

PHOTOELECTROCATALYSIS

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Summary

The use of semiconductors for the photocatalytic detoxification (oxidation of organics) and disinfection (inactivation of bacteria) steps in the treatment of water has been widely reported but the photonic efficiency is low. This is because the lifetimes of the UV-generated charge carriers, the key intermediates in the photocatalytic process, are too low because of their high recombination rates. Theory predicts that by applying a small positive potential to a semiconductor (often TiO₂) anode the charge carrier recombination responsible for low photonic efficiency can be reduced and efficiency increased. The predicted improvement has been demonstrated experimentally in the laboratory. This review describes the preparation and characterization of the necessary photoanodes and focuses on their use in three applications: oxidation of phenolic compounds, decoloration of dilute solutions of dye molecules and the inactivation of

bacteria. The basic concept has been demonstrated to be correct. Some of the problems inherent in any scale-up of photoelectrocatalytic process are identified and it is suggested that at present photoelectrocatalytic activities are too low for commercial exploitation.

The same processes responsible for the oxidation of organics can, in the absence of dissolved molecules reduce water molecules to produce hydrogen and oxidize them to produce oxygen. The problems of carrying out this reaction photocatalytically are indicated and the advantages of photoelectrocatalysis summarized and some examples of hydrogen production using TiO_2 , SiC and Fe_2O_3 electrodes are described.

1. Definition and Scope

Photoelectrocatalysis increases the rate of a chemical reaction by applying an electrical potential to (usually) a semiconductor electrode which is simultaneously irradiated by a stream of photons.

Irradiation of a semiconductor by photons with an energy greater than the electronic band gap causes photocatalysis (PC). The term ‘photoelectrocatalysis’ (PEC) is used when an electrical potential is applied simultaneously to the semiconductor. Since 1993 photoelectrocatalysis research has focused mainly on PEC for water-treatment. There has also been a revival of studies focused on photoelectrocatalytic splitting of water in order to generate hydrogen as a clean fuel. This article will focus on these two topics.

2. Photoelectrocatalysis for Water Treatment

2.1. Photocatalysis by Semiconductors

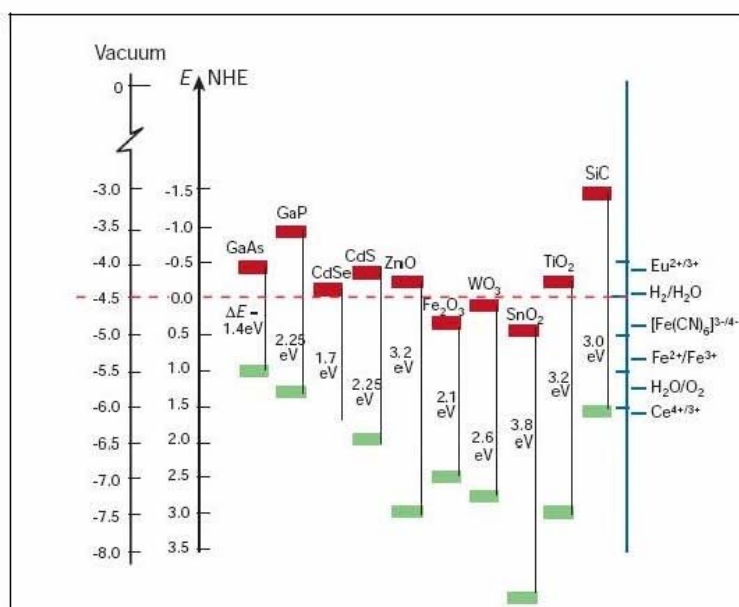


Figure 1. Band positions of several semiconductors in contact with aqueous electrolyte at pH1 taken from Gratzel Nature 414 338 (2001)

In semiconductors, electrons only have energies within narrow ranges of closely spaced levels, i.e. within specific energy level bands. Electrons first fill the bands of lowest energy, and then fill successively higher energy bands. The very highest energy level bands are normally empty. The highest of the filled energy bands, called the valence band, is separated from the first of the unfilled bands, the conduction band, by an energy gap, or band gap, whose size, ΔE , depends on the semiconductor of interest. For a semiconductor such as gallium arsenide the band gap is ~ 1.4 eV, for both TiO_2 and ZnO it is ~ 3 eV. (Fig. 1)

Since a band gap of 3 eV corresponds to wavelengths of 400 nm, UV light with wavelengths below 400 nm has sufficient energy to excite electrons from the valence band to the conduction band in TiO_2 and ZnO . Because the valence band is normally completely filled, the electrons that occupy it do not move freely across the crystal and electrical conductance is very low. However, as shown in Fig. 2, the absorption of sufficiently energetic photons may excite an electron from the filled valence to the conduction band. Because the conduction is almost empty, the mobility of the excited electron within it is high; therefore, the excited electron can migrate to the surface of the semiconductor, where it is able to initiate chemical reactions. At the same time the removal of an electron from the previously filled band permits some charge carrier mobility in the valence band of the irradiated semiconductor. This absence of an electron is usually referred to as a positive hole (or simply a 'hole') because excitation has generated a gap, or hole, which is positively charged relative to the surrounding negative electrons. The photon induced formation of an excited electron and its associated positive hole, and their subsequent migration to the semiconductor surface, is the basis of photocatalysis (PC). The application of a small electrical potential to the semiconductor modifies the properties of these excited charge carriers and leads to the phenomenon of photoelectrocatalysis (PEC).

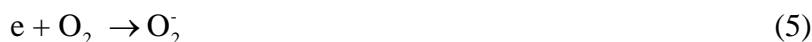
The most widely used photocatalyst is titanium dioxide for which the band gap, ΔE , is 3.05 (for the rutile polymorph) or 3.25 eV (for the anatase polymorph). This means that photons with wavelengths, λ , below ~ 405 nm are sufficiently energetic ($hc/\lambda > \Delta E$ where c is the speed of light and h , 6.6×10^{-34} Js, is Planck's constant) to excite the electrons in rutile, and wavelengths < 385 nm to excite anatase. The catalytic sequence may then be represented by schemes such as



where e represents an excited electron and p represents the positive hole that is formed in the valence band as a result of irradiation by light of wavelength λ such that $hc/\lambda > \Delta E$. This hole can oxidize adsorbed species either directly or via the formation of a hydroxyl radical.



The OH^\bullet radical is strongly oxidizing and its redox potential of 2.8 V vs. the normal hydrogen electrode (NHE) is surpassed only by that of F_2 among common chemical oxidants. The excited electron can react with an electron acceptor, usually oxygen with which it may form reactive species such as O_2^-



These O_2^- superoxide radical ions may then react further with water to form perhydroxyl radicals OOH^\bullet or H_2O_2 . The H_2O_2 is also a strong oxidant ($E^0=1.78$ V vs NHE), but less so than OH^\bullet . The capture of the electron by O_2 , which is necessary if charge is not to build up on the photocatalyst, is frequently considered to be the rate determining step in photocatalysis (Gerischer, 1993).

Semi-conducting films of titanium dioxide on glass have been widely used both for self-cleaning of glass surfaces and for the oxidation of trace organic pollutants in the atmosphere and these applications are particularly effective if the source of energetic photons is the UV component of solar radiation (Mills and Lee, 1994). However, despite widespread interest, photocatalytic treatment of water has been restricted to relatively few niche applications and has not achieved widespread commercial success. The main reason for this failure is that the efficiency with which absorbed photons are converted into catalytically active holes and excited electrons is too low, normally less than 5% for the generally available photocatalysts. Therefore, much of the energy input into UV lamps is wasted, if they are the source of radiation. Although solar radiation may be used, its UV component is small, ~5%. Hence, a compromise must be made between the expense of concentrating the solar UV by e.g., the use of parabolic reflectors and the need to limit the flows of water to be treated. Further information on semi-conductor photocatalysis may be found in *Photocatalysis*.

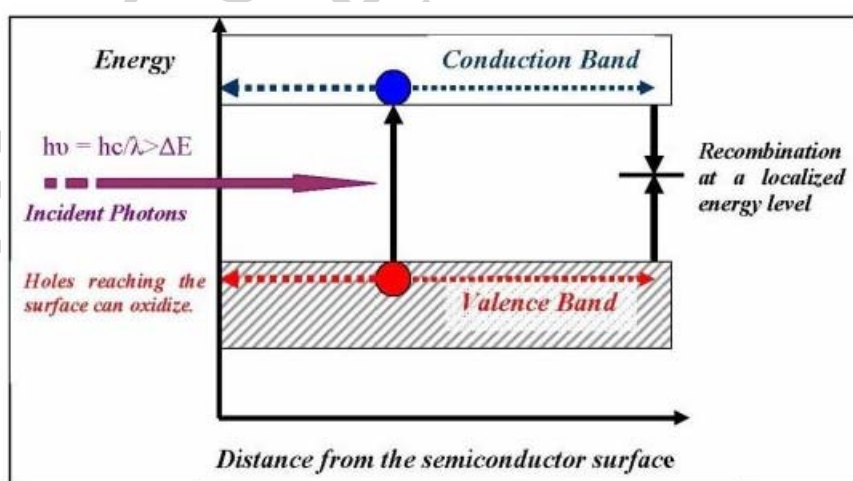


Figure 2. Absorption of photons with a wavelength $\lambda < \Delta E / hc$ excites electrons from the valence band to the conduction band of a semi-conducting solid. The excited electron, e, is represented by \bullet and the positive hole, p, by \bullet . Localized energy levels are normally associated with defects or dopants.

2.2. Photoelectrocatalysis by Semi-Conductors.

2.2.1. The Underlying Concept

The main reason for the low efficiency for the conversion of absorbed photons to hydroxyl radicals or other oxidation intermediates is that most, > 95%, of the photogenerated holes recombine with excited electrons before they can migrate to the semiconductor surface. (In formal terms, L_p the diffusion length of the positive holes is small.) This recombination is almost exclusively non-radiative so the energy of the excited electron is simply converted to heat – as a result of shining light on the catalyst it gets warm! Consequently, an important objective in the development of photoelectrocatalytic methods of water treatment has been to improve the efficiency with which the absorbed light is used. Conceptually, the dominance of charge carrier recombination might be reduced by using particles that are smaller than L_p . In practice this approach is limited because, even if recombination in the particle bulk can be eliminated, surface recombination can still occur. In addition, the necessary removal of catalyst particles from treated water becomes more costly as the catalysts particle size is reduced. Therefore, a secondary objective has been to use immobilized semiconductors instead of dispersion (slurry) of semiconductor particles. A third desirable objective, to use semiconductors which can use some of the visible photons which are available in the solar spectrum has, at the time of writing, received much less attention in photoelectrocatalysis than it has in photocatalysis.

Photoelectrocatalysis seeks to improve the utilization of light by reducing the charge carrier recombination that is the major cause of the low quantum efficiency of conventional photocatalytic processes, by applying a small positive bias to a semiconductor electrode. At the conductor/semi-conductor interface of a single crystal or polycrystalline semiconductor, the band energies are lowered by the application of the positive potential. However, at the semi-conductor/electrolyte interface the band energies are substantially unaltered. Consequently a potential energy gradient - an electric field - is generated within the semiconductor. As a result, the simple energy diagram for photocatalysis shown in Fig. 1, must be modified as shown in Fig. 2. This shows a field extending over a depth W into the semiconductor from the semiconductor/electrolyte interface, and this surface zone is commonly called the depletion-layer.

The electrolyte concentration is usually larger than N_d the density of dopants in the semiconductor and the depletion layer thickness increases as the square root of the applied potential according to the equation.

$$W = \left(2\varepsilon\varepsilon_0 |V - V_f| / eN_d \right)^{1/2} \quad (6)$$

where V is the potential at the conduction band edge, V_f is the flat band potential, ε is the relative permeability in the direction perpendicular to the interface, ε_0 is the permittivity of free space and e is the charge on the electron. The background theory is discussed in text books by Morrison, among many others.

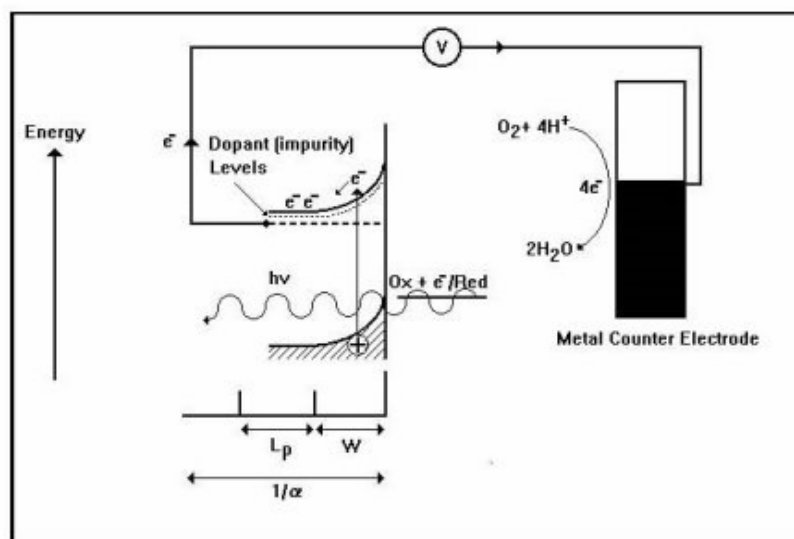


Figure 3. The application of a positive potential of ~ 1 V to a semiconductor electrode lowers the energy of the conduction band at metal/semiconductor interface. As a result a field develops at the electrode/electrolyte interface and extends over a depth W into the semiconductor. L_p is the diffusion length of the positive hole. The UV is considered to penetrate into the semiconductor by a distance $1/\alpha$ where α is the wavelength dependent absorption coefficient of the semi-conductor.

Typically, for anatase films formed by sputtering, 90% of incident UV is absorbed in ~ 200 nm (for 370 nm radiation) or 50 nm (for 345 nm radiation), i.e. $1/\alpha$ is of the order of 100 nm. In PC only those holes generated within a distance L_p reach the semiconductor surface. In PEC holes generated within a distance $(W + L_p)$ have a good chance of reaching the surface as holes generated at a depth between W and $(W + L_p)$ have a good chance of diffusing to the edge of the depletion layer and of then moving ‘uphill energetically’ towards the semiconductor/electrolyte interface. Electrons, e , move ‘down hill’ towards the conducting substrate. Therefore, electrons tend to separate from the holes and calculations suggest that, for reasonable dopant concentrations, an applied bias of ~ 1 V is sufficient to cause the separation. The separation increases the photonic efficiency because it reduces charge-carrier recombination. In addition electrons that have been attracted towards the conducting substrate, by the potential difference between the TiO_2 photoanode and the cathode, are driven around the external circuit to the cathode at which the counter electrode reaction, usually oxygen reduction, occurs. Hence oxygen reduction is no longer rate limiting, in contrast to photocatalysis, (Gerischer, 1993). For a fixed UV intensity the ‘electric field effect’ is predicted to increase the rate of photocatalysis, as shown schematically in Fig. 5.

The treatment of the semiconductor depletion layer assumes that the distance over which an electric field is established, the thickness of the depletion-layer, is small in comparison with the electrode thickness – as will occur for single crystal or polycrystalline electrodes. However, the form of the equation shows that for low dopant levels, N_d , W will be large. For particulate electrodes, such as those prepared by

deposition of commercially available powders or by the sol-gel preparation methods described below, the particle size may be too small, 30 nm or less, to allow the depletion layer to fully develop at individual particle/electrolyte interfaces. As discussed by Vinodgopal, Hotchandani and Kamat, even though the classical treatment of the semiconductor/electrolyte interface is no longer appropriate, and charge separation can only be achieved from the differences between the rates of hole and electron transfer at the electrode/electrolyte interface, application of a potential bias provides a potential gradient within the film that drives the photogenerated holes to the electrode/electrolyte interface. Electrons are attracted to the back contact, at which, as a result of the potential difference between the TiO₂ photoanode and the cathode, they are driven around the external circuit to the counter electrode, where, the counter electrode reaction, usually oxygen reduction, is driven separately.

2.2.2. The Basic Experiment

Fig. 4 represents the basic photoelectrocatalytic experimental arrangement. A UV source irradiates a semiconductor electrode and generates holes which oxidize the solution species R. The semiconductor electrode is biased relative to a reference electrode and the cathodic reaction, the reduction of X to X⁻ takes place at a nickel counter electrode. The reactant solution must be electrically conducting and it is usual to add a supporting electrolyte. Often, but not always, this is Na₂SO₄ or NaClO₄.

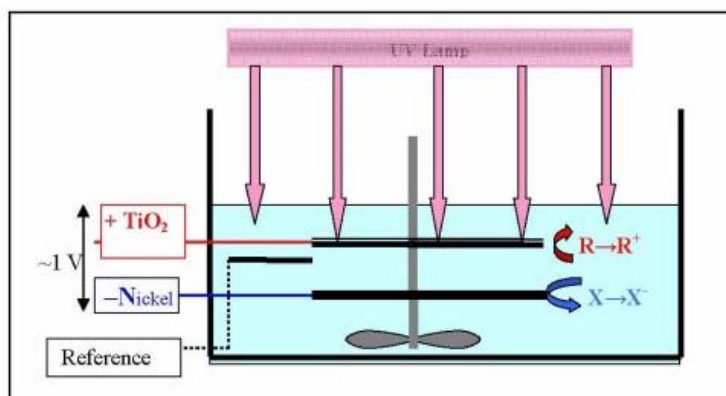


Figure 4. A schematic representation of the type of reactor used in many Photoelectrocatalysis experiments. A titanium dioxide anode –typically deposited on a conducting glass – is separated from a metallic (often nickel) cathode. A third, reference, electrode is present if reliable current voltage curves are to be measured.

A schematic representation of a reaction which is started by switching on a UV lamp, after 5 minutes is shown in Fig. 5. In the absence of a semi-conducting electrode, direct photochemical reaction may occur, and this is represented by the violet line designated 'UV'. If, however, a potential is applied to a semi-conducting electrode immersed in the reactant solution a 'dark' electrochemical reaction, represented by the black dashed line marked 'field' may take place even in the absence of UV irradiation. Alternatively, in the absence of an applied field, photocatalysis may occur if the semiconductor surface is irradiated; this is represented by the full black line, 'photocatalysis', in Fig. 5. Finally, if a potential is applied to the UV-irradiated semiconductor electrode,

photoelectrocatalysis can occur – the red line. If this is truly photoelectrocatalytic the % reaction is be greater than the combined reaction (blue line) due to the sum of the individual dark electrochemical and photocatalytic reactions. Clearly, a large number of control experiments must be carried out if photoelectrocatalysis is to be unambiguously identified.

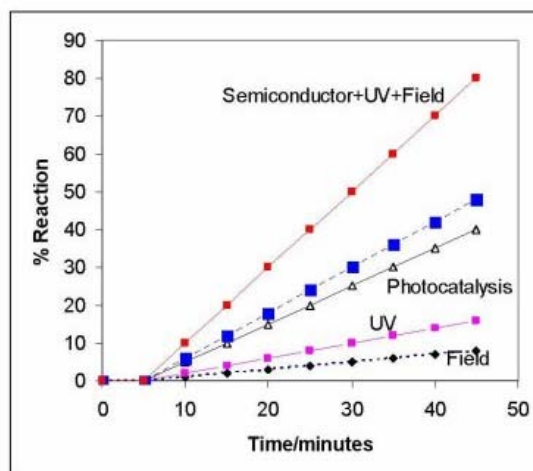


Figure 5. A schematic representation of the typical results obtained during a PEC experiment. For true photoelectrocatalysis, the reaction in the presence of simultaneous irradiation and potential bias should exceed the sum (—■—■—■—) of the individual effects of irradiation (photocatalysis) —△—△—△— and of the electrical field by itself (electrochemical)◆.....◆.....◆......

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Biographical Sketch

Dr. Terry Egerton's current research interests focus on the growth and surface modification of titanium dioxide, its UV absorbing and photocatalytic properties and on polymer degradation. His early research on catalysis and spectroscopic characterization of catalysts was followed by lectureships in the Departments of Chemistry at Makerere University, Uganda, and Cardiff University, Wales. He then worked for twenty four years in the Research and Redevelopment Department first of BTP Tioxide and , following Tioxide's absorption into ICI, in ICI Tioxide business. After retiring from industry, as an ICI

Company Research Associate, he moved to Newcastle University, UK where he is currently a senior lecturer in the School of Chemical Engineering and Advanced Materials.

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