PHOTOCHEMICAL AND PHOTOELECTROCHEMICAL WATER SPLITTING

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Contents

1. Introduction

The twenty-first century has been predicted to be the “age of light,” and, in anticipation of this, we have been interested in light-related chemical phenomena, that is, using light to induce chemical and electrochemical reactions. We have focused our main attention on reactions that might be useful for maintaining our environment, including hydrogen production, carbon dioxide reduction, and the destruction of pollutants. This article will focus principally on hydrogen production, due to the increasing interest in hydrogen as a clean energy storage medium.

The total amount of solar energy impinging on the earth’s surface in one year is about 3×10^{24} J, or approximately 10^4 times the worldwide yearly consumption of energy. The search for the efficient conversion of solar energy into other useful forms is, in view of the increasing anxiety over the exhaustion of fossil energy resources and attendant global warming, one of the most important challenges for future research and technology development.

In systems designed for the purpose of converting solar energy into electricity and/or chemicals, two principal criteria must be met. The first is absorption, by some chemical substance, of solar illumination, leading to the creation of electrons and holes. The second is the effective separation of these electron–hole pairs with little energetic loss, before they lose their input energy through recombination.

Living plants effectively capture solar energy, which enables them to grow. During this process, they produce oxygen by oxidizing water and organic material by reducing carbon dioxide. In other words, they achieve the oxidation of water and the reduction of carbon dioxide by means of solar energy. Following the model of natural photosynthesis, we began to investigate the photoelectrolysis of water using light energy.

Photo-induced charge separation can proceed effectively if an electric field (potential gradient) is established at the position where the primary photoexcitation takes place. In general, a potential gradient can be produced at an interface between two different substances or phases.

For example, a very thin (approximately 50 Å) lipid membrane separating two aqueous solutions inside the chloroplasts of green plants is believed to play an essential role in the process of photosynthesis, which is one of the most remarkable solar energy conversion systems in existence.

Another well-known example is the solar photovoltaic (PV) cell, in which the photogenerated electron–hole pairs are driven efficiently in opposite directions by an electric field existing at the boundary between n- and p-type semiconductors or at that between a semiconductor and a metal (Schottky junction).

A potential gradient can also be created at the interface between a semiconducting material and a liquid electrolyte. Hence, if a semiconductor is used as an electrode that is connected to another (counter) electrode, photoexcitation of the semiconductor can generate electrical work through an external load and simultaneously drive chemical (redox) reactions on the surfaces of each electrode.

Similarly, when semiconductor particles are suspended in a liquid solution, excitation of the semiconductor can lead to redox processes in the interfacial region around each particle, but no electrical work is done, because the oxidation and reduction reactions are short-circuited.

These types of systems have drawn the attention of a large number of investigators over the past twenty years, primarily in connection with the conversion of solar energy to electrical energy and chemically stored energy. During the last five years, the area of particulate semiconductors has also seen tremendous growth in terms of photocatalyzed air and water purification.

This article deals with the principles and recent advances in the investigation of light energy conversion systems based on semiconductor/liquid junctions, focusing on hydrogen generation from water. We will also make brief mention of photoelectrochemical CO_2 reduction and TiO_2 photocatalysis, because of their close relationships to the main topic. Specific topics covered include the following: photoelectrochemical water electrolysis, including the TiO_2–Pt system; photoelectrochemical photovoltaic systems; photocatalytic water splitting; photoelectrochemical reduction of CO_2 at p-type semiconductor electrodes; and photocatalytic decomposition of air and/or water pollutants with illuminated semiconductors.

2. Photoelectrochemical Approaches

2.1 Basics Aspects of Photoelectrochemistry

When a non-illuminated semiconductor electrode is in contact with an electrolyte solution containing a redox couple, equilibration takes place at the interface, just as in the case of a Schottky junction, with the Fermi level in the semiconductor shifting to match that of the solution redox couple.

This may result in the formation of a space charge layer within a thin region close to the surface of the semiconductor, in which the electronic energy bands (valence and conduction) are bent upwards or downwards, depending on the relationships between the respective Fermi levels in the semiconductor and the solution redox couple (Figure 1a).

The thickness of the space charge layer is usually of the order of 1–10^3 nm, depending on the carrier density and dielectric constant of the semiconductor. Thus, for an n-type material, for example, the electrons in the semiconductor continue to reduce the oxidized form of the redox couple, during which time the Fermi level decreases until it matches that of the couple.

If the illuminated semiconductor is illuminated by photons with energies greater than that of the semiconductor band gap, E_G, electron–hole pairs are generated and separated in the space charge layer.

In the case of an n-type semiconductor, the electric field existing across the space charge layer drives photogenerated holes toward the interfacial region (i.e., solid–liquid) and electrons toward the interior of the electrode and from there to the electrical connection to the external circuit. On open circuit, as the electrons are driven toward the bulk of the semiconductor, they begin to accumulate, which raises the bulk Fermi level (Figure 1b).

The latter will continue to rise, depending on the light intensity and recombination rate, until a steady state is reached. At this point, one can measure an open circuit voltage EOC of the illuminated semiconductor electrode with respect to the counter electrode, which is in equilibrium with the redox couple and thus has an electron energy corresponding to the couple's Fermi level.

Naturally, if current is drawn off in an external circuit, there will no longer be as many electrons accumulated in the semiconductor, and its Fermi level will fall until a new steady state is reached (Figure 1c).

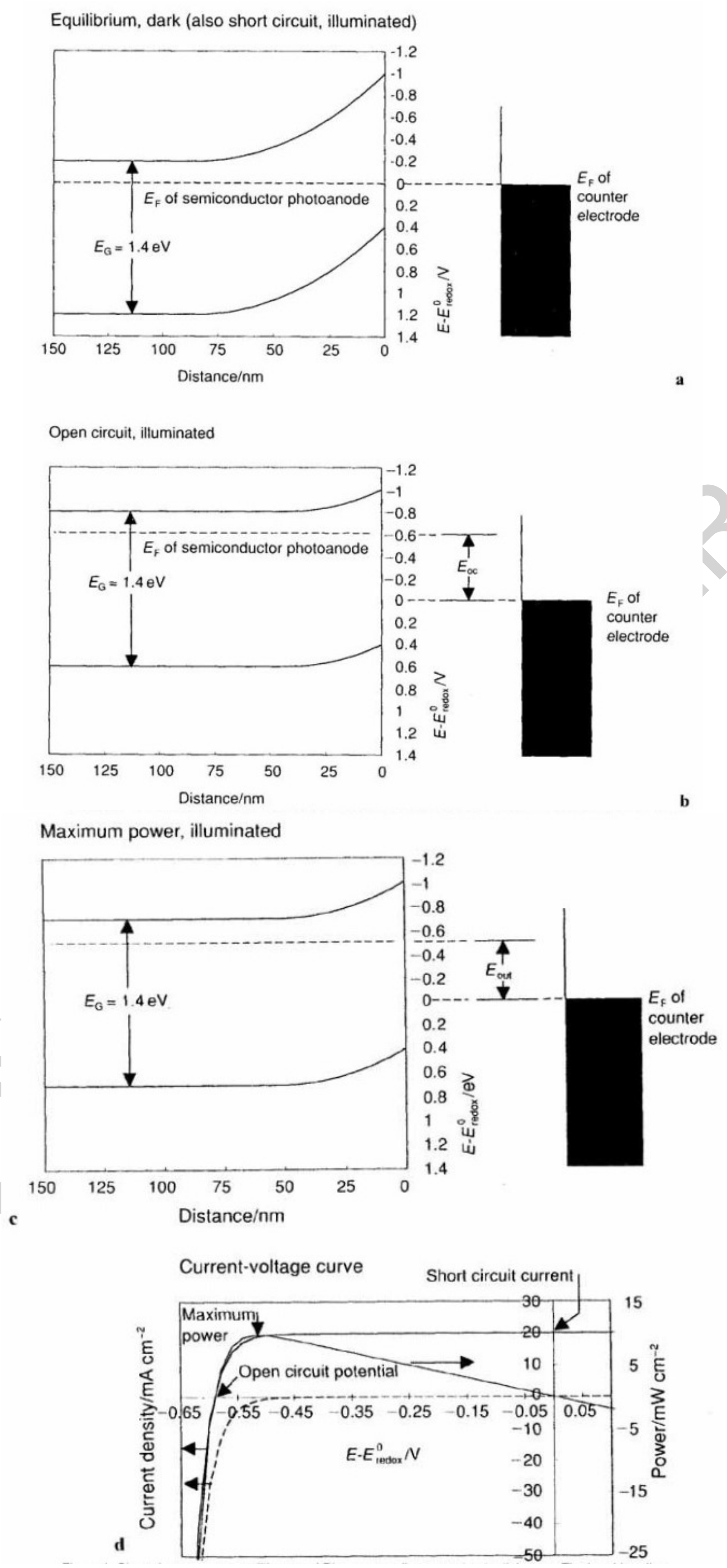
Equilibrium, dark (also short circuit, illuminated)
E_F of semiconductor photoanode
E_G = 1.4 eV
E_F of counter electrode
-1.2 -1 -0.8 -0.6 -0.4 -0.2 0 0.2 0.4 0.6 0.8 1 1.2 1.4
E-E^0_{redox}/V
150 125 100 75 50 25 0
Distance/nm
a
Open circuit, illuminated
E_F of semiconductor photoanode
E_G = 1.4 eV
E_{oc}
E_F of counter electrode
−1.2 −1 −0.8 −0.6 −0.4 −0.2 0 0.2 0.4 0.6 0.8 1 1.2 1.4
E-E^0_{redox}/V
150 125 100 75 50 25 0
Distance/nm
b
Maximum power, illuminated
E_G = 1.4 eV
E_{out}
E_F of counter electrode
−1.2 −1 −0.8 −0.6 −0.4 −0.2 0 0.2 0.4 0.6 0.8 1 1.2 1.4
E-E^0_{redox}/eV
150 125 100 75 50 25 0
Distance/nm
c
Current-voltage curve
Short circuit current
Maximum power
Open circuit potential
−0.65 −0.55 −0.45 −0.35 −0.25 −0.15 −0.05 0.05
E-E^0_{redox}/V
30 20 10 0 −10 −20 −30 −40 −50
Current density/mA cm^{-2}
15 5 −5 −15 −25
Power/mW cm^{-2}
d

Figure 1. Schematic diagram of energy levels for a generic n-type semiconductor in a regenerative PEC. (a) Equilibrium, dark conditions and also short circuit, illuminated conditions. (b) Open circuit, illuminated conditions. (d) Maximum power conditions. (d) Corresponding current–potential curve. The band-bending curves were calculated based a carrier density of 10^{17} cm^{-3} and a dielectric constant of 8. For the current–voltage curves, the photocurrent density and the reverse saturation current density were assumed to be 20 mA cm^{-2} and 10^{-12} A cm^{-2}, respectively.

Note that there is no net change in the amounts of oxidized and reduced forms of the redox couple, because exactly the same number of moles of the reduced form are oxidized at the semiconductor as there are of the oxidized form that are reduced at the counter electrode.

Thus, this type of photoelectrochemical cell (PEC) is referred to as “regenerative.” All of these processes are very similar to those occurring in p-n and particularly Schottky junction cells and have been discussed in a number of reviews (see Bibliography).

As already mentioned, the operating principles of the PEC are very similar to those of the solid-state junction photovoltaic cell. The latter have enjoyed continuous development, with the efficiency now reaching over ~24% in laboratory cells, although practical wafer-based cells are in the 12–16% range.

One of the driving forces behind the PEC approach is the perceived ability to form rectifying junctions in simpler ways compared to the relatively sophisticated techniques required in solid-state processing. Another is that barrier height can in principle be varied easily by choosing appropriate match-ups between semiconductors and redox couples. These types of ideas continue to drive research in this area, and interesting results continue to be obtained.

Of course, there are also disadvantages of the PEC approach. For example, the manufacturing process is more complicated if there is a liquid electrolyte. For another, the liquid can evaporate, or water and oxygen can get in and contaminate the electrolyte. For these reasons, there has also been a continuing interest in solid polymer electrolytes.

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Biographical Sketches

Dr. Akira Fujishima received his undergraduate engineering degree from Yokohama National University in 1966 and his doctorate from the University of Tokyo in 1971. He took his first academic position as a Lecturer at Kanagawa University in 1971, then moving back to the University of Tokyo (School of Engineering), first as Assistant Professor in 1975, as Associate Professor in 1978), as Professor in 1986. He retired from the University in 2003 and is now a special Professor Emeritus. He has also held various increasingly responsible positions at the Kanagawa Academy of Science and Technology (KAST), beginning in 1997, culminating in 2003 in the position he now holds, of Chairman. Dr. Fujishima has received many awards and prizes, including the Asahi Prize, the Inoue Harunari Prize, the Chemical Academy Award, the Gerischer Award, the Japan Prize, the Japan Academy Award, and the Prime Minister's Award for Contributions to Industry-Academia-Government Collaboration.

Donald A. Tryk received his undergraduate degree in chemistry from the University of Florida in 1969 and his doctorate from the University of New Mexico in 1980. Then, he went on to Case Western Reserve University, where he was a Senior Research Associate in the Chemistry Department until 1995. He was at the University of Tokyo as a Research Associate and Special Associate Professor in the group of Professor Akira Fujishima until 2001. He was then a Visiting Professor, first at Tokyo Metropolitan University, then in 2003 at the University of Puerto Rico, and then again, in 2005, at Tokyo Metropolitan University. His principal research interests are in electrochemistry, **photoelectrochemistry and photocatalysis.**