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THE MECHANISM OF SPECTRAL SENSITIZATION IN THE LIGHT OF ELECTROCHEMICAL EXPERIMENTS: THE SYSTEM ZINC OXIDE-RHODAMINE B

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The electrochemical technique, in which semiconductors are used as one electrode of an electrochemical cell with sensitizing dyes adsorbing at the semiconductor surface from the electrolyte, is very well suited for a systematic investigation of sensitization reactions. A survey of the information is given which can be derived from already existing experimental data. The results show that both exchange of electrons and energy transfer are possible between excited dye molecules and semiconductors, and that the mechanism of sensitization has to be determined for the particular system involved. The mechanism of spectral sensitization of ZnO by Rhodamine B is studied in some detail. The Rhodamine B-sensitized photocurrent across the ZnO/electrolyte interface is strongly dependent on the pH value of the electrolyte. It is shown that this effect is produced by a pH-dependent double layer and not by a pH-dependent change of an electronic property of Rhodamine B. The potential jump in the double layer cannot influence energy transfer reactions; however, electron transfer is affected. Consequently, excited Rhodamine B at a ZnO-electrolyte interface sensitizes this semiconductor by electron transfer into the conduction band. This conclusion is supported by calculation of the pH-dependence of sensitization.

I. Introduction

Although the process of spectral sensitization of inorganic semiconductors by adsorbed dyes has been the subject of intensive investigation for more than 50 years, its mechanism is still a matter of controversy. Ample experimental evidence for two mechanisms - primary electron transfer and primary energy
(1-5) transfer - has been suggested.[1-5] A decisive interpretation of experimental data in terms of a special mechanism of spectral sensitization has turned out to be extremely difficult. Only recently, experiments in which sensitization of silver bromide could be obtained across isolating molecular layers, could be ex-
(6) plained convincingly in terms of an energy transfer mechanism of sensitization.[6] These experiments, however, do not include the important case where sensitizing molecules are in direct contact with the substrate.

The difficulties met in the studies of the mechanism of spectral sensitization are mainly due to the fact that sensitization effects were usually studied at semiconductor surfaces in contact with a vacuum or a gas. Experimental methods of investigation, applicable to such a system (e.g. surface conductivity, photographic effects) are hardly suitable for the study of heterogeneous photochemical reactions: neither the physical situation in the semiconductor surface (space charge layer, concentration of charge carriers in the surface) can be controlled and varied in a well-defined way, nor can photochemical reaction parameters (molecular environment of photoactive molecules) easily be changed and the turnover of reacting molecules determined.

To obtain the advantage of a more flexible and adequate system for the investigation of the mechanism and the kinetics of spectral sensitization, attempts have been made to study sensitization reactions at surfaces of inorganic semiconductors which are in contact with an electrolyte and used as electrode of

(7-15) an electrochemical cell.[7-15] In the same arrangement, sensitization effects
(16) at organic semiconductors have been investigated.[7,16]

Experimental indications that sensitization effects can also be observed at semiconductor-electrolyte interfaces are very old. As early as 1893 it was
(17) found by Rigollot[17] that copper electrodes, oxidized by glowing, when placed in contact with an electrolyte and "dyed", showed a sensitized photoeffect. It is now difficult to decide whether Rigollot has seen a Bequerel effect which may arise from a semiconductor property of the dye layer and can also be seen
(18) with dye layers, deposited at platinum electrodes,[18] or whether he saw a real sensitization effect which was produced by monomeric dye molecules adsorbed to a semiconducting cuprous oxide layer at his electrodes.

Only in recent times has the electrochemical method become practical for the investigation of spectral sensitization, because only in the last two decades has the electrochemical behaviour of semiconducting electrodes become sufficiently elucidated, and suitable single crystal semiconductors become available for investigations.

The technique of studying sensitization reactions at inorganic semiconductors which are used as one electrode of an electrochemical cell[7-15] turned out to be very effective, mainly for the following reasons:

1) The space charge layer and thus the concentration of carriers in the surface of the semiconductor electrode can be conveniently controlled and varied by means of the electrode potential which can be measured against a reference electrode.

2) Excited dye molecules generate a sensitized photocurrent across the semiconductor-electrolyte interface which is controllable with the electrode potential.

3) Chemical agents can conveniently be added to the electrolyte; they were found to influence the sensitization effect in a specific way.

4) The appearance of sensitized photocurrents across the semiconductor surface is coupled with a chemical turnover of agents which participate in the sensitization reaction. The Faraday law can therefore be used to determine reactants.

5) Various techniques of electrochemical kinetics can be applied to investigate the mechanism of spectral sensitization: dynamic current-voltage characteristics, potential-jump experiments, alternative current experiments (capacity measurements), experiments at rotating disc electrodes (diffusion controlled reactions), change of composition of electrolyte, etc.

Sensitization effects, produced by excited dyes, have been found at various inorganic (p- and n-conducting) semiconductor electrodes (ZnO,[7-12,15] CdS,[14,15]
(19) Cu_2O,[14] GaAs,[14] GaP,[13] SnO_2,[19] SiC[19]). Dyes of very different classes (triphenylmethane, phencarboxonium, cyanine, fluoresceine dyes, dyes of the chlorophyll group) showed sensitizing activity, provided semiconductors with appropriate electronic structure are used as semiconductor electrodes.

In their interaction with semiconductor electrodes, sensitizing dyes have shown a remarkable specificity: excited Rhodamine B, for example, generates electrons in the conduction bands of ZnO and CdS (both n-type semiconductors), thus giving rise to sensitized anodic photocurrents, when a positive potential is applied to the electrode. With GaP or Cu_2O (p-type) as electrodes, the same dye generates holes in the valence-band of the semiconductor, thus producing a cathodic sensitized photocurrent, when a negative potential is applied to the electrode. Similarly, pseudo-isocyanine aggregates, which show a very narrow characteristic polymer band in their spectrum, generate

electrons in the conduction band of ZnO and holes in the valence band of GaP. Methylene blue, which generates holes in p-GaP, however, does not show noticeable sensitization of ZnO. On the other hand, molecules of the chlorophyll group, which generate electrons in the conduction band of ZnO, do not show sensitization of p-GaP.

Although excited dye molecules at semiconductor electrodes sensitize anodic or cathodic electronic photocurrents across the semiconductor-electrolyte interface, and although these sensitized photocurrents reflect the oxidation or reduction of some participants of the sensitization reaction, this does not prove a sensitization by electron transfer. In principle, both sensitization by electron transfer and by energy transfer to suitable acceptors in the semiconductor surface can generate a photocurrent across an electrode surface. This is shown in Figures 1 and 2 for both p- and n-conducting semiconductor electrodes.

If the process of sensitization occurs by exchange of electrons between one of the electron levels of the excited dye molecules and one of the energy bands of the semiconductor (electron injection into conduction band or hole injection into valence band) (Fig. 1), there has to be an energetic correlation between energy bands of the semiconductor and electronic levels of the excited molecule. During the process of sensitization, the sensitizing dye becomes oxidized or reduced. In the case of a primary energy transfer by dipole-dipole, dipole-quadrupole or exchange-interaction, a correlation of energy levels of the dye and the semiconductor is not needed. However, suitable energy acceptors have to be present within the semiconductor surface. Since in the investigated cases the transferred energy is usually smaller than the energy gap between valence band and conduction band of the semiconductor, the energy

acceptors will constitute irregularities or impurities in the crystal lattice or surface states. Also in the case of a primary energy transfer a sensitized photocurrent across the semiconductor surface can be generated, provided holes (or electrons) which are produced at discrete levels within the energy gap can reach the electrode surface (Fig. 2), and initiate a suitable electrochemical reaction which enables the transition from electronic into ionic conduction (e.g. oxidation or reduction of the sensitizing dye).

The electrochemical technique offers various experiments to distinguish between sensitization by electron transfer or by energy transfer. In most cases which have been investigated up to now, experiments support a sensitization mechanism by direct injection of electrons or holes into the conduction or valence band of the semiconductor electrode.[10,13] However, in a few cases, strong evidence for the occurrence of energy transfer reactions from excited dyes to the semiconductor has also been found.[13]

Among others, the following experimental evidence can be cited in support of a mechanism of spectral sensitization by electron transfer:

a) Reactions of sensitizing dyes with redox agents. Redox agents which are known to reduce excited sensitizing molecules in homogeneous solution, or at least form complexes with them, remarkably increase electron liberation in an n-type semiconductor electrode (ZnO), suppress the consumption of the sensitizing dye (e.g. chlorophyll in the presence of hydroquinone[15]), and get oxidized themselves. This behaviour can only be explained by a reaction in which the sensitizing dye exchanges electrons with both semiconductor and reducing agent.

b) Comparison of quantum efficiency of spectral sensitization and of the semiconductor bulk photoeffect. The quantum efficiency for charge separation after photon absorption in p-GaP is only 1% (due to surface recombination of

electron hole pairs). The quantum efficiency of spectral sensitization (e.g. Rhodamine B), however, reaches values of approximately 30%.[13] Since energy transfer would generate electron hole pairs in the same way as photon absorption, this difference in quantum efficiency is very difficult to understand. It can, however, be easily understood if holes are injected by Rhodamine B, since there are no surplus electrons in p-GaP to recombine with them.

c) Kinetics of impurity-level photocurrents. If sensitization would occur by energy transfer, the transport of holes or electrons over impurity levels and their electrochemical reactions at the semiconductor surface would enter as rate-limiting steps in the kinetics of sensitized electrode photocurrents (Fig. 2). The kinetics of impurity photocurrents can be studied independently in the absence of sensitizing dye when the semiconductor is illuminated beyond the absorption edge in the tail of absorption. It does not show any similarity to that of sensitized photocurrents. It is especially remarkable that sensitized photocurrents (e.g. Rhodamine B, chlorophyll a at ZnO, and Rhodamine B at GaP) reach a limiting, light-dependent saturation value at very low electrode potentials, whereas impurity level photocurrents strongly increase with the applied potential over a large range of potential. The kinetics of sensitized photocurrents is, however, easily explainable in terms of a sensitization by electron or hole transfer. On the other hand, there are also clear indications that energy transfer reactions between adsorbed dyes and a semiconductor are possible under favorable conditions. This conclusion is derived from experiments with gallium phosphide electrodes to which dyes like Rhodamine B, rose bengale or crystal violet were adsorbed.[13]

It has been observed that the spectra of sensitized photocurrents, which have been found to be generated by hole injection from the adsorbed dyes into

the valence band of the semiconductor, were cut off in the spectral region of the edge of the absorption of the semiconductor. The only possible explanation for the cut-off of a part of the sensitization band was the action of energy transfer reactions from the thermally non-equilibrated excited molecules to acceptor levels in the semiconductor which begin to reach a high density near the absorption edge. In contrast to the hole injection, the quantum efficiency for charge liberation and thus generation of sensitized photocurrents by energy transfer remained low because of the high recombination probability for electron hole pairs in the electrode surface.

Thus, the experimental evidence shows that both sensitization mechanisms, electron (or hole) transfer and energy transfer are possible. In the case of an electron exchange, an energetical correlation between the levels of the excited dyes and the energy bands of the semiconductors must exist; in the case of energy transfer reactions, suitable acceptor levels in sufficiently high density have to be present in the semiconductor surface.

As indicated by the experiments with GaP electrodes, a high probability of energy transfer is not sufficient for a high quantum efficiency of sensitization by energy transfer; it is also necessary that one of the levels of the acceptor belongs to an energy band and that the probability for a recombination of electron hole pairs is low.

In the case of sensitization by electron or hole injection, it has been found that a quantum efficiency of more than ten percent can be reached under favorable conditions (hole injection in the presence of oxidizing agents, electron injection in the presence of reducing agents). In the absence of reducing agents, the efficiency of sensitization reaches values in the order of a few percent. It is clear that these values of quantum efficiency are average values. Recent experiments with chlorophyll molecules

adsorbed to semiconductor electrolyte interfaces have shown that adsorbed molecules are distributed over a variety of adsorption sites with different probability for sensitization and that a portion of molecules might be adsorbed at such unfavorable sites that they practically do not participate at all in sensitization reactions.[15] Therefore, sensitization effects should have average quantum efficiencies of less than one, even under very favorable conditions (in the presence of suitable redox agents, optimal realizable surface conditions). (See, however, ref. 12.)

The suitability of electrochemical measurements for the determination of the mechanism of spectral sensitization for individual semiconductor/dye systems should be demonstrated here for the case of Rhodamine B adsorbed at ZnO, a system which has already received considerable attention.[10,12]

II. Experimental Section

As semiconductors, plate-shaped ZnO single crystals, obtained from the 3-M Company, were used. The preparation of the crystals and the electrochemical cell arrangement which allowed the crystal to rotate to control the diffusion of dye molecules to the surface of the electrode and of reaction products away from the surface (rotating disc electrode) have been described elsewhere.[10] A simple scheme of the arrangement in shown in Fig. 3. The electrode surface was prepared by grinding, and was subsequently etched in the electrolyte used. Both polar surfaces, 0001 and $000\bar{1}$, were used in the experiments and no qualitative differences were found. In the experiments, the electrode surface was illuminated across the rotating semiconductor electrode. The electrode potential was controlled against a 1 n Kalomel electrode (not depicted in

Fig. 3). As electrolyte, 1 M KCl was used. The pH of the electrolyte was adjusted by addition of small quantities of acid (HCl) or base (KOH). The electrolyte was flushed with nitrogen.

Absorption and fluorescence measurements of Rhodamine B have been performed in the same electrolyte as used for the electrochemical experiments (aqueous 1 M KCl).

III. Measurements

When Rhodamine B is excited at the surface of a ZnO single crystal electrode (positive electrode potential), anodic photocurrents are sensitized across the electrode surface. The photocurrents reach a maximum at Rhodamine concentration of approximately 10^{-3} M in the electrolyte.[10] The analysis of the spectrum of sensitized photocurrents shows that both Rhodamine B monomers and dimers contribute to the photocurrent. At a Rhodamine B concentration of 10^{-6} M in the electrolyte (when only a very small fraction of the electrode surface is covered by adsorbed Rhodamine B) the sensitization spectrum corresponds to that of Rhodamine B monomers. The maximum of the Rhodamine B sensitization, however, is shifted towards longer wavelengths, when compared with the absorption peak of Rhodamine B in the electrolyte (Fig. 4). This allows the conclusion that photocurrents are sensitized by adsorbed dye molecules only. This conclusion is supported by the observation that addition of methanol to the aqueous electrolyte (which increases solubility), effectively decreases Rhodamine B-sensitized photocurrents. It is also supported by the observation that addition of salt (KCl) to the electrolyte increases sensitization.

The production of a sensitized anodic photocurrent is accompanied by the oxidation of the sensitizing Rhodamine B molecule.[9,12] This conclusion is supported by quantitative measurements of the bleaching of Rhodamine B in the electrolyte, by studies of the kinetic behavior of sensitized photocurrents after onset of illumination, and by the observation of diffusion-limited photocurrents at high light intensities (experiments at rotating disc electrodes). The consumption of the dye during the sensitization reaction can also be observed visually at the semiconductor surface after longer periods of photocurrent generation by excited Rhodamine B. In illuminated areas of the electrode surface a red dyed layer of reaction products is deposited.

Especially remarkable is a strong dependence of the Rhodamine B-sensitized photocurrent on the pH of the electrolyte. With increasing pH value, the photocurrent decreases between pH 2 and pH 10 by two orders of magnitude (Fig. 5). The dependence of the injected photocurrents follows an exponential law. When allythiourea is added to the electrolyte, the photocurrents' increase, however, maintain their logarithmic pH-dependence. When the electrode surface is not renewed with every change of the pH of the electrolyte (renewal made before every measurement of Figure 5), but the pH gradually changes by addition of acid or base, the pH dependence of sensitized photocurrents shows a hysteresis. When the experiment starts with an alkaline electrolyte and gradually acid is added, the value of sensitized photocurrents does not follow the logarithmic line, but a loop below this line. Similarly, when an acidified electrolyte is slowly neutralized, the values follow a loop above the line. Renewal of the surface brings the values of the sensitized photocurrents back to the logarithmic line.

The observation of a hysteresis of the pH dependence of Rhodamine B-sensitized photocurrents clearly indicates that a pH-dependent double layer at the ZnO surface is involved in the sensitization reaction. It is known
(20,21) from capacity measurements[20,21] that this pH-dependent double layer actually exists, and, when produced at high or low pH, equilibrates only very slowly at neutral pH.

To get further indications of whether the pH dependence is caused by a pH-dependent property of the semiconductor surface or of a property of the dye, the pH dependence of the energy transfer property of Rhodamine B was determined. According to well known relations on energy transfer reactions, this examination requires the measurement of the pH dependence of the Rhodamine B absorption, fluorescence, concentration-dependence of fluorescence and dimerization. It was found that the absorption spectrum of Rhodamine B is practically independent of pH between pH 3 and 12. Towards lower pH the absorption slowly decreases because of increasing protonation and bleaching of Rhodamine B. A similar relative independence of pH was found for the intensity and the spectral distribution of the fluorescence in a wide range of concentration (Fig. 6). These results imply the conclusion that a pH-dependent property of Rhodamine B in its ground state or excited state cannot account for the observed pH dependence of Rhodamine B-sensitized photocurrents at ZnO electrodes.

Discussion

Since absorption, fluorescence, and concentration quenching of fluorescence (in part caused by the formation of non-fluorescing dimers) is constant

between pH 3 and pH 10, it can be concluded that the energy transfer capacity of excited Rhodamine B molecules itself is not dependent on the proton concentration in this range. Therefore, the strong pH dependence of Rhodamine B-sensitized photocurrents has to be caused by a pH-dependent property of the ZnO surface.

From other investigations,[20,21] it is known that there is actually a surface parameter of a ZnO electrode which is strongly dependent on the pH value of the electrolyte; it is a pH-dependent double layer which is produced by an exchange of H^+ and OH^- ions between the ZnO surface and the electrolyte. The dependence of the double layer (Helmholtz layer) on the pH can be obtained by determining the flatband potential (electrode potential, at which the space charge layer in the electrode surface vanishes) by means of capacity measurements.

(22) According to Lohman,[22] the potential drop in the double layer of ZnO is linearly dependent on the pH of the electrolyte. A relation for the potential drop in the Helmholtz layer has been derived, and was found to be very well in accordance with experimental data:

$$\Delta\Psi_H = \text{const} - \frac{2{,}3\ RT}{F}\ pH \qquad (1)$$

Since the pH-dependent double layer appears to be the only plausible reason for the observed strong pH dependence of Rhodamine B-sensitized photocurrents, an important conclusion for the mechanism of sensitization can be drawn: A gradual change of sensitized photocurrents with pH over more than two orders of magnitude cannot be interpreted with an energy transfer mechanism of spectral sensitization. A potential drop in the Helmholtz layer cannot influence

energy transfer; and secondary phenomena like changes in the refraction index or the adsorption state could not account for the magnitude of the effect.

An electron transfer mechanism of spectral sensitization, on the other hand, is completely consistent with the observed pH dependence of spectral sensitization. This will be shown by the following calculation:

The calculation of the transfer of an electron from an excited molecule to an electrode may be performed along similar lines of thought as the
(22-24) electron transfer between ground state molecules in solution[22,23] and at electrodes.[24]

(25) In analogy to electron transfer reactions from ground state molecules,[25] several theoretical treatments are, in principle, applicable to sensitization reactions by electron transfer:

a) A calculation can be based on the theory of absolute rates, and pro-
(26) cedures of thermodynamics and statistical mechanics may be applied.[22,26] Contributions of quantum mechanical interactions during the electron transfer reaction may be introduced as corrections into the activation energy of the activated complexes. This treatment is mainly applicable to electron transfer reactions with strong electronic interaction of the reactants (adiabatic electron transfer), and thus high electron transfer probability.

b) A quantum mechanical approach can be made which is mainly applicable to electron transfer reactions with weaker electronic interaction between reactants (non-adiabatic electron transfer) and uses perturbation theory for the calculation of electron transfer rates.[23] When simplified and restricted to appropriate cases, the results of the perturbation calculations can be shown to lead to analogous relations like the thermodynamical-statistical approach, which is more easily evaluated.[25] For both adiabatic and non-adiabatic electron transfer reactions,the electronic energy in the activated

complex is not as high as the classical potential energy barrier. Hence, electron transfer is a quantum mechanical tunneling process, in which the electron passes through the potential barrier rather than over it. This situation has led to attempts to calculate transmission coefficients by another approach, namely

(27) c) In terms of the penetration of the potential barrier by a plane wave[27] (tunneling coefficients). (This approach has also already been used for the calculation of sensitization by electron transfer.) However, the height and shape of the energy barrier and the total energy of the electron, which are needed for the calculation of tunneling, are difficult quantities to estimate reliably. Besides, this approach does not permit one to take account of possible spin- or symmetry-forbidden transitions.

Conventional time-dependent perturbation methods are more realistic, and a thermodynamical-statistical approach (corrected for quantum mechanical interactions) is easier to handle. This latter approach (a), which should be applied here, is based on the assumption that the theory of absolute rates is applicable and that rate constants may be written as:

$$k = \kappa Z \exp\left(\frac{-\Delta G^{\ddagger}}{RT}\right) = k_o \exp\left(\frac{-\Delta G^{\ddagger}}{RT}\right) \qquad (2)$$

(κ = transmission coefficient; $\kappa \approx 1$ = adiabatic electron transfer; $\kappa << 1$ = non-adiabatic electron transfer; Z = collision frequency)

Consequently, the photocurrent sensitized by transfer of electrons from excited Rhodamine B into a ZnO electrode at sufficiently high anodic potential (sensitized photocurrent is quantum-limited) can be written as:

$$j = k D_a^* \qquad (3)$$

(D_a^* = concentration of adsorbed dye molecules in their excited state)

A quantitative calculation of electron transfer is very complicated, as the involved free energy of activation is composed of a series of contributing free energy changes which arise from several mechanisms of interaction:

$$G^{\ddagger} = \sum_{i=1}^{n} G_i^{\ddagger} \tag{4}$$

An important factor in the activation energy of an electron transfer reaction in solution and at electrode/electrolyte interfaces is the state of solvatation of the reactants. Outer-sphere activated complexes (inner coordination shells of reactants left intact as to number and kind of ligands, however, usually distorted) or inner-sphere complexes (inner shell ligand replaced) may be formed during electron transfer, and the corresponding free energies of rearrangement will contribute to the energy of activation. Further contributions arise from the free energy change due to coulombic interaction of reactants at the nuclear configuration of the collision complex, from quantum mechanical exchange interactions and from a change of entropy due to change of electronic quantum numbers during electron transfer. In an electron transfer reaction at an electrode surface, additional contributions to the free energy of activation are essential: free energy of adsorption, free energy changes due to image forces and polarization, and especially, potential gradients in the double layer (Helmholtz layer) at the electrode surface.

In the present study of the influence of a pH-dependent double layer on sensitized electron transfer, only the latter contribution needs to be considered explicitly: This double layer may be looked upon as an inner ligand layer of the ZnO electrode which has to be surmounted during the electron transfer reaction. Consequently, the pH-dependent potential jump (1) in this layer has to be considered in the free energy of activation:

$$\Delta G^{\ddagger} \longrightarrow \Delta G_o^{\ddagger} + \alpha \cdot F \cdot \Delta\Psi_H \tag{5}$$

In this relation, α is a factor ($0 < \alpha \leqslant 1$), dependent on the shape of the activation barrier, which determines the fraction of the potential drop which actually contributes to the activation energy (Fig. 7). An influence of the pH on other parameters which contribute to the free energy of activation is not evident and will be neglected here. The sensitized photocurrent may thus be written as

$$j = k_o \, e^{-\frac{1}{RT}(\Delta G_o^{\ddagger} + \alpha F \Delta\Psi_H)}$$

and with relation (1) for the potential drop in the double layer, after writing the logarithm:

$$\log j = -\alpha(pH) - \frac{\Delta G_o^{\ddagger}}{2{,}3\ RT} + \frac{const}{2{,}3\ RT} + \log k_o D_a^{*}$$

$$\log j = -\alpha(pH) + i_o \{\Delta G_o^{\ddagger}, k_o, I_L\} \tag{6}$$

with $\alpha \approx 0.21$, relation (6) exactly describes the observed pH dependence of Rhodamine B-sensitized photocurrents (Fig. 5). The parallel shift of the photocurrent dependence, caused by the presence of a suitable reducing agent (allyl-thiourea) in the electrolyte is also described by relation (6) and confirms the assumed mechanism of supersensitization by these agents:[10] reducing agents might react with excited molecules by forming complexes or by directly reducing them, thus decreasing the activation energy ($\Delta G_o^{\ddagger}$) for electron transfer or delaying (or preventing) the recombination of the excited electron (increase of total collision number [k_o]).

This calculation of the pH dependence of Rhodamine B-sensitized photocurrents at a ZnO electrode confirms our conclusion that Rhodamine B sensitizes ZnO by transfer of an electron from its excited level into the conduction band of the semiconductor. This mechanism of spectral sensitization is very well in accordance with other experimental results previously mentioned, and is consistent with conclusions from other investigators.[12] In addition, the small factor of α obtained means that electron transfer occurs only across a fraction of the pH-dependent double layer, indicating that the Rhodamine B wave function is in close contact with the electrode surface, and electron transfer occurs from within the Helmholtz layer.

The results which have been obtained for a semiconductor which is in contact with an electrolyte cannot easily be generalized and applied to sensitization effects at semiconductor gas interfaces, at which many of the experiments in the past have been performed. At least with respect to the conditions existing in photographic emulsions, however, a semiconductor/electrolyte interface seems to be a more realistic system to study sensitization effects than a clean semiconductor surface in a high vacuum; and it is evident that the electrochemical technique,with its flexibility with respect to kinetic studies and the possibility to change reaction parameters easily and in a controlled way, will allow a systematic investigation and elucidation of the mechanism of spectral sensitization.

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Figure Legends

Fig. 1. Energy-potential scheme for semiconductor and adsorbed dye during sensitization by electron transfer. (D^* = excited dye; CB = conduction band; VB = valence band; E_F = Fermi level; R = reducing agent; O = oxidizing agent).

a) Sensitization by electron injection at n-type semiconductor.

b) Sensitization by hole injection at p-type semiconductor.

Fig. 2. Energy-potential scheme for semiconductor and adsorbed dye during sensitization by energy transfer.

a) Sensitization of anodic photocurrent at n-type semiconductor.

b) Sensitization of cathodic photocurrent at p-type semiconductor.

Fig. 3. Scheme of electrochemical cell (rotating electrode arrangement) for the investigation of spectral sensitization. 1 = rotating electrode support; 2 = semiconductor single crystal electrode; 3 = electrode surface to which dye molecules adsorb; 4 = electrolyte in which sensitizing dyes are dissolved; 5 = Pt-counter electrode; 6 = metal contact for semiconductor electrode; 7 = gliding electric contact.

Fig. 4. Comparison of absorption spectrum (dotted line) and spectrum of sensitized photocurrents (at ZnO) of Rhodamine B. Absorption spectrum taken in aqueous 1 M KCl, 10^{-5} M Rhodamine B. Sensitization spectrum: electrolyte: 1 M KCl, 10^{-6} M Rhodamine B.

Fig. 5. Dependence of Rhodamine B-sensitized photocurrent at a ZnO electrode on the pH of the electrolyte. Electrode potential: +0.5 Volt; electrolyte: 1 M KCl. Open squares, 10^{-4} M Rhodamine B; open circles, 10^{-4} M Rhodamine B plus 10^{-1} M allylthiourea.

Fig. 6. Dependence of Rhodamine B fluorescence intensity (at 582 nm) on the pH of the solution at various concentrations. Solution: 1 M KCl in H_2O.

Fig. 7. Influence of a potential jump, $\Delta\Psi_H$, in the double layer on the free energy of activation ($\Delta G_o^{\ddagger}$) for the transfer of an electron from an excited level of a dye (D*) into the conduction band of a semiconductor (ZnO).

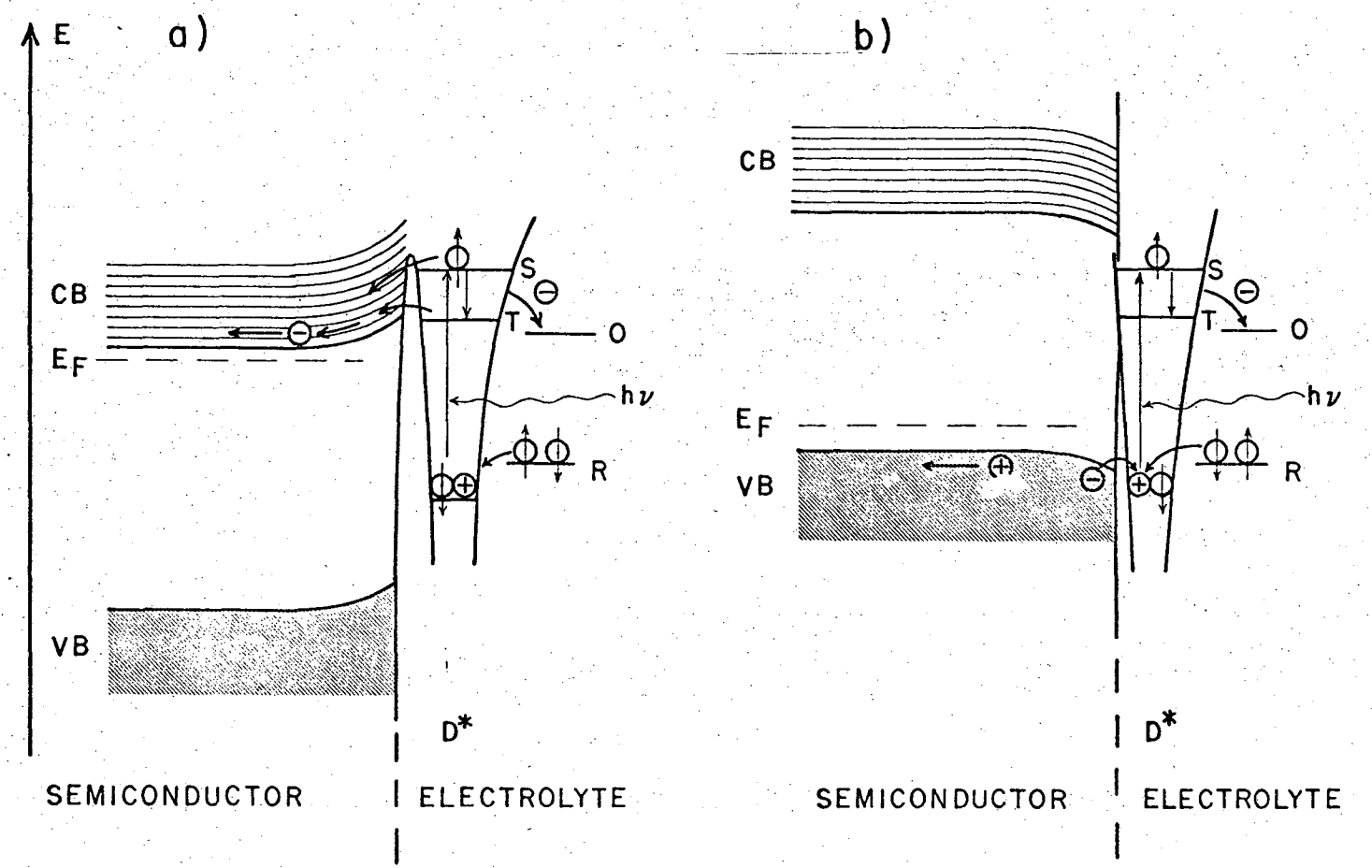

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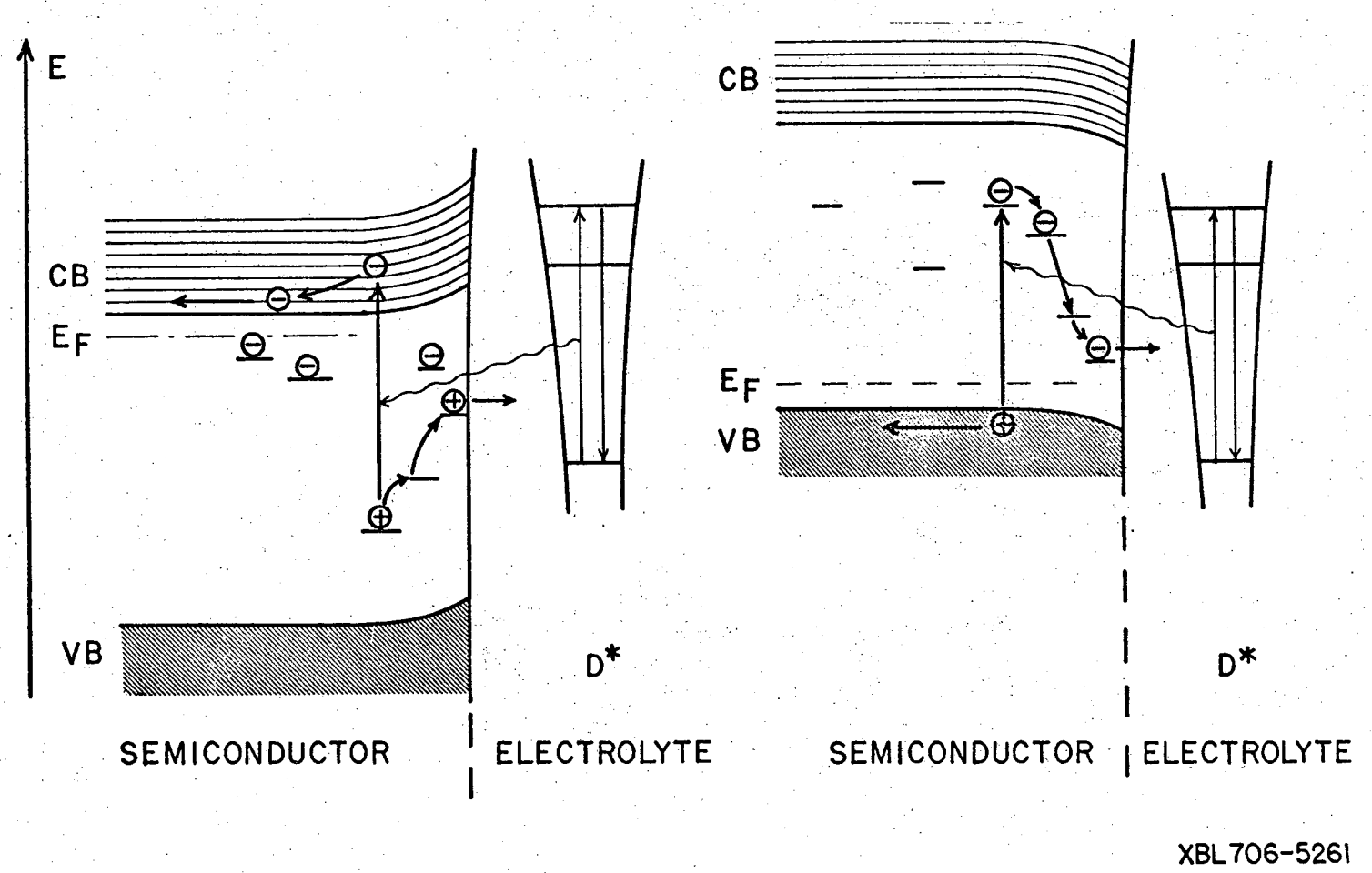
Fig. 1


E
CB
E_F
VB
D*
SEMICONDUCTOR
ELECTROLYTE
CB
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D*
SEMICONDUCTOR
ELECTROLYTE
XBL706-5261

Fig. 2

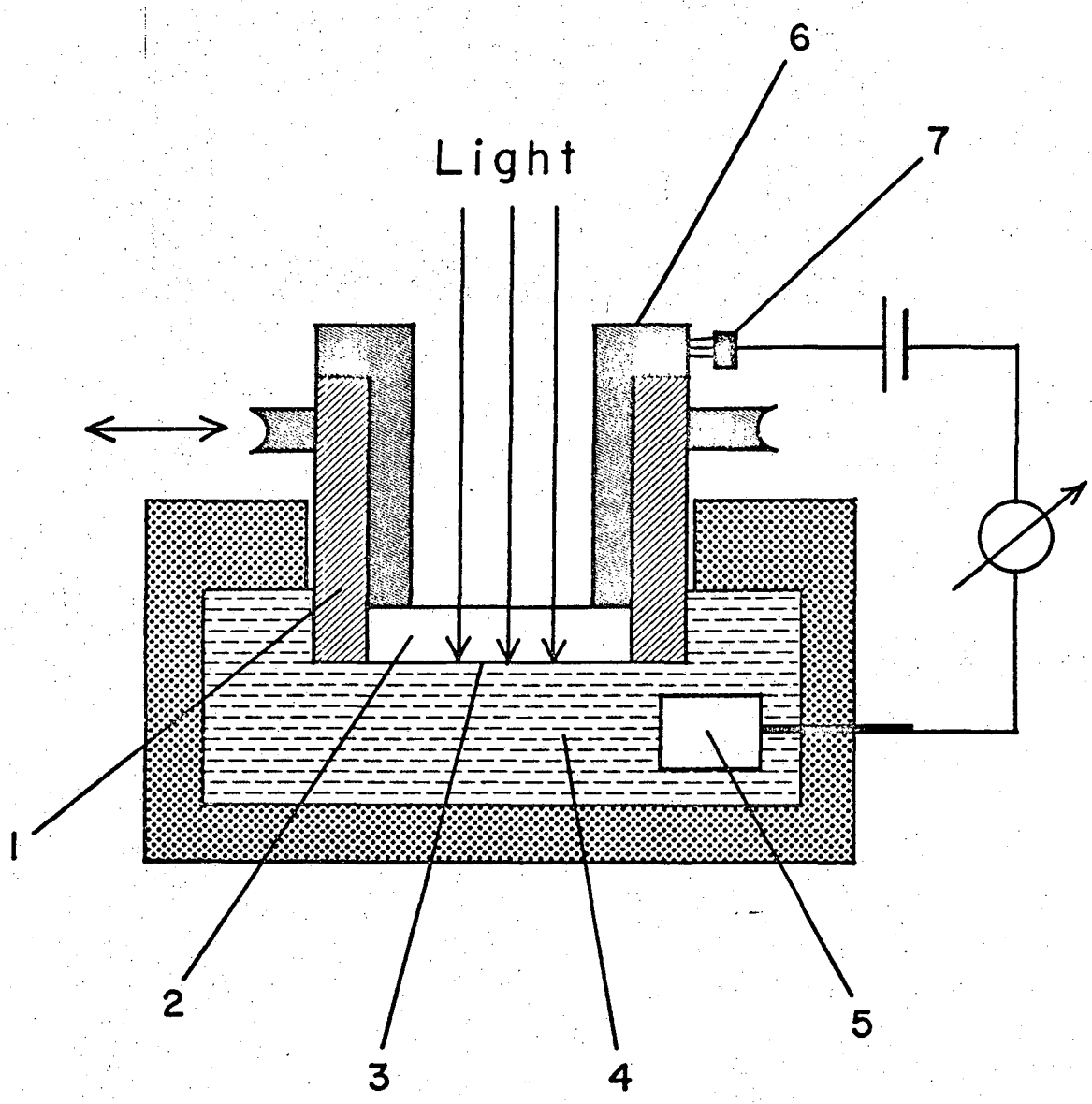

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Fig. 3

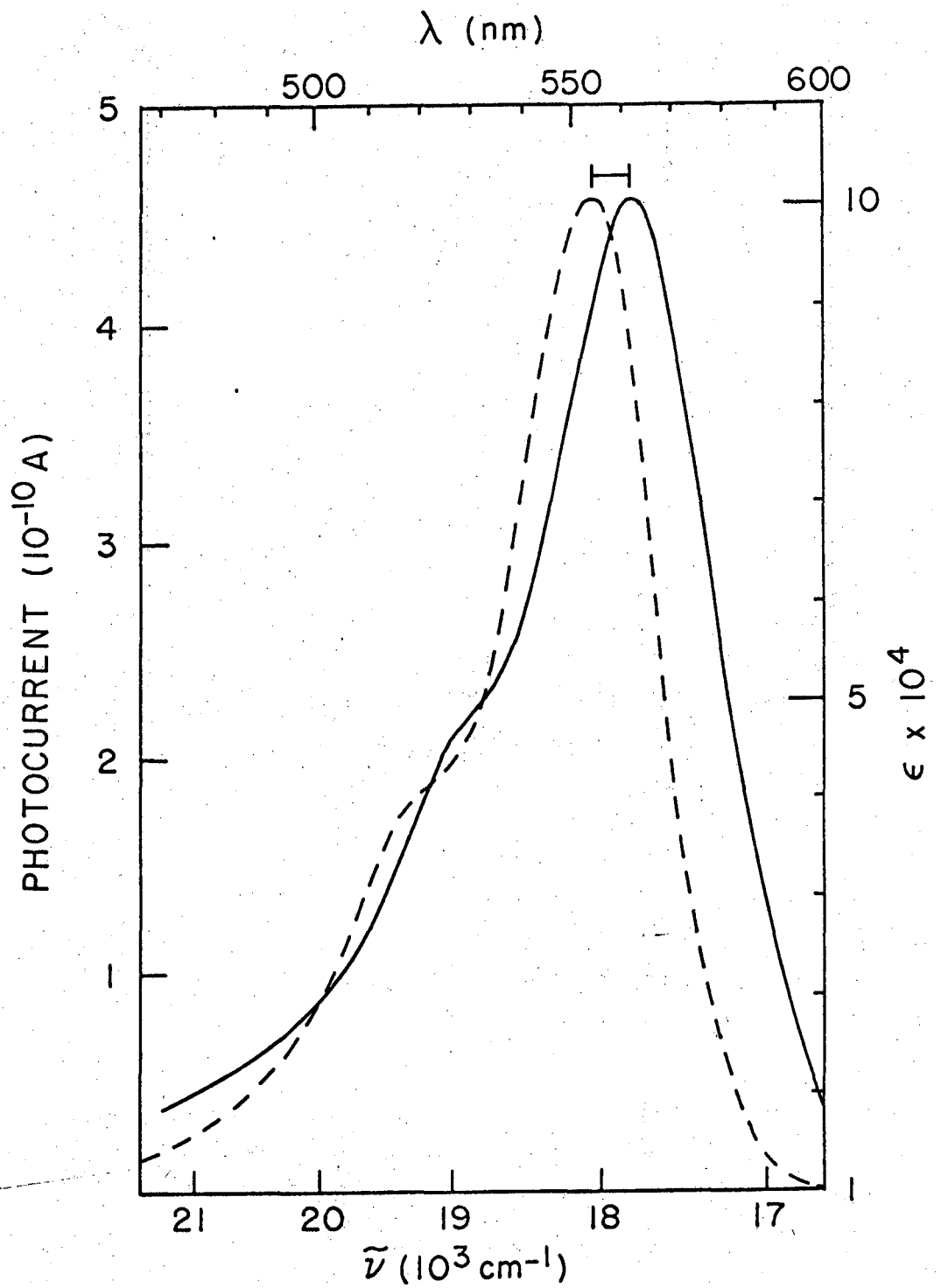

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Fig. 4

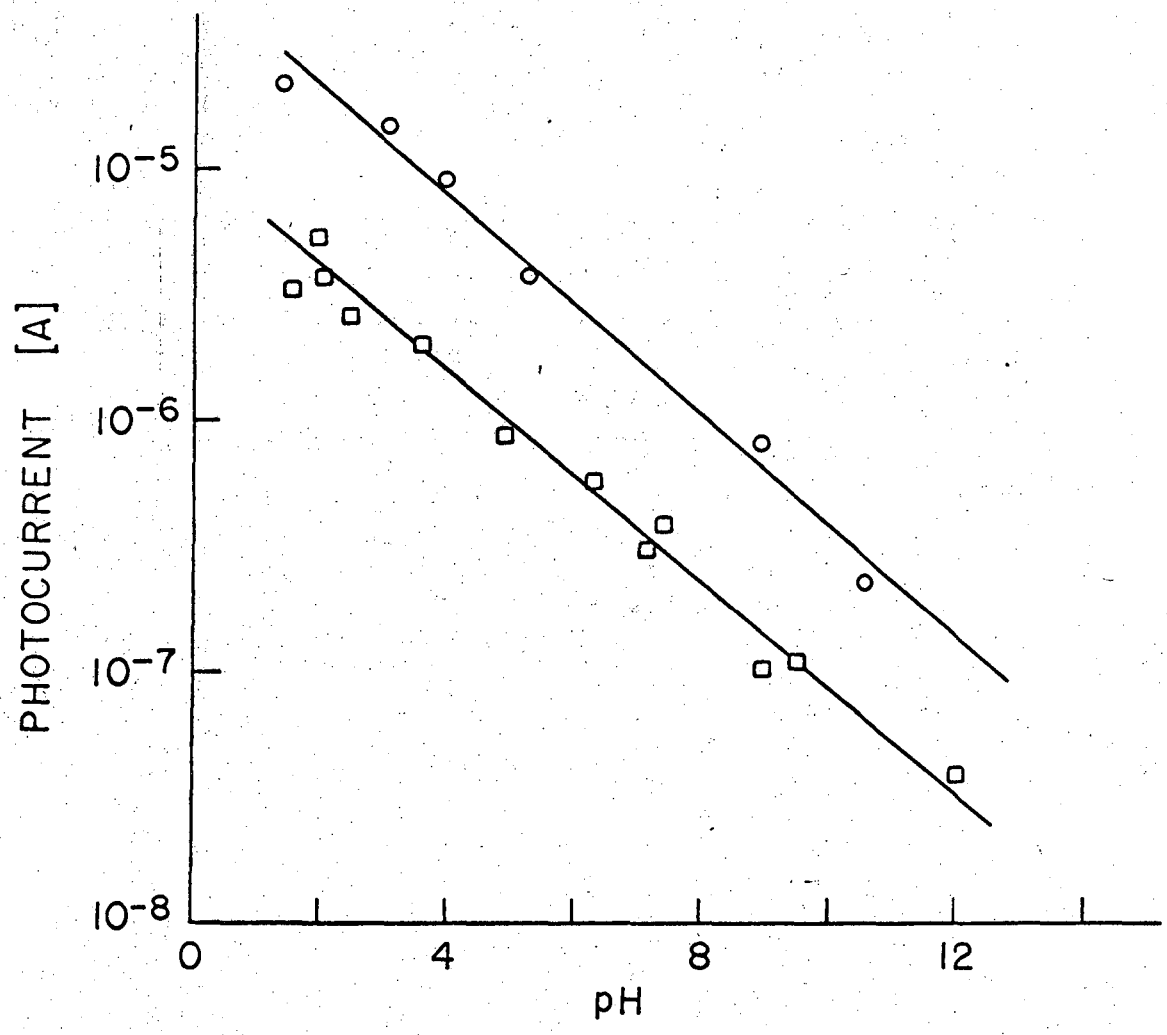

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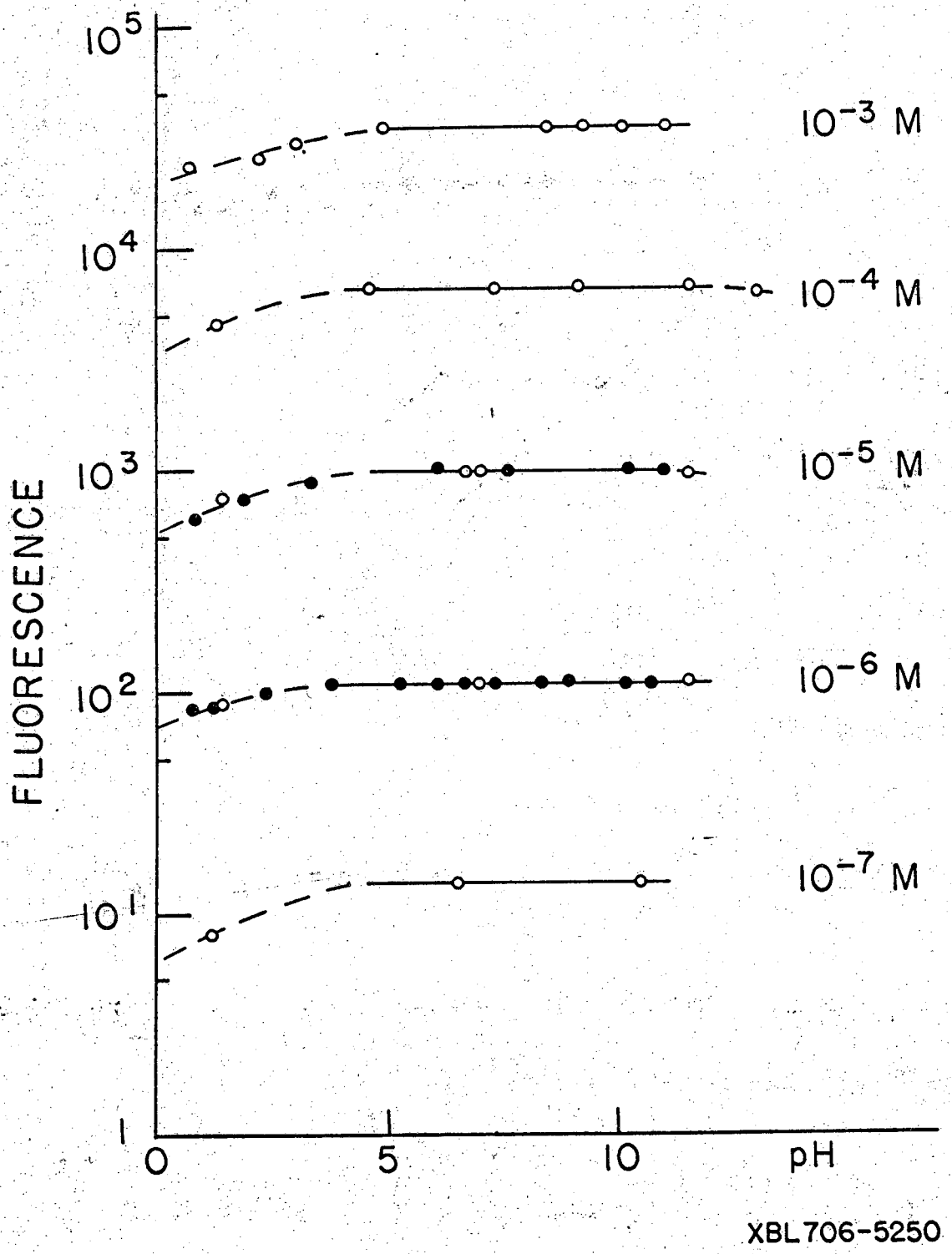
Fig. 5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10^3
10^2
10^1
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10
pH
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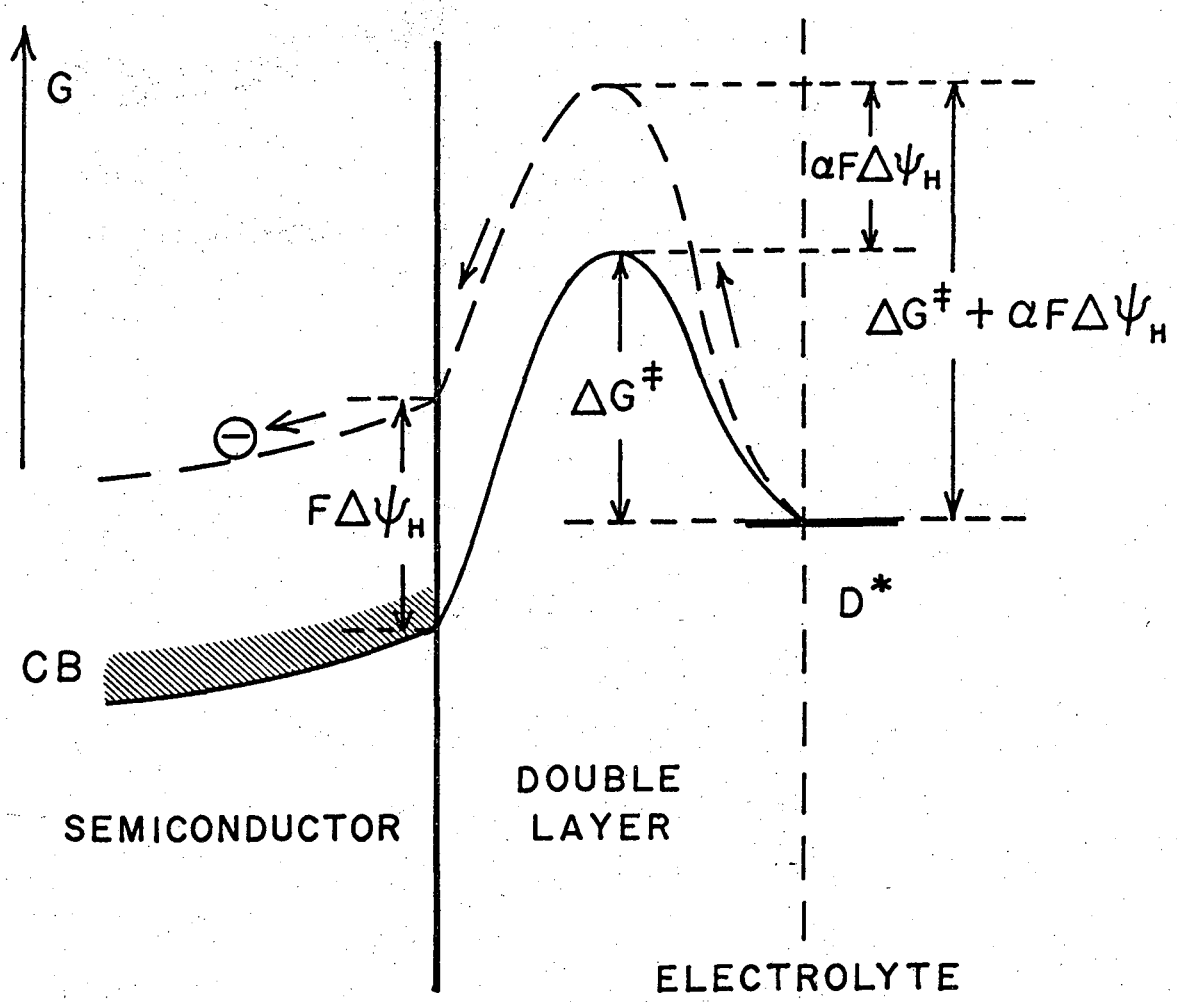
10^{-7} M
XBL706-5250

Fig. 6



XBL716-5242

Fig. 7

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