/or electrical energy by photoelectrochemical (1, 2) and photocatalytic (3, 4) methods has been studied very extensively. Both methods have advantages and disadvantages. In the photoelectrochemical method, the products can be obtained separately. That is particularly useful when water is decomposed photoelectrochemically. Electricity can be generated, but the presence of electrolyte is essential in this system. On the other hand, the photocatalytic method does not require electrolyte, but the products, *e.g.*, oxygen and hydrogen, are generated in the same compartment. Thus an extra separation process is required and no electricity can be obtained.

The advantages of a solid polymer electrolyte (SPE) in water electrolysis (5), organic electrochemistry (6), and fuel cells (7) have been well recognized and the application of SPE to photoelectrochemical cells should also be advantageous. Recently, Skotheim and Lundström have constructed all-solid photoelectrochemical cells using poly(ethylene oxide) as the SPE (8).

Here, we propose a new type of SPE photoelectrochemical cell that contains layers of a semiconductor as a sensitizer, a metal, an ion exchange membrane as an SPE, and a metal. We report the photoelectro-

chemical characteristics of  $\text{TiO}_2$ -Pt/SPE and  $\text{TiO}_2$ -Au/SPE as well as those of  $\text{TiO}_2$ -Pt/SPE/Pt and  $\text{TiO}_2$ -Au/SPE/Pt. By using this type of cell, even electrolyte-free photoelectrolysis of water may be possible, as shown in Fig. 1.

## Experimental

Nafion 315 perfluorinated cation exchange membrane was used as an SPE material. The deposition of metal on the SPE was carried out by the electrolytic plating method suggested by Takenaka and Torikai (9, 10). After a swelling treatment in boiling water for 30 min, the membrane was set as a separator in the cell shown in Fig. 2. The upper compartment was filled with a metal salt ( $\text{H}_2\text{PtCl}_6$  or  $\text{HAuCl}_4$ ) solution and the other compartment was filled with an  $\text{NaBH}_4$  (1M)- $\text{NaOH}$  (1M) solution.  $\text{NaBH}_4$  diffused through the membrane and reduced the metal salt to the metal on the membrane surface at the upper compartment. After several hours, the solution of the upper compartment became colorless, suggesting most of the salt was reduced, and the surface of the membrane at the upper compartment became black. The amount of metal deposited was 4-12  $\text{mg} \cdot \text{cm}^{-2}$ . Hereafter this configuration is called Pt/SPE or Au/SPE. In some cases, after washing the membrane thoroughly with distilled water, the other side of the membrane was also coated with a metal

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Key words: energy conversion, semiconductor, photoelectrochemistry, solid polymer electrolyte.

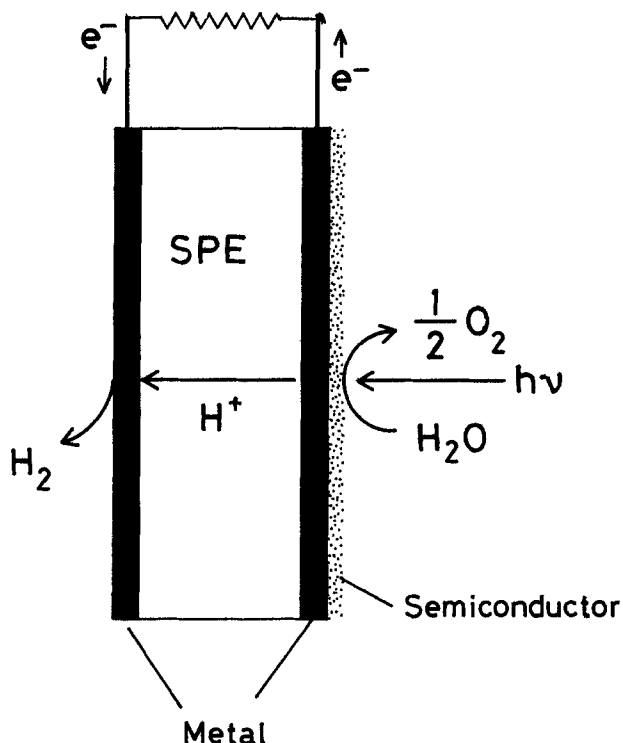


Fig. 1. Schematic diagram of proposed SPE photoelectrochemical cell.

in the same way. At least one side of the membrane was coated with platinum. This configuration is called Pt/SPE/Pt or Au/SPE/Pt. The side coated with either Pt or Au will be called side 1 and the side always coated with Pt will be called side 2 in the rest of this paper. Side 1 was further coated with TiO<sub>2</sub> by drops of a TiO<sub>2</sub> (Merck, Anatase) powder suspension (2g TiO<sub>2</sub>/25 cm<sup>3</sup> distilled water), following the method used by Davidson *et al.* for the coating of Pt wire with TiO<sub>2</sub> (11). The membrane was then dried in an oven at 70°C for 15-20 hr. After this treatment, most of the TiO<sub>2</sub> powder came off but some remained on the metal. This configuration is

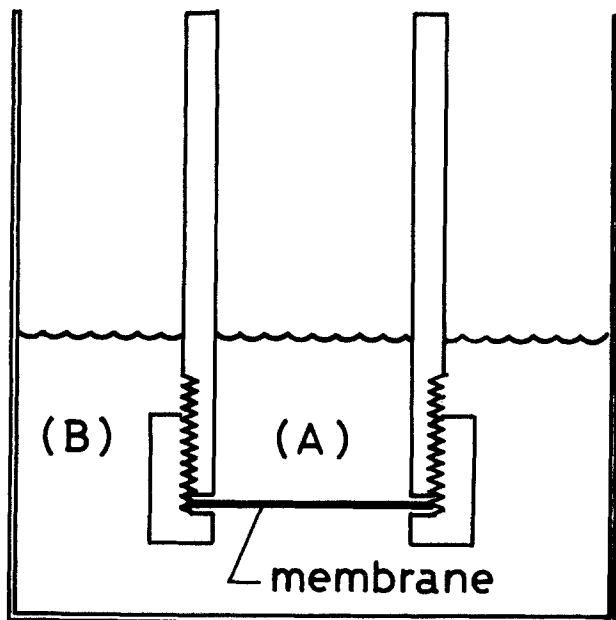


Fig. 2. Schematic diagram of the cell used for the electroless plating of SPE. Solution (A) is a metal salt solution and solution (B) is an NaBH<sub>4</sub>(1M)-NaOH(1M) solution.

called TiO<sub>2</sub>-Au/SPE, TiO<sub>2</sub>-Pt/SPE, TiO<sub>2</sub>-Au/SPE/Pt, or TiO<sub>2</sub>-Pt/SPE/Pt.

The (photo)electrochemical characteristics of TiO<sub>2</sub>-Pt/SPE and TiO<sub>2</sub>-Au/SPE electrodes were studied in the cell shown in Fig. 3.

A potentiostat (Nikko Keisoku, NPGS-301S) was used to control the electrode potential. A platinum wire and a silver/silver chloride electrode were used as a counter and a reference electrode, respectively. The working electrode, TiO<sub>2</sub>-Pt or TiO<sub>2</sub>-Au, is disk shaped and 2.5 cm in diameter. A gold ring was used as a current collector.

The photoelectrochemical characteristics of whole cells, TiO<sub>2</sub>-Pt/SPE/Pt and TiO<sub>2</sub>-Au/SPE/Pt, were studied in a cell shown in Fig. 4.

Results

The cyclic voltammograms of Pt/SPE and TiO<sub>2</sub>-Pt/SPE in 0.5M H<sub>2</sub>SO<sub>4</sub> are shown in Fig. 5. It is clear from the figure that the electrochemical characteristics of Pt/SPE are similar to those of a Pt electrode. The real surface area of Pt was calculated as ca. 1125 cm<sup>2</sup>, i.e., the roughness factor was ca. 230, from the area of the oxide reduction peak. By comparing the

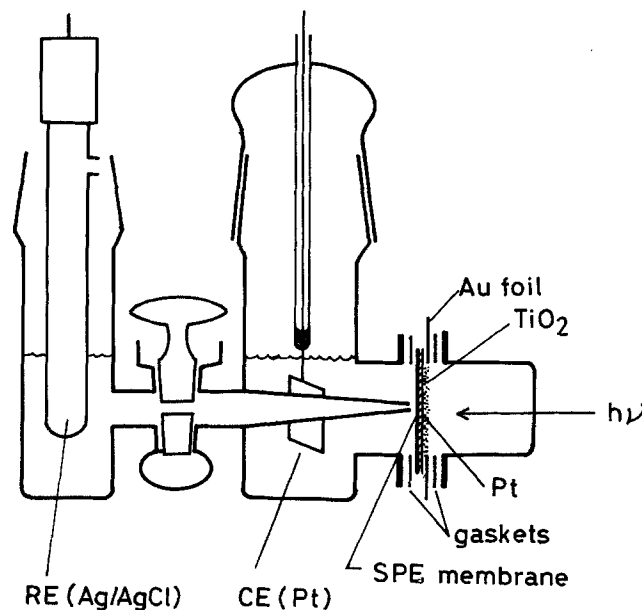


Fig. 3. A cell used for the measurements of (photo)electrochemical characteristics of TiO<sub>2</sub>-Pt/SPE and TiO<sub>2</sub>-Au/SPE electrodes.

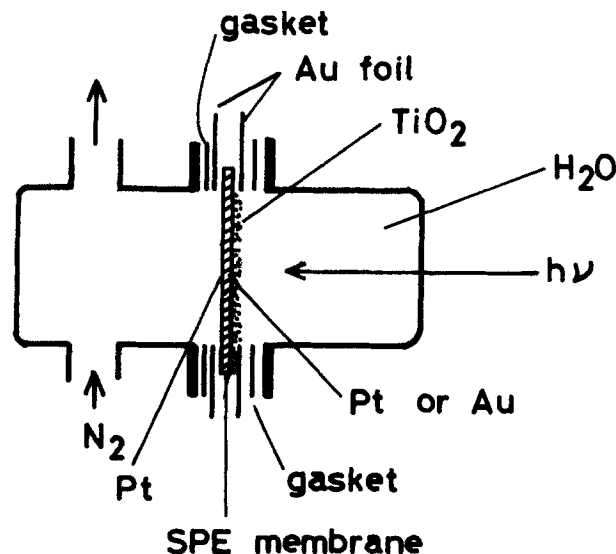


Fig. 4. A cell used for the measurements of photoelectrochemical characteristics of TiO<sub>2</sub>-Pt/SPE/Pt and TiO<sub>2</sub>-Au/SPE/Pt.

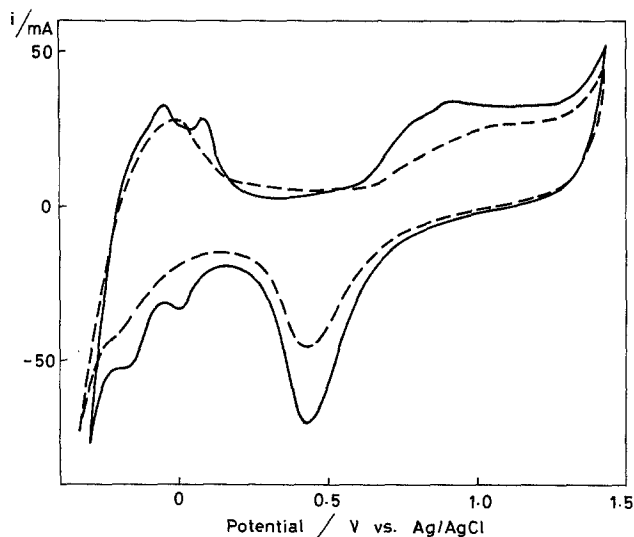


Fig. 5. Cyclic voltammograms of Pt/SPE (—) and TiO<sub>2</sub>-Pt/SPE (---) in 0.5M H<sub>2</sub>SO<sub>4</sub>. Sweep rate was 30 mV · sec<sup>-1</sup>.

area of the oxide reduction peak in the cyclic voltammogram of TiO<sub>2</sub>-Pt/SPE with that of Pt/SPE, the coverage of the Pt surface by TiO<sub>2</sub> was calculated as ca. 35%, i.e., a significant portion of Pt was still exposed, as observed with TiO<sub>2</sub>-coated Pt wire. The cyclic voltammograms of TiO<sub>2</sub>-Au/SPE in 0.5M H<sub>2</sub>SO<sub>4</sub> before and after photoelectrochemical measurements are shown in Fig. 6. From the cyclic voltammogram of Au/SPE which is not shown here, the real area of Au was calculated as ca. 100 cm<sup>2</sup>, i.e., roughness factor was ca. 20. By comparing the cyclic voltammogram of Au/SPE and that of TiO<sub>2</sub>-Au/SPE, the coverage of Au surface by TiO<sub>2</sub> was calculated as 75%. The cyclic voltammogram of TiO<sub>2</sub>-Au/SPE after the photoelectrochemical measurements shows that the nature of gold on the SPE changed and indeed a change in the appearance of the membrane surface was observed. Thus a better method for depositing Au on the SPE should be developed. When the TiO<sub>2</sub>-metal side was illuminated by a 500W Xe lamp through an infrared absorbing filter, a negative photovoltage was developed, as observed with Pt wire coated with TiO<sub>2</sub>, and is shown in Fig. 7. The time course of photovoltage of TiO<sub>2</sub>-Pt illuminated by 360 nm monochromatic light is also shown in Fig. 7. The photovoltage was small and the time constant was large when the electrode was illuminated with monochromatic light. The wavelength dependence of the photovoltage is shown in Fig. 8 and is similar to

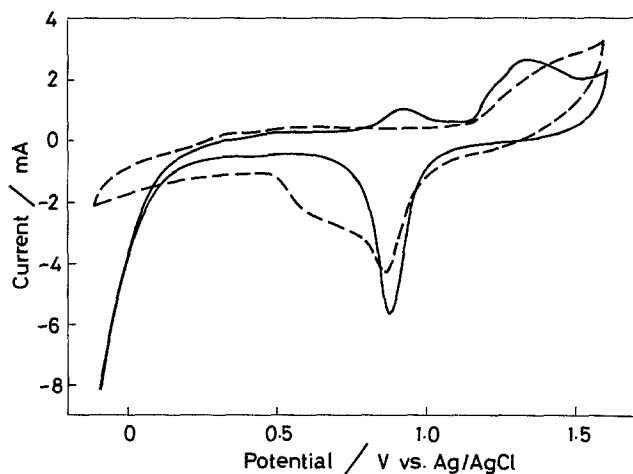


Fig. 6. Cyclic voltammograms of TiO<sub>2</sub>-Au/SPE in 0.5M H<sub>2</sub>SO<sub>4</sub> before (—) and after (---) photoelectrochemical measurements. Sweep rate was 100 mV · sec<sup>-1</sup>.

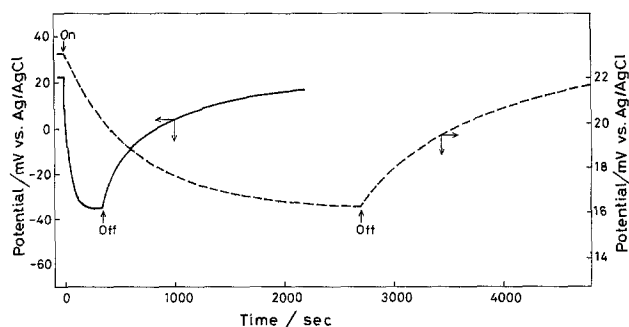


Fig. 7. Photoeffect on the potential of TiO<sub>2</sub>-Pt on SPE in 1M NaOH illuminated by 500W Xe lamp with infrared absorbing filter (—) and by 360 nm monochromatic light (---).

that of Pt/TiO<sub>2</sub> powders (12). These results support the view that the photoresponse was due to absorption of light by TiO<sub>2</sub>. Anodic photocurrents were also observed potentiostatically. A typical photocurrent-time relation at TiO<sub>2</sub>-Pt/SPE is shown in Fig. 9.

The photocurrent-potential relations at TiO<sub>2</sub>-Pt/SPE and TiO<sub>2</sub>-Au/SPE are shown in Fig. 10 and are quite different from those of TiO<sub>2</sub> electrodes. It is clear that the photocurrents were strongly affected by the underlying metals. There are peaks in the relations and the peak potentials coincide with those at which oxides of the metals are formed.

The results reported so far are all for TiO<sub>2</sub>-Pt/SPE and for TiO<sub>2</sub>-Au/SPE and not those for whole cell systems, i.e., TiO<sub>2</sub>-Pt/SPE/Pt or TiO<sub>2</sub>-Au/SPE/Pt. For the whole cell systems, both compartments of the cell shown in Fig. 4 were filled with distilled water, not an electrolyte solution, and then the water in the Pt side (side 2) of the compartment was drained off. This compartment was then filled with N<sub>2</sub> gas. When the TiO<sub>2</sub>-metal side (side 1) and the Pt side (side 2) were connected by an electrometer and the TiO<sub>2</sub>-metal side was illuminated by light, the potential of TiO<sub>2</sub>-metal became more negative than that of Pt. When the two sides were connected with a resistor of finite resistance, a photocurrent (TiO<sub>2</sub>-metal as an anode and Pt as a cathode) was observed. Thus the conversion of light to electricity without electrolyte solution was achieved. A typical time course of the

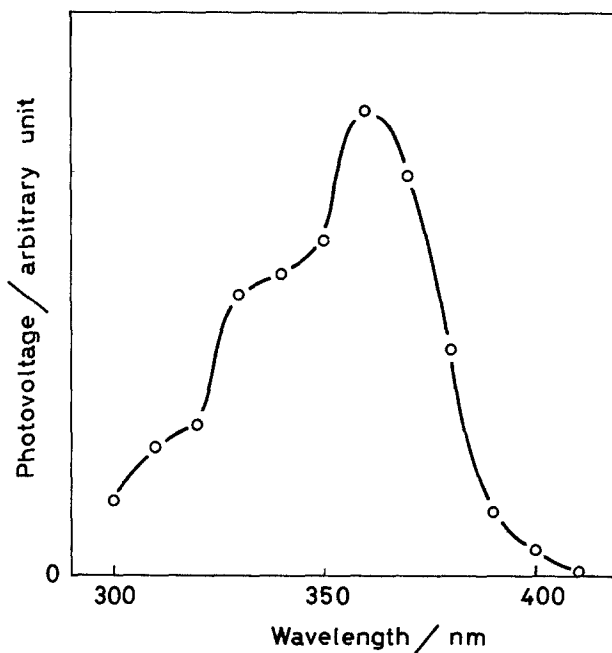


Fig. 8. Photovoltage-wavelength dependence of TiO<sub>2</sub>-Pt/SPE in 1M NaOH. The photovoltages are not calibrated for photon numbers.

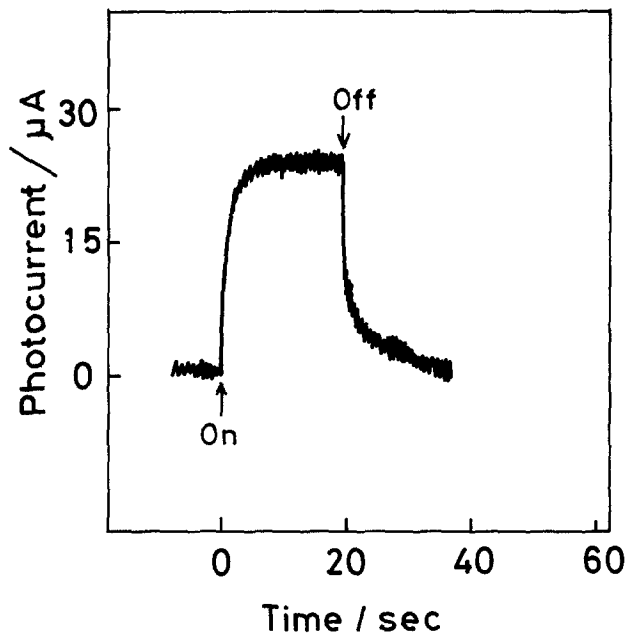


Fig. 9. A typical photocurrent-time relation of TiO<sub>2</sub>-Pt/SPE in 1M NaOH at 0.5V (vs. Ag/AgCl).

photocurrent is shown in Fig. 11. The larger the resistance, the larger the time constant of this process. The wavelength dependence of the photocurrent, which is shown in Fig. 12, again confirms that photocurrents were due to the absorption of light by TiO<sub>2</sub>. After the measurements, TiO<sub>2</sub> remained on the metal surface as shown by the reflection spectrum in Fig. 13.

The cell performance of TiO<sub>2</sub>-Pt/SPE/Pt cell was determined by changing the resistor which connected the TiO<sub>2</sub>-metal side to the Pt side and is shown in Fig. 14. The characteristics of the cells were relatively poor compared with those of TiO<sub>2</sub> electrodes (13).

The quantitative detection of the reaction product by using a membrane polarographic detector (MPD) (14) was tried but failed because of too low an efficiency.

By adding ethanol to the water of the TiO<sub>2</sub>-metal compartment, the photocurrent increased by several times but by not as much as observed in photocatalytic systems (15, 16).

### Discussion

When the TiO<sub>2</sub>-metal side (side 1) of the TiO<sub>2</sub>-metal/SPE was illuminated by light of greater than bandgap energy, electron-hole pairs was generated

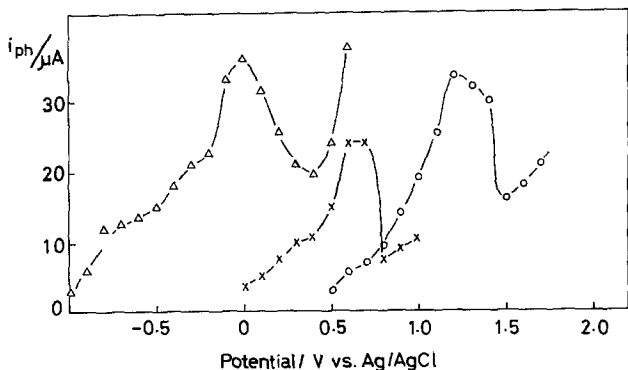
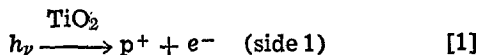


Fig. 10. Photocurrent-potential relations of TiO<sub>2</sub>-Pt/SPE in 1M NaOH (—△—) and in 0.5M H<sub>2</sub>SO<sub>4</sub> (—×—) and of TiO<sub>2</sub>-Au/SPE in 0.5M H<sub>2</sub>SO<sub>4</sub> (—○—).

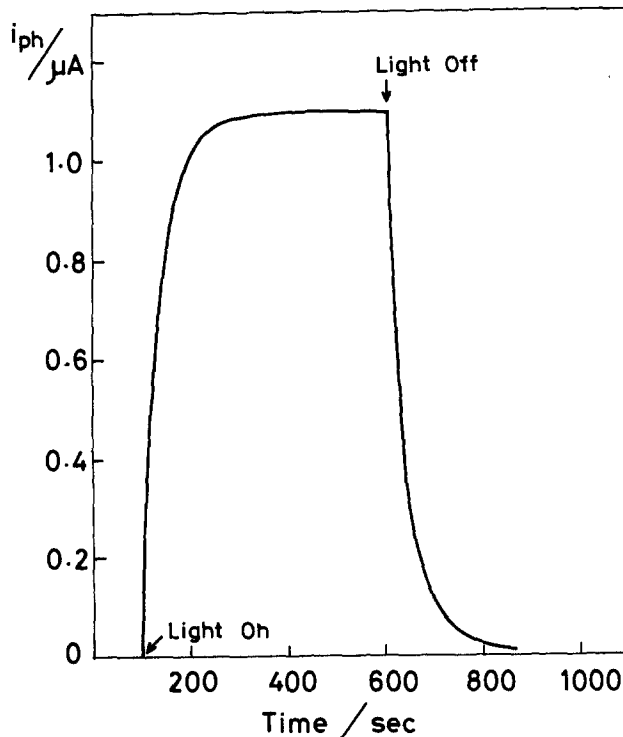
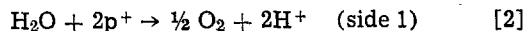


Fig. 11. A typical time course of photocurrent of H<sub>2</sub>O/TiO<sub>2</sub>-Pt/SPE/Pt/N<sub>2</sub> cell when H<sub>2</sub>O/TiO<sub>2</sub>-Pt side was illuminated by 360 nm monochromatic light.

where p<sup>+</sup> and e<sup>-</sup> are the hole and electrons generated at side 1 by the light. In analogy to ordinary photoelectrochemical systems, the holes oxidized water



When the circuit was open, the electrons accumulated on side 1, the Fermi level of TiO<sub>2</sub>-metal was raised and the potential of TiO<sub>2</sub>-metal became negative by the illumination as shown in Fig. 7. In the potentiostatic condition, electrons could be removed from TiO<sub>2</sub>-metal through an external wire and anodic photocurrent was observed, as shown in Fig. 9. The reason for the effect of the metal substrate on the photocurrent potential is not clear, but the coincidence of photocurrent peak potential with oxide formation potential suggests that change of the po-

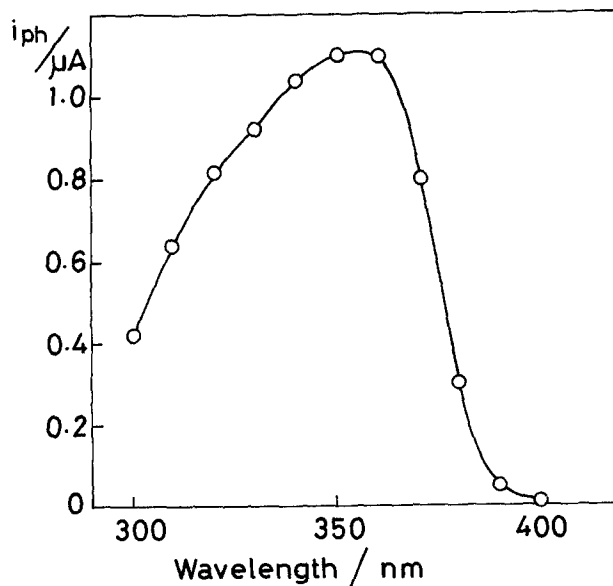


Fig. 12. Photocurrent-wavelength dependence of H<sub>2</sub>O/TiO<sub>2</sub>-Pt/SPE/Pt/N<sub>2</sub> cell.

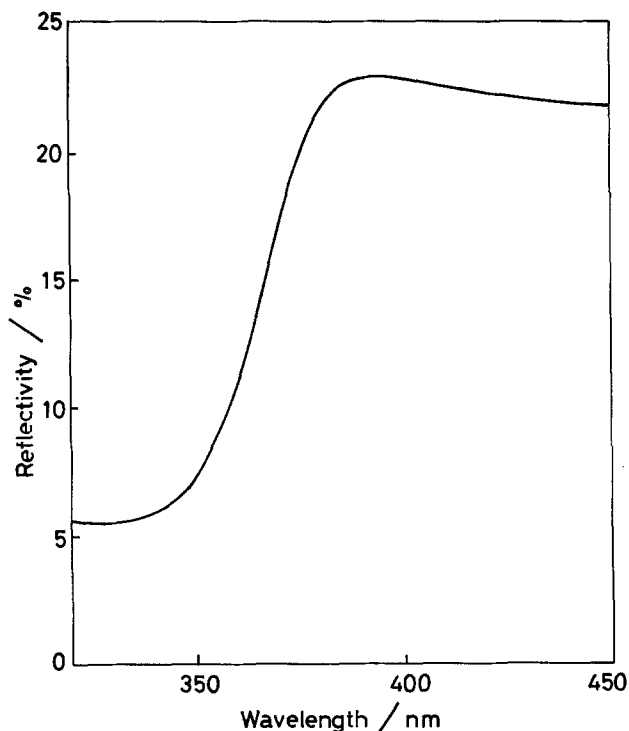
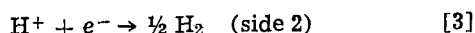


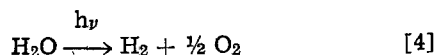
Fig. 13. Reflection spectrum of TiO<sub>2</sub>-Pt/SPE after the photoelectrochemical measurements.

tential distribution at TiO<sub>2</sub>-metal(oxide) interface has some effect on the relations. The relatively large exposure of metal substrate is a complicating factor.

In whole cell systems, *i.e.*, TiO-Au/SPE/Pt and TiO<sub>2</sub>-Pt/SPE/Pt, reactions [1] and [2] also occurred and, at open circuit, electrons accumulated at the TiO<sub>2</sub>-metal side (side 1) and the potential of TiO<sub>2</sub>-metal became more negative than that of Pt (side 2). When the TiO<sub>2</sub>-metal and Pt were connected with a resistor of finite resistance, electrons flowed through the resistance and H<sup>+</sup> moved through the SPE to Pt of side 2 as confirmed by anodic photocurrent. One of the possible reactions at side 2 was the hydrogen evolution reaction

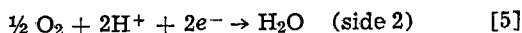


Thus a possible net reaction is photodecomposition of water



However, in the present experimental condition, this reaction did not take place as the potential of the TiO<sub>2</sub>-Pt side was much more positive than the reversible hydrogen electrode potential as shown in Fig. 7.

The comparison between the photovoltage generated by 500W Xe lamp illumination and the one generated by 360 nm monochromatic light suggests that the potential of TiO<sub>2</sub>-Pt may become negative enough to proceed through reaction [4] by increasing the intensity of light. The reaction which seemed to take place at side 2 in the present experimental condition was the reduction of oxygen due to the small amount of oxygen in side 2 despite the nitrogen purge



The light-electricity conversion efficiency was also very low, possibly for several reasons. The short-circuit reactions at the TiO<sub>2</sub>-metal surface (side 1), such as oxygen reduction and hydrogen evolution reactions, consumed electrons at side 1 and, thus, reduced the conversion efficiency

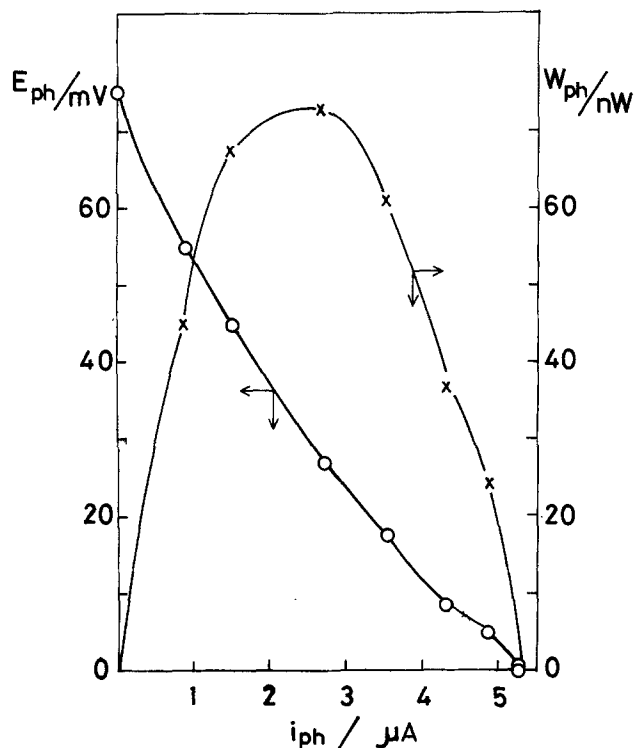
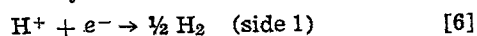
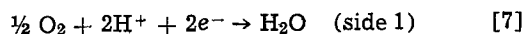
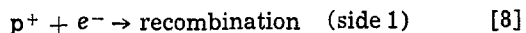


Fig. 14. Photovoltage ( $E_{ph}$ )-output power ( $W_{ph}$ )-photocurrent ( $i_{ph}$ ) relations of H<sub>2</sub>O/TiO<sub>2</sub>-Pt/SPE/Pt/N<sub>2</sub> cell under illumination of 500W Xe lamp with infrared absorbing filter (Toshiba, IRA-20).



The use of a metal which is an inactive catalyst for reactions [6] and [7] as a substrate may improve the efficiency. The rate of reaction [2] seemed to be slow and the recombination reaction [8] effectively competed with reaction [2] and reduced the conversion efficiency



The increase of the photocurrent by the addition of ethanol supports this argument. The prevention of reactions [6], [7], and [8] and the acceleration of reaction [2] would increase not only the light-electricity conversion efficiency but also the electrochemical potential of the electron at the TiO<sub>2</sub>-Pt side, *i.e.*, the possibility of electrolyte-free photoelectrolysis of water.

It must be noted that most of the photoelectrochemical and photocatalytic systems presently available can be constructed as SPE photoelectrochemical cells, *e.g.*, Ru(bpy)<sub>3</sub>Cl<sub>2</sub>-M/SPE/M (17) and Ru(bpy)<sub>3</sub>Cl<sub>2</sub>-RuO<sub>2</sub>·TiO<sub>2</sub>-M/SPE/M (18) where M is the metal substrate.

### Conclusion

The SPE photoelectrochemical cell is proposed as a new device to convert solar energy to electrical and/or chemical energy. The conversion of light to electricity without the intervention of an electrolyte solution was achieved in TiO<sub>2</sub>-Pt/SPE/Pt and TiO<sub>2</sub>-Au/SPE/Pt cells. An increase of light intensity with a smaller contribution of short-circuit reactions at the TiO<sub>2</sub>-metal surface may make electrolyte-free photoelectrolysis of water possible, although it was not attained in this work.

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## Electrochemical Solar Cells with Layer-Type Semiconductor Anodes

### Stabilization of the Semiconductor Electrode by Selective Polyindole Electrodeposition

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#### ABSTRACT

The electropolymerization of indole has been investigated on platinum and molybdenum diselenide electrodes. When performed in the dark, the electropolymerization is selectively directed to the surface defects of the semiconductor. The effect of this surface treatment is investigated and discussed. The results indicate that the electropolymerization of indole effectively blocks the defect sites and produces a stable improvement on the output characteristics of photoelectrochemical cells with layer-type semiconductor anodes.

Photoelectrochemical cells based on layered semiconductors (*i.e.*, MoSe<sub>2</sub> or WSe<sub>2</sub>) have both good solar to electrical energy conversion efficiency and stability against photocorrosion (1). However, the performance of these cells is largely influenced by the surface morphology of the semiconductor (2-5). Crystals with surface defects, such as steps between the van der Waals layers, show poor photoresponses. The unsaturated atoms at the edge of a step have dangling bonds exposed to the electrolyte, introducing new surface states close to the conduction band. These states act as recombination centers and promote, by tunneling of the majority carriers, back reactions of photogenerated redox species. Moreover, the contact of a surface parallel to the *c*-axis with the electrolyte creates a new electric field which drives the photogenerated carriers toward this region where they eventually recombine (2-5).

Consequently, large effort is presently devoted to the study of surface treatments capable of controlling these undesired morphological limitations (4, 6). Bard *et al.* (7) have proposed stabilizing the semiconductor surface by dark electropolymerization of *o*-phenylenediamine, specifically directed toward the blockage of the defective sites. Such a selective action is favored by the fact that only the surface defects of the semiconductor allow passage of appreciable current in the dark.

Following this direction, we have started a systematic study on electrocrystallization and electrodeposition processes on layered semiconductors. In a previous work (8), the feasibility of selective electrodeposition, in general, has been analyzed and discussed. In this paper, the effect of this type of surface treatment is further investigated by examining the polyindole electrodeposition on a single-crystal molybdenum diselenide photoanode.

#### Experimental

The molybdenum diselenide, MoSe<sub>2</sub>, crystals were kindly provided by Dr. F. Lévy of the Polytechnic of Lausanne. The semiconductor crystals were attached with a conductive silver paste to a brass current collector. This was then potted and sealed with epoxy resin on a Teflon holder. The counterelectrode was a platinum wire, spirally arranged around the semiconductor photoanode.

Conventional three-electrode glass cells have been used for the electrodeposition and output characteristic studies. These studies were performed by controlling the voltage with a potentiostat driven by a function generator and recording the current-voltage curves with an X-Y recorder or a computerized acquisition data system.

A halogen lamp was used to irradiate the photoelectrodes. The illumination intensity and uniformity were controlled by a light intensity meter.

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