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International Symposium on

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NEW TRENDS IN
PHOTOELECTROCHEMISTRY

Altavilla Milicia (Pa), Italy, 22-26 September 1991

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EXTENDED ABSTRACTS

International Symposium on

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International Symposium on

NEW TRENDS IN PHOTOELECTROCHEMISTRY

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PROGRAMME

Monday, Sept. 23 Morning Session

Chairman: *H. Gerischer*

9 - 10 a.m.: Opening lecture
"Functionalized Electrochemistry"
K. Honda, Tokyo Institute of Polytechnics, JAPAN

10.00 - 10.30 a.m.:
"Effect of Excitation Wavelength on the Photo induced Electron Transfer of Metalophtalocyanines"
K.Tokomaru, University of Tsukuba, JAPAN

10.30. - 11.000 a.m.:
"Polymer-Based Electrochromic Devices"
M. Mastragostino, University of Bologna, ITALY

11.00 - 11.30 a.m.: *Coffee break*

Chairman: *L. Peraldo Bicelli*

11.30 - 12.00 a.m.:
"Imaging Techniques of Passive Oxides and Metals on Semiconductors"
R. Peat, Harwell Laboratory, ENGLAND

12.00 - 12.30 p.m.:
"Effect of visible light on Hydrogen Permeation in Metals"
G."Razzini, Polytechnic of Milano, ITALY

12.30 p.m.: *Lunch*

Monday, Sept. 23 Afternoon Session:

Chairman: ***A. Fujishima***

5.30 - 6.30 p.m.: Invited Lecture
"Microwave (Photo)electrochemistry: New Insight Into Illuminated Interfaces"
H. Tributsch, Hahn-Meitner-Institut, Berlin GERMANY

6.30 - 7.00 p.m.:
"Some Basic Working Principles of Heterogeneous Photocatalysis by Semiconductors"
M.Schiavello, University of Palermo, ITALY

7.00 - 7.30 p.m.:
"Photo-oxidation of Organic compounds at Semiconductor-Water Interface"
E. Pelizzetti, C. Minero and E. Pramauro
University of Torino, ITALY

7.30-8.00 p.m.:
"Picosecond Time-Resolved Measurements and Theoretical Concepts of Charge Exchange Between Semiconductors and Molecules (Redox Ions)"
F. Willig, Fritz-Haber Institut der Max-Planck Gesellschaft, Berlin GERMANY

8.00 p.m.: *Dinner*

Tuesday, Sept. 24 Morning Session

Chairman: *H. Tributsch*

9.00 - 10.00 p.m.:Invited lecture
"From Photocorrosion to Photoelectrochemical Etching"
F. Decker, University of Rome, ITALY

10.00 - 10.30 a.m.:
"Photoelectrochemical Properties of Photoelectroetched n-Silicon"
A. Lagoubi, M. Neumann Spallart and C. Levy-Clément, Laboratoire de Physique des Solides, CNRS, Paris, FRANCE

10.30 - 11.00 a.m.:
"Photoelectrochemical Etching of Deep, Random, Microstructures onto n-InP Using White Light"
D. Soltz, L. Cescato and F. Decker
University of Campinas, BRASIL

11.00 - 11.30 a.m.: *Coffee Break*

Chairman: *F. Decker*

11.30 - 12.00 a.m.:
"Photoelectrochemical Methods for Semiconductor Device Processing".
P.A. Kohl, Georgia Institute of Technology, Atlanta, U.S.A.

12.00 - 12.30 p.m.:
"Use of AFM and STM for Characterization and Modification of Semiconductor Surfaces"
B.Parkinson,Colorado State University, USA

12.30 p.m.: *Lunch*

Tuesday, Sept. 24 Afternoon Session

Chairman: *Y. Pleskov*

5.30 - 6.30 p.m.: Invited Lecture
"Investigation of Oxide Films on Ti,Al,Zn and Hf"
W.H. Smyrl, University of Minnesota, Minneapolis, U.S.A.

6.30 - 7.00 p.m.:
"The Photoelectrochemistry of Thin Passive Layers Investigation of Anodic Oxide Films on Titanium Metal"
S. Piazza, C. Sunseri and F.Di Quarto
University of Palermo, ITALY

7.00- 7.30 p.m.:
"The Role of the Surface Intermediates in the Photoelectrochemical Behaviour of Anatase and Rutile TiO_2*"*
J.Augustinski, University of Geneve, Switzerland

7.30-8.00 p.m.:
"Characterization of electrodeposited TiO_2 *films"*
D. Zane, F. Decker and G. Razzini
University of Rome and Polytechnic of Milan, ITALY

8.00 p.m.: *Dinner*

Wednesday, Sept 25 Morning Session

Chairman: ***W.H. Smyrl***

9.00 - 10.00 a.m.:Invited Lecture
"Biochemical Application of Photoelectrochemistry -Photokilling of Malignant Cells with Ultrafine TiO_2 *Powder"*
A. Fujishima, The University ofTokyo JAPAN

10..00 - 10.30 a.m.:
"Non-Linear Phenomena Observed During Reduction of H_2O_2 *at Chalcopyrite (Photo)cathodes".*
S. Cattarin and H. Tributsch
IPELP, CNR, Padova ITALY
Hahn-Meitner-Institut, Berlin GERMANY

10.30 - 11.00 a.m.:
"Natural Pyrite-Based Electrodes of Photoelectrochemical Applications"
V. Antonucci, A.S. Aricò, I. Ielo, E. Modica G. Candiano., G. Monforte and N. Giordano
CNR Institute for Transformation and Storage of Energy, Messina ITALY

11.00 - 11.30 a.m.: *Coffee Break*

Chairman: ***B.Parkinson***

11.30 - 12.00 a.m.
"Protected Silicon Photoanode for Photoelectrolysis"
Pleskov, Institute of Electrochemistry Academy of the Sciences of USSR, Moscow

12.00 - 12.30 p.m.:
"Application of Photoelectrochemistry to Memory Device and Display Device"
K.Hashimoto, The University of Tokyo, JAPAN

12.30 p.m.: *Lunch*

Wednesday, Sept. 25 Afternoon Session

Chairman: *K. Honda*

5.30 - 6.00 p.m.:
"Photoelectrochemical Devices Composed of Coated Polymer Membranes for Photoenergy Conversion"
M. Kaneto, The Institute of Physical and Chemical Research, Wako, Sakama, JAPAN

6.00 - 6.15 p.m.:
"Investigation of Photoelectrochemical Properties of Semiconductor-Electrolyte Interface in Armenia".
V. Arutyunyan, Yerevan State University, U.S.S.R.

6.15-6.30 p.m:
"Thin-film Multijunction Solar Cell for Water Photoelectrolysis"
A.Selvaggi, Eniricerche, Monterotondo, Rome, ITALY

6.30 - 7.30 p.m.: Closing Lecture
"Photoelectrochemical Catalysis by Small Semiconducting Particles"
H. Gerischer, Fritz-Haber Institut der Max-Planck-Gesellschaft, Berlin, GERMANY

7.30 - 8.00 p.m.: Closing remarks
B. Scrosati, University of Rome, ITALY

8.30 p.m.: *Dinner*

Investigation of photoelectrochemical properties of semiconductor-electrolyte interface in Armenia.

Vladimir Arutyunyan
Yerevan State University
Yerevan, 375049, Armenia, USSR

At present photoelectrochemistry of semiconductors covers a wide range of border problem, is stimulating discoveries and studies of new materials, and promises interesting applications in various branches of modern technology, including energetics and control system.

This review paper discusses results of investigations carried out last two year in Yerevan State University.

Photoelectrochemical characteristics and properties of photocathodes made yttrium barium ceramics were investigated. Sintered by standart solid state techniques samples with various nominal compositions were degenerative p-type semiconductors. It is shown that these low cost electrode can be use rather well instead of metalic cathode (platinum etc.).

It is shown that the use of a number of polar semiconductors as the photoanode in photoelectrochemical cells can lead to increasing of the efficiency of conversion of solar energy to hydrogen if semiconductors characterised by great value of exciton transitions oscillation strength. For such semiconductors as ZnO, InSe etc. it becomes essential to take into account charge carriers generated by exciton thermal or field dissociation. We have carried out the analisis of exciton field dissociation influence on the photocurrent in exciton absorption region. The possibility of sensitization of semiconductors by a surface field formed on contact with an electrolyte is discussed as well as the influence of deep states on the capacitance-voltage characteristics of interface.

A automatic plant allowing to obtain the distribution of surface photovoltage signal from the surface of semiconductor plate was constructed. It allow us to get rapidly an information about unhomogeneity of semiconductor plate.

Photoelectrochemical Devices Composed of Coated Polymer Membranes for Photoenergy Conversion

Masao KANEKO
The Institute of Physical and Chemical Research
Wako, Saitama, 351-01 Japan

Electrode coating by functional polymer membranes is one of the prominent methodology to fabricate photoelectrochemical devices for photoenergy conversion. These devices can be divided into the following four types.

Type 1: Photoexcitation center is incorporated into the coated polymer layer, and the electron transfer between the excited state and other acceptor (or donor) induces response at the electrode (photochemical diode).

Type 2: Photochemical reaction of a compound incorporated into the coated polymer layer induces current changes.

Type 3: Semiconducting polymer layer forms a liquid-junction with an electrolyte solution, and induces photocurrent.

Type 4: Liquid-junction inorganic semiconductor is coated with a polymer membrane whose function is charge transport/storage, catalysis, etc. for stabilization, energy storage, photocatalysis and so on.

Our works (Table) will be reviewed together with recent results.

Ref) M.Kaneko et al. Adv. Polym.Sci.<u>84</u>,141(1987). J.Phys. Chem.<u>95</u>,1748(1991).J.Chem.Soc.Chem.Commun.<u>1989</u>,1338.

Table Photoelectrochemical devices composed of polymer membranes

Type	Excitation center	Electrode	Coated polymer layer composed of		Redox reagent in soln.
			1st	2nd	
1	MPc	ITO	MPc	-	O_2or MV^{2+}(+O_2
	〃	〃	〃	BV^{2+}	None or O_2
	$Ru(bpy)_3^{2+}$	ITO or BPG	$Ru(bpy)_3^{2+}$	-	O_2or MV^{2+}(+O_2
	〃	BPG	〃	MV^{2+}	None or O_2
	〃	〃	〃	PB	-
2	$Fe(CN)_6^{3-}$	ITO or GC	$Fe(CN)_6^{3-}$	-	-
3	PB	BPG	PB	-	-
	PAn	〃	PAn	-	-
	PP	〃	PP	-	-
	PT	〃	PT	-	-
	PT	ITO	PT	PB	-
4	GaAs	GaAs	$Ru(bpy)_3^{2+}$	-	$Fe^{3+/2+}$
	CdS	CdS	$Ru(bpy)_3^{2+}$+RuO_2+$Fe(CN)_6^{3-/4-}$		-
	〃	〃	$Ru(bpy)_3^{2+}$+RuO_2	-	X^-
	〃	〃	〃 〃	-	H_2O
	〃	〃	Ru-red	-	H_2O
	〃	〃	PB	-	-

APPLICATION OF PHOTOELECTROCHEMISTRY TO MEMORY DEVICE AND DISPLAY DEVICE

K. HASHIMOTO, Z. F. LIU, J. N. YAO and A. FUJISHIMA

Department of Synthetic Chemistry, Faculty of Engineering,
The University of Tokyo,

7-3-1, Hongo, Bunkyo-ku, Tokyo 113, Japan

High-density information storage is one of the key technologies of modern society. The *heat-mode* techniques of the current optical memory, in which only the thermal energy of laser light is utilized in recording process and hence the information is usually stored as a *physical change* of the storage media, are, in principle, subjected to the diffraction limit of light. To achieve higher storage density, a *photon-mode* technique is indispensable. Since the information is stored as a photon-induced *chemical change* of the storage media in this case, the frequency domain of light is also available for increasing storage density of information. In this paper, we present two new types of *photon-mode* storage technique. One is established upon a photochemical and electrochemical hybrid phenomenon found in azobenzene system. The other is based on the photoelectrochromic behavior of amorphous MoO_3 thin films.

(1)Photoelectrochemical Recording System with Azo Compound LB Film.

As is known, there are two typical reversible reactions, i.e., the photochemical trans/cis isomerization and the electrochemical reduction/oxidation, in an azobenzene system. Our basic concept consists of a deliberate organization of these two reversible processes for a *photoelectrochemical* recording of information. The monolayer film of azobenzene derivaitve was deposited onto a transparent SnO_2 glass substrate, the working electrode, in the trans form using the conventional Langmuir-Blodgett method. In the applied potential range no reduction and oxidation peaks were observed in the trans-ABD film, whereas significantly large reduction and oxidation peaks were obtained in the cis-ABD film. The cis-ABD was reduced to hydra-ABD. The hydra-ABD, on the other hand, was found to be exclusively oxidized to the energetically stable trans-ABD because no electrochemical activity was observed after its oxidation in the electro-inactive potential range of trans-ABD.

The thermally stable hydra-ABD is used as the *storage state* for information instead of the thermally unstable cis-ABD. The photoelectrochemical hybrid feature of the present system gives rise to two possible means of high-density storage: either high-resolution *optical writing* or high-resolution *electrochemical writing*.

(2)Photoelectrochromic Recording System using MoO_3 Thin Film.

It is known that some transitional metal oxides such as WO_3 and MoO_3 can be deeply blued by either conventional optical band-gap irradiation (photochromism) or by applying a negative potential in an electrolyte (electrochromism). We found that a prepared MoO_3 amorphous thin film can be converted to a visible light sensitive photochromic film material. Since freshly vacuum evaporated MoO_3 is initially colorless and transparent, it does not show photochromism by the visible light irradiation, yet after being slightly blued by electrochromism in nonaqueous electrolyte, it become sensitive to visible light.

The molybdenum bronze formed is very stable under air, therefore, this material has the potential to be applied to photon-mode memory device. The advantage in using this process is that inexpensively, commonly used semiconductor lasers can be used as a photochromic reaction light source.

"PROTECTED SILICON PHOTOANODE FOR PHOTOELECTROLYSIS"

Yu. Pleskov

A.N. Frumkin Institute of Electrochemistry
Acedemy of Sciences of the USSR
MOSCOW, USSR

To protect the silicon photoanode against photocorrosion in aqueous solutions, thin film of mixed ruthenium and titanium oxide is deposited thereon by pyrolysis of salts solution. The film is fairly transparent for visible light, conductive, and electrocatalytically active in the reaction of electrolysis of halides in aqueous solution. Very high potential (schottky) barrier was estimated at the silicon/the mixed oxide interface. Hence, efficiency of the PEC cell for KCL photoelectrolysis is as high as six to 11 per cent with simulated sun light.

NATURAL PYRITE-BASED ELECTRODES FOR PHOTOELECTROCHEMICAL APPLICATIONS.

V. Antonucci, A. S. Aricò, I. Ielo, E. Modica, G. Candiano, G. Monforte and N. Giordano.

CNR Institute for Transformation and Storage of Energy, Salita S. Lucia sopra Contesse 39, 98126, Pistunina, Messina, Italy

ABSTRACT

Natural pyrite-based photoelectrodes have been manufactured by the screen printing technique. Solid state investigation of the starting material as well as of the thermally activated powders has been carried out by X-ray diffraction (XRD) and Energy-Dispersive X-ray analysis (EDX). Information on the electrochemical reactivity of the surface has been obtained by Cyclic Voltammetry in alkaline solution. The air - treated electrodes have shown to be photoactive when tested as photoanodes in polyiodide - containing photoelectrochemical cells. The maximum obtained efficiency for solar energy conversion was 0.5%. Formation of an heterostructure composed of FeS_2 and Fe_2O_3 phases is considered to be a promising way for the development of low-cost devices in the direct conversion of solar energy.

NON-LINEAR PHENOMENA OBSERVED DURING REDUCTION OF H_2O_2 AT CHALCOPYRITE (PHOTO)CATHODES.

S. CATTARIN[1] and H. TRIBUTSCH[2]

1. IPELP del C.N.R., Corso Stati Uniti 4, 35100 Padova, ITALY
2. Hahn-Meitner-Institut, Glienicker Str. 100, D-1000 Berlin 39, GERMANY

The current-voltage curves of H_2O_2 reduction at $CuFeS_2$ and $CuInSe_2$ cathodes in alkaline medium show a non-monotonous profile. In the potential region with a negative i/U slope, the cell responds to potential changes as an element with negative (differential) resistance: the cathodic current increases when the potential is swept in a positive direction and *viceversa* (1, 2). In the same region, illumination causes anodic photocurrents at p-$CuInSe_2$ and cathodic photocurrents at n-$CuInSe_2$, opposite in sign to what is expected .

XP-spectra of $CuFeS_2$ electrodes taken after polarization experiments show products of surface corrosion and - depending on the potential of emersion - changes in the oxidation state of copper which may be correlated with the shape of the i/U curve (3). It is proposed that the variations of interfacial reactivity observed for the process of H_2O_2 reduction result from the activation of a catalytic reduction pathway on copper sites.

Sustained oscillatory phenomena occur by properly adjusting the polarization conditions: potential oscillations under galvanostatic control and current oscillations under potentiostatic control, in the presence of a suitable external resistance (1, 4). Oscillations can be triggered by adequate potential or light stimuli and may show an all-or-nothing excitation law. A cell including a $CuInSe_2$ electrode may behave as a rudimentary light sensor, responding with current (or potential) pulses to variations of photon flux (4).

An "electrical" analysis of the oscillatory phenomena is proposed, focused on the conditions of polarization control and resulting circuit (in)stability, which accounts qualitatively for the experimental findings.

1. S. Cattarin and H. Tributsch, *J. Electrochem. Soc.*, **137**, 3475 (1990).
2. S. Cattarin, H. Tributsch and U. Stimming, *J. Electrochem. Soc*, submitted.
3. S. Cattarin, S. Fiechter, C. Pettenkofer and H. Tributsch, *J. Electrochem. Soc.*, **137**, 3484 (1990).
4. S. Cattarin and H. Tributsch, *J. Electrochem. Soc.*, submitted.

Biochemical Application of Photoelectrochemistry
---Photokilling of Malignant Cells with Ultrafine TiO_2 Powder---

Akira Fujishima
Department of Synthetic Chemistry, The University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113, Japan

Photo-irradiated TiO_2 particles drive various chemical reactions due to their strong oxidation and reduction ability. This effect is applied in order to kill cancer cells, e.g. HeLa cells, with TiO_2 particles. During 10-min UV irradiation period, HeLa cells were completely killed in the presence of TiO_2 (100μg/cm^3). However, without irradiation these particles showed little cytotoxicity up to 360μg/cm^3. It is concluded that the cells were killed by hydroxyl radicals(OH•) and hydrogen peroxide (H_2O_2) produced from the irradiated TiO_2 particles, and also that the cells were directly oxidized by photogenerated holes in TiO_2.

The distribution of TiO_2 powders in the cells was observed using a transmission electron microscope. The TiO_2 powders existed on the cell membrane, and in the cytoplasm. Thus, the cells were damaged by photoexcited TiO_2 powders not only on the cell membrane, but also inside of cytoplasm.

As in vivo experiment, the antitumor activity of photoexcited TiO_2 particles against the human heart cancer Ycr-1 transplanted into nude mice was also investigated. In the control group, remarkable tumor growth was observed. Likewise, no effect of TiO_2-treated alone on the tumor growth was observed. However, the tumor growth of the light-TiO_2-treated was found to have been significantly suppressed up to 22 days. These observations suggest that the effect of photokilling of cells with TiO_2 particles can be applied for photodynamic therapy.

CARACTERIZATION OF ELECTRODEPOSITED TiO_2 FILMS

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and
G.Razzini
Dipartimento di Chimica Fisica Applicata, Centro di Studio sui
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Stress variations of semiconducting n-TiO_2 films prepared by anodic oxidation in concentrated akaline solutions, are here illustrated and discussed with particular attention to the relation between stress and photoelectrochemical response. By comparing the behaviour of the elecrodeposited TiO_2 samples with that of thermally prepared samples, one may conclude that the specific properties of the former are related to the presence of sodium ions in the oxide reticular lattice.

The role of the surface intermediates in the photoelectrochemical behaviour of anatase and rutile TiO_2

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The photocatalytic degradation of certain categories of organic pollutants as well as photocatalytic synthesis of some organic compounds at semiconductors have become major centers of interest in present day photoelectrochemistry. Such reactions are usually carried out using suspensions (or, sometimes, fixed beds) of semiconductor particles in aqueous solutions irradiated with near-UV light. Because of their relative stability, oxide semiconductors are preferred for this kind of applications and, among them, the most widely used is titanium dioxide. Interestingly, according to numerous reports,(1) activity of the anatase form of TiO_2 towards photodegradation of various pollutants is, in general, much higher than that of rutile.

One of the purposes of this presentation is to emphasize the important differences in the surface behaviour of anatase and rutile. While anatase, in the course of the photo-oxidation process, becomes rapidly covered with at least a monolayer of surface peroxo species, no significant amount of any surface species can be detected at rutile.

This implies that the mechanism of the photooxidation reactions occuring at anatase and rutile must be necessarily different.

The use of polycrystalline TiO_2 electrodes to mimic the behaviour of a suspension of TiO_2 particles allows, in addition to controlling the potential of the illuminated TiO_2, the application of conventional electrochemical techniques capable of detecting reaction intermediates. Such measurements enabled us to show up that very stable (persisting for hours) surface species were formed at illuminated anatase electrodes in alkaline(2), as well as in neutral, solutions. However, even in the case of anatase photoelectrodes, some photo-oxidation reactions (for example, those involving compounds causing photocurrent doubling) occur, in a restricted region of potentials close to the open-circuit potential, in the absence of the surface peroxo species(3).

The comparison of the photoelectrochemical behaviour of anatase and rutile will be further extended to the case of the extensively investigated photo-oxidation reaction - of 4-chloro-phenol.

References

(1) E. Pelizzetti and M. Schiavello, Eds., Photochemical Conversion and Storage of Solar Energy, Kluwer Acad. Publ. Dordrecht, 1991.
(2) M. Ulmann, N.R. de Tacconi, J. Augustynski, J. Phys. Chem., 90, (1986) 6523.
(3) J. Augustynski, Structure and Bonding, 69 (1988) 1-61.

THE PHOTOELECTROCHEMISTRY OF THIN PASSIVE LAYERS. INVESTIGATION OF ANODIC OXIDE FILMS ON TITANIUM METAL

S. Piazza, C. Sunseri and F. Di Quarto

Dipartimento di Ingegneria Chimica dei Processi e dei Materiali, Università di Palermo, Viale delle Scienze, 90128 Palermo (Italy).

Photoelectrochemistry is a powerful tool for the investigation of thin passive layers on metals. In previous work we have studied the photoelectrochemical behaviour of anodic oxides on different metals. Our studies have evidenced the strong influence of the amorphous or strongly disordered structure of the films on their solid state properties (1) and photoelectrochemical behaviour (2).

In spite of the large number of investigations performed on anodic oxide films grown on titanium there is still a lack of knowledge on the influence of the solid state properties of the films on their photoelectrochemical behaviour (3,4). In our opinion, this must be attributed to the complex influence of the preparation method on the properties of the films (5). In fact, depending on the preparation procedure both amorphous and crystalline films can be obtained.

In this work we present a photoelectrochemical study performed on anodic oxide films grown on titanium in 0.5 M H_2SO_4 solution. The passive layers were grown at high growth rate (≥ 2 V/s) up to different thicknesses. Both the photoelectrochemical behaviour and the growth curves suggest that the films undergo an amorphous → crystalline transformation by increasing the thickness.

It will be shown that until about 40 V the films have a highly disordered structure with optical band gap ranging between 3.35 and 3.1 eV, whilst at higher thicknesses the optical band gap measured (3.0 eV) is in agreement with the values reported for crystalline TiO_2.

The photocurrent vs. potential curves show a strong dependence on the wavelength of the inciding light: as a general trend, at long wavelengths the photocharacteristics have a supralinear behaviour, whilst at shorter wavelengths they are sublinear. This finding will be interpreted on the basis of a model which takes into account the disordered nature of the films and the effect of geminate recombination (1,2).

REFERENCES

(1) F. Di Quarto, S. Piazza and C. Sunseri, Electrochim. Acta **35**, 99 (1990).
(2) F. Di Quarto, S. Piazza, R. D'Agostino and C. Sunseri, J. Electroanal Chem. **228**, 119 (1987).
(3) K. Leitner, J.W. Schultze and U. Stimming, J. Electrochem. Soc. **133**, 1561 (1986).
(4) D.J. Blackwood and L.M. Peter, Electrochim. Acta **34**, 1505 (1989).
(5) G. Blondeau, M. Froelicher, M. Froment and A. Hugot-Le Goff, Thin Solid Films **42**, 147 (1977), and references therein.

INVESTIGATION OF OXIDE FILMS ON Ti, Al, Zn, AND Hf

by
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Oxide films moderate interactions with the environment, and may reduce the corrosion rate of substrates by orders of magnitude. The properties of oxide films and the characteristic processes that control their stability, growth and breakdown are major objectives that have practical consequences. Local structural and electronic properties of then films are also important in catalysis, optical films, and microelectronics, and local, in situ measurements have become important for development in these technological areas. One of the techniques which continues to have the potential for major impact is photoelectrochemical microscopy, which will be the focus of this paper.

In crystalline oxide films such as TiO_2 on Ti, the structural and photoelectrochemical properties depend on the growth rate and substrate crystallographical orientation, as has been shown in our laboratory. The oxide structure for slow growth mode (SGM) TiO_2 was found by reflection electron microscopy and grazing incidence angle X-ray scattering (GIXS) to show partial ordering (epitaxy) for some grain orientations. This in turn influences the nature and concentration of defects in the anodic oxide film. The structure of thin films was found to be the rutile form of TiO_2.

Photospectroscopy of the SGM oxide films is nearly identical to that of single crystal rutile as reported by Koffeyberg. Theoretical modeling studies indicate that oxygen vacancies behave as localized states in the bulk, and experimental results of sub-bandgap illumination show that the vacancies alter the local surface recombination rates. The lateral nonuniform distribution of oxygen vacancies causes the work function to vary in the oxide film on different grains, as has been revealed recently by a scanning Kelvin probe. The work function map (determined in air), along with the photoelectrochemical map made of the same surface in acidic aqueous solution, when used together show that the oxide/electrolyte interface controls the photoresponse through surface recombination. More complete analysis has revealed that the photoelectrochemical behavior of the SGM films follow the Gaertner model surprising well, except that the photocurrent depends on film thickness. The latter property is accomodated by modifying the Gaertner model to include the effects of multiple internal reflections.

The final model for the TiO_2/Ti system that emerges is an oxide film which is controlled by the concentration of defects, probably oxygen vacancies, and that the oxide/electrolyte interface is especially important. Other oxide-metal systems such as ZnO/Zn appear to behave like the titanium system. However, wide bandgap materials such as HfO_2 and Al_2O_3, when grown as anodic films on the parent metals, are controlled by the metal/metal oxide interface. Internal photoemission measurements in aqueous solutions reveal that the energy barriers at this interface are substantial and determine the photoresponse. An example of an internal photoemission map of Al_2O_3 on Al will be discussed.

Use of AFM and STM for the Characterization and Modification of Semiconductor Surfaces

Bruce Parkinson
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USA

Researchers are in the beginning stages of utilizing scanning probe microscopies for the characterization of electrode surfaces at an atomic level. In this talk I will review the progress in applying this technology for *in situ* studies of metal and semiconductor electrode surfaces.

The scanning tunneling microscope (STM) and atomic force microscope (AFM) have also proven to be a useful tools for the manipulation of matter on an extremely fine scale. The many new nanolithography techniques which have been developed for this instrument can be loosely divided into several categories based on the method of substrate modification. These categories include: 1. continuous and pulsed high voltage or high current applied to the tip, 2. chemical or electrochemical deposition or etching and 3. mechanical deformation or abrasion via direct tip surface interactions. A review of the literature in these areas will be presented.

Recent results, from my laboratory, on the modification of the surfaces of 2D chalcogenide materials with the STM and AFM will be discussed in more detail. Speculative applications of this technology to photoelectrochemistry will also be discussed.

PHOTOELECTROCHEMICAL METHODS FOR SEMICONDUCTOR DEVICE PROCESSING

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Throughout the evolution of the semiconductor industry, electrochemistry has been an active area of investigation because it is the basis for many processes used in the fabrication of semiconductor devices. Wet etching, electrodeposition, oxide formation, corrosion and defect etching are some of the electrochemical processes.

More recently, photoelectrochemical (PEC) processes have been used to produce semiconductor devices with unique features, such as integral lenses on light emitting diodes, gratings for distributed feedback lasers, and through-wafer via connections for GaAs field effect transistors. These processes usually involve the photo-anodic dissolution of n-type semiconductors where the semiconductor is stable in the dark and easily undergoes photoanodic dissolution to form highly soluble products. In these processes, photo-selectivity and control are excellent because of the simplicity and thermodynamic favorability of the reactions. PEC processes for materials other than stable, n-type semiconductors are highly desirable for spatially selective etching and deposition reactions.

In this paper, PEC processes involving less favorable materials will be examined. The first process is the PEC etching of p-InP. In order to achieve photo-selective etching, conduction band electrons must initiate the semiconductor decomposition. A two step process has been investigated where photo-initiated electrons first reduce the semiconductor surface and form an insoluble product. The second part of the process is to step the potential to a value where valence band holes can oxidize the reduction products without inducing significant anodic decomposition of the bulk material. The effect of potential, temperature, crystal orientation, and competitive reactions will be discussed.

The photoelectrochemical etching of small band gap, less stable, n-type III-V semiconductors is of interest for opto-electronic devices which operate in the infrared region. The photoelectrochemical behavior of GaSb (Eg=0.72 eV) and InAs (Eg=0.36 eV) will be discussed. The anodic decomposition of the semiconductor due to thermally generated holes (dark current) is much greater than with InP or GaAs because of the small gap and the ease of oxidation (2). The conditions for PEC etching will be discussed.

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Photoelectrochemical Etching of Deep, Random, Microstructures onto n-InP *Using White Light*

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High aspect-ration microstructures were observed on n-InP (100) samples that were etched with white light. These random structures present some degree of regularity which increases with etching time. Shape and orientation of the etching profile is determined by the etch-stop planes of the crystal.

The process of PEC etching was monitored in real time with a HeNe laser probe by measuring the light reflected and scattered by the sample. Information on the reaction rate and surface texture compared *well with* values calculated from the photo-current and SEM images. The structures obtained present interesting anti-reflecting properties that may be useful for photo-voltaic applications.

PHOTOELECTROCHEMICAL PROPERTIES OF PHOTOELECTROETCHED n-SILICON

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A new photoelectrochemical etching (PECE) technique for the passivation of surface recombination centers in Si based PEC's and Schottky junctions is presented in this communication.

PECE of silicon carried out in diluted HF under reverse bias strongly modifies its surface properties. After PECE the Si surface became less shiny and darker, the surface roughness increasing with the charge passed. SEM analysis shows the presence of etch pits.

The (photo)current-potential curves of n-Si ($N_D = 10^{15}/cm^3$) in 57% HI is dramatically affected after PECE: the onset potential is shifted by -0.25 V and a high photocurrent (> 35 mA/cm^2 when extrapolated to 100 mW/cm^2) is observed. The charge passed across the interface corresponds mainly to the oxidation of I^-, as indicated bv the darkening of the solution in the vicinity of the electrode. The initial plateau current decreased by only 5% after 45 min. This is in contrast with previous observations of strong photocorrosion of illuminated n-Si/aqueous electrolyte junctions, even in concentrated HI. Chemically etched n-Si exhibits external quantum efficiencies of 60% in 57% HI, while for PECE-Si quantum efficiencies reach 80% over a broad spectral range.

Electroless deposition of Au on n-Si ($N_D = 10^{15}/cm^3$) after chemical etching leads to an enhanced rate of electroless Au plating and improved spectral response of the so formed Schottky junctions.

In order to understand the mechanism of the PECE complementary experiments have been done to characterize the Si surface before and after *PECE*. Chemical composition of the photoelectroetched Si was investigated using infrared multiple internal reflectance and XPS. The cathodic shift of the onset of the photocurrent, the Photoluminescence at low temperature (1.8K) and the photoreflectance results were in favor of the hypothesis that PECE passivated the surface recombination centers and unpinned the Fermi level.

PECE seems to be promising for the treatment of polycrystalline Si. Possible technological applications of PECE will be discussed.

FROM PHOTOCORROSION TO PHOTOELECTROCHEMICAL ETCHING

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In this lecture, a review of the effects of corrosion reactions at illuminated semiconducting electrodes will be given. Deleterious for the duration of PEC solar cells, corrosion reactions can be useful in the preparation of semiconductor surfaces for a variety of applications. Several examples of photoelectrochemical etching procedures with elemental, II-VI and III-V compound semiconducting electrodes will be discussed.

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Abstract for:
NEW TRENDS IN PHOTOELECTROCHEMISTRY,
Altavilla Milicia, Italia

PICOSECOND TIME-RESOLVED MEASUREMENTS AND THEORETICAL CONCEPTS OF CHARGE EXCHANGE BETWEEN SEMICONDUCTORS AND MOLECULES (REDOX IONS).

Photoelectrochemical processes have been investigated vigorously in many laboratories for more than 20 years but there is still very little experimental information available about electron transfer across the interface of such systems. Experimental observations are often rationalized with the help of so called distribution curves for the energy levels of redox ions or molecules. When the photocurrent is big the maximum of the distribution curve is assumed to lie at or above the band edge of the semiconductor electrode. We will show that this notion implies electron transfer on the pico-second time scale. The distribution curves will be related to fundamental theoretical concepts concerning electron transfer reactions. Specific properties of interfacial electron transfer reactions will be outlined. Recent results of time-resolved experiments on electron transfer between molecules and semiconductors will be reported covering the relevant time scales from pico-seconds to seconds. These results will be compared with new experimental information about closely related model systems and with theoretical concepts.

PHOTO-OXIDATION OF ORGANIC COMPOUNDS AT SEMICONDUCTOR-WATER INTERFACE

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Photocatalyzed redox processes occurring at illuminated semiconductor materials (e.g.TiO_2) are finding application in the degradation of a variety of organic compounds, aliphatic and aromatic, of environmental concern.

The improvement of the photocatalytic activity of the catalyst as well as the need of practical immobilization of the photocatalyst require a detailed understanding of the mechanism by which TiO_2 photodegrades pollutant species.

While complete mineralization of these organics to CO_2 and corresponding anions has been demonstrated, active current debate concerns the nature of photoactive species (direct electron transfer to the holes vs. reactions with oxidizing radicals, such as hydroxyl radicals) and, taking OH as oxidant, the site of the reactions (at the catalyst surface vs. in the bulk solution). Some recent results are presented and discussed.

EFFECT OF VISIBLE LIGHT ON HYDROGEN PERMEATION IN METALS

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The influence of light on hydrogen permeation through a thin metallic membrane has been investigated. The measurements have been performed in a modified Devanathan- Stachursky cell where hydrogen is evolved on the inlet (cathodic) side of the membrane and monitored on the outlet (anodic) side of the same membrane.

Visible light dramatically affects the hydrogen permeation current in iron and in AISI 304 stainless steel. Floodlighting the inlet side of metal sheets cathodically polarized at constant current (10 to 200 uA/cm^2) the hydrogen permeation current drops to very low values. This result is interpreted as due to the photodesorption of the hydrogen adsorbed on the metal surface during the discharge process of H$^+$ ions. The same result is obtained in spite of the presence of promoters such as S^{2-} in the electrolyte. Indeed, the light competes with the promoters drastically decreasing the amount of hydrogen adsorbed on the metal surface and consequently the hydrogen absorption into the metal.

It is well known that the hydrogen permeation current is due to the hydrogen electro-oxidation to proton on the anodically polarized side of the membrane surface in the second compartment of the testing cell. When this surface is illuminated, a photocurrent is measured as a result of the hydrogen photo-oxidation. Moreover, the permeation current is decreased likewise to what occurs when the inlet side of the membrane is illuminated. Also this light effect is interpreted as due to a photo-desorption process of the hydrogen atoms which competes with their electrochemical oxidation to protons. So, the hydrogen atoms diffusing in the metal membrane and reaching the outlet side which is anodically polarized and under illumination are oxidized and photo-oxidized to protons. Moreover when the photon intensity is large enough, the photodesorption process may overcome the electrochemical process reducing to zero the permeation current.

These light effects on the permeation current may be utilized for the "in situ" topological investigation of hydrogen diffusing through metals.

MICROWAVE (PHOTO)ELECTROCHEMISTRY : NEW INSIGHT INTO ILLUMINATED INTERFACES

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Microwave (photo)electrochemistry is a contact free experimental technique, based on the measurement of the relative change of microwave power reflected from semiconductor liquid interfaces as a consequence of changes of electrode potential, illumination or time 1-6). It is a technique which, like (photo)electrochemistry, probes the behavior of charge carriers and dipoles in solid/liquid interfaces, but via an independent circuit, which does not involve the RC constants of the electrochemical circuit and certain polarization effects accompanying direct current measurements. A time resolution of at least 30 ps and a sensitivity permitting detection of 10^8 charge carriers are characteristic advantages as well as the possibility of monitoring photoactivated charge carriers which do not reach the external circuit.

In (photo)electrochemistry the expected photocurrent change Δi is typically in a non-linear way dependent on the applied potential change. The reciprocal complex impedance, $1/\Delta Z$, is the variable proportionality factor , which can be separated into a real part ($\Delta\sigma^*$) and an imaginary part ($\Delta\beta^*$). The real part is proportional to the conductivity change across the electrode/electrolyte interface. The imaginary part ($\Delta\beta^*$) is dependent on the dielectric constant (ε_r) and determines the phase shift. It can be used to measure the interfacial capacitance :

$$\frac{\Delta i(V,h\nu,t)}{\Delta V} = \frac{1}{Z(V,h\nu,t)} = B\,\Delta\sigma^*(V,h\nu,t) + i\Delta\beta^*(V,h\nu,t) \qquad (1)$$

The relative microwave power ($\Delta P/P$) reflected from an electrode/electrolyte interface can be considered proportional to the change of the complex propagation constant for microwaves (γ) due to a change of potential, illumination or time. Its real part is proportional to the induced change of conductivity ($\Delta\sigma$) of both charge carriers and dipoles (n_i is concentration of charge carriers of type i; μ_i is their mobility)

$$\Delta\sigma = \sum_i \Delta n_i \mu_i e + \sum_d \Delta\sigma_d \qquad (2)$$

The imaginary part describes the change of the phase factor ($\Delta\beta$) which depends on the change of the dielectric constant (ε_r) responsible for the phase shift. The change of the reflected microwave power as a consequence of an imposed potential change can therefore be written (A = proportionality constant) :

$$\frac{\Delta P(V,h\nu,t)}{\Delta V} = \frac{P}{\Delta V} \{ A\, \Delta\sigma(V,h\nu,t) + i\, \Delta\beta(V,h\nu,t) \} \qquad (3)$$

Although the conductivity change $\Delta\sigma$ (relation (2) and (3)) of microwave conductivity measurements and $\Delta\sigma^*$ of electrochemical measurements (relation (1)) are typically not identical, the analogy between relations (1) and (3) show that similar parameters are accessible by (photo)electrochemical and microwave conductivity measurements. This includes the dunamics of charge carriers and dipoles, photoeffects, flatband and capacitive behaviour and the effect of surface states.

Experience with illuminated semiconductor electrodes (e.g. ZnO, WSe_2, p/n -Si) show that the potential dependent curves obtained for photocurrents and microwave conductivity are typically very different and that the latter provide some important complementary information:

- they measure the integral concentration of photogenerated charge carriers in the semiconductor electrode and not only those entering the external circuit. They detect, during their lifetime, charge carriers, which are finally lost in recombination processes
- they monitor charge carriers jammed towards the interface, when surface recombination and the potential dependent interfacial charge transfer rate is low
- they allow under certain conditions the differentiation between photocurrent limitation by recombination or interfacial charge transfer.
- as in scanning laser photoelectrochemistry, space resolved microwave conductivity measurements are possible and allow identification of inhomogeneities in surface behavior.

Like dynamic photocurrent curves, microwave conductivity curves are, due to the relatively large number of parameters involved, difficult to calculate and have mainly to be explored experimentally or theoretically described with simplified formula.

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SOME BASIC WORKING PRINCIPLES OF HETEROGENEOUS PHOTOCATALYTIC PROCESSES

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The paper tries to outline some principles which are the base for the behaviour of a *heterogeneous photocatalytic process*, performed using irradiated semiconductors.

One key aspect is the charge separation step: the description of this point stems from the theories currently applied in photoelectrochemistry. Other aspects of the photocatalytic behaviour are more physicochemical in nature: also these aspects are briefly outlined.

Case studies are finally presented, in which the photocatalytic mechanism is described taking into account the principles above oulined.

POLYMER-BASED ELECTROCHROMIC DEVICES

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The doping process of conjugated polymers induces evolution of their band electronic structure, causing changes in the polymer's color. The high contrast in color between doped and undoped forms, together with the reversibility of electrochemical doping process, makes conducting polymers attractive as electrochromic materials for display devices. The evolution of the electronic structure and of the optical properties of several conjugated polymers is reviewed. The electrochromic properties of these polymers are also surveyed with particular emphasis on electrochromic efficiency values, response time, switching stability and optical memory, to evaluate the possibility of pratical use of these materials in display devices. In addition the electrochromic performance of conducting polymers is compared to that of other electrochromic materials.

Imaging techniques of passive oxides and metals on semiconductors.

R. Peat, A. J. Kucernak and D. E. Williams

ABSTRACT

Imaging of spatial variability of electrode processes using signals stimulated by a focussed light spot is described. Photocurrent images showing the photoetching of GaAs-GaAlAs layered structures, the space charge distribution around metal particles and the corrosion of high sulphur rich steel are presented as examples of the contrast types that are observed. The theory of contrast in photocurrent images is presented: methods using intensity modulated light are compared with those in which the spot is scanned rapidly without intensity modulation. Effects of variation of intensity, modulation frequency and spot scan speed are calculated; *blurring, streaking and shadowing effects* are explained. The feasibility is assessed, for systems which are not photoactive, of an imaging procedure based upon the small thermal effect induced by the focussed spot on the current for an electrode process.

Effect of Excitation Wavelength on the Photoinduced Electron Transfer of Metalophthalocyanines

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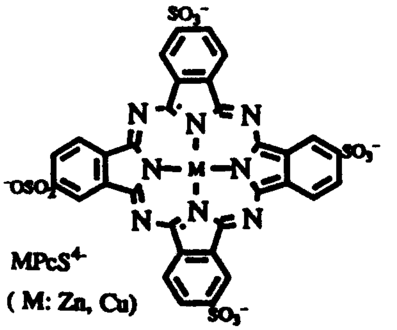
Phthalocyanines are widely used as durable dye-pigments. However, we now wish to report a remarkable effect of wavelength of the irradiating light for the photoreduction of tetrasodium salt of zinc phthalocyanin ($ZnPcS^{4-}$); thus, reddish light to excite its long wavelength absorption is not effective but near UV light to excite its shorter wavelength absorption is effective to induce its reduction in deaerated aqueous solution of triethanolamine (TEOA) as an electron donor.

On steady light irradiation, $ZnPcS^{4-}$ (8×10^{-6} mol dm^{-3}) was irradiated in degassed TEOA (0.8 mol dm^{-3}) aqueous solution with a high pressure mercury lamp through appropriate filters. The irradiation with 365 nm resulted in the decrease of the absorption at 670 nm accompanied by the increase of the absorption at near 580 nm as shown in Fig.1; the quantum yield for photoreduction of $ZnPcS^{4-}$ was 5×10^{-3}; on the contrary, irradiation with 656 nm did not lead to any detectable change at all. Laser flash photolysis of $ZnPcS^{4-}$ with 308 nm produced absorption due to a reduced species (580 nm) as well as $ZnPcS^{4-}$ triplet state (500 nm); however, 670-nm laser did not afford at all the reduced species though giving only $ZnPcS^{4-}$ triplet state.

$CuPcS^{4-}$ behaved in a similar way, however, more efficiently than $ZnPcS^{4-}$.



$MPcS^{4-}$
(M: Zn, Cu)

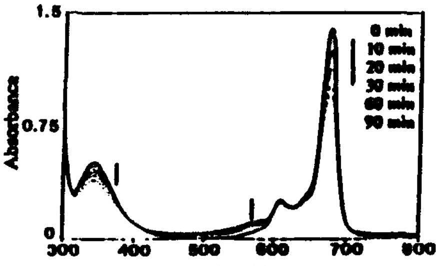


Fig. 1. A spectral change of ZnPcS on 365-nm light irradiation in water in the presence of TEOA (0.8 mol dm^{-3}).

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FUNCTIONALIZED PHOTOELECTROCHEMISTRY

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The photoelectrochemical process is essentially the electron transfer across the solid-solution heterophase interface where either the solid phase, say electrode or the chemical species in the solution in contact with the interface is electronically excited.

At the early stage of its evolution, the photoelectrochemistry has been developing with much concern with the light energy conversion.

On the other hand, the photochemistry itself has been expanding its area of application based on the evolution new interdisciplines between the conventional photochemistry and other disciplines such as the electrochemistry, the biochemistry, surface chemistry, polymer chemistry, solid state physics, imaging science and so on. Accordingly, the results of the growth of the above interdisciplines have given rise to a variety of new functions related to the photoelectrochemistry.

In the course of the photoelectrochemical processes, the various types of energy and information conversion among the optial, electrical, chemical,thermal, mechanical, biological and other signal inputs take place, offering the novel functions such as sensor, display, imaging, recognition, memory and others. Some of these are expected to be applied to the metallurgy, the medical therapy, environmental problem and the synthesis of new materials.

Research trend toward the functionalized photoelectrochemistry reported in the literature is summarized.

THIN-FILM MULTIJUNCTION SOLAR CELL FOR WATER PHOTOELECTROLYSIS.

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Tandem and triple stacks of a-Si:H and a-SiC:H in the typical multiple p-i-n configuration is under development in our laboratories. The a-Si:H and a-SiC:H layers were deposited on SnO2 coated glass by a (DC) glow discharge method .Triple-junction devices,irradiated by a 100 mW/cm2 simulated solar radiation, exhibit open-circuit voltage higher than 2 V and short-circuit current of about 5 mA/cm2; with an overall photovoltaic efficiency exceeding 6% . Such units can sustain water electrolysis in solforic acid solution and therefore it can be used as photoelectrodes in integrated photovoltaic-electrochemical systems. Characterizzation of both electrochemical and photovoltaic properties is in progress.

PHOTOELECTROCHEMICAL CATALYSIS IN SOLUTION BY SMALL SEMICONDUCTOR PARTICLES

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The photocatalytic action of semiconductor particles is due to the reactivity of electrons and holes generated therein by light absorption. The holes oxidize species which cannot directly react with the oxidant present in the solution (usually oxygen) because the activation barrier for this process is too high. For compensation the electrons reduce the oxidant.

In the steady state both reactions occur at equal rate. The quantum efficiency is limited by recombination in the bulk and at the surface. The rate of both processes is affected by the rate of the interfacial redox reactions. Another loss of the yield is caused by the reverse reactions of electrons and holes with the products of oxidation or reduction, respectively.

Models for the kinetics of all the relevant processes in a spherical particle and at its surface are discussed and the conditions for obtaining a high quantum yield are derived. The controlling parameters are the light intensity and the absorption efficiency, the radius of the sphere, the rate constants of the reactions involved, and the diffusion coefficients. The consequences for the photocatalytic oxidation by dissolved dioxygen are discussed in more detail.