CATALYSIS OF PHOTOCHEMICAL REACTIONS BY COLLOIDAL SEMICONDUCTORS

A. Henglein

Hahn-Meitner-Institut für Kernforschung Berlin, Bereich Strahlenchemie
D-1000 Berlin 39, Federal Republic of Germany

Abstract – Illumination of semiconductor colloids such as ZnS, CdS and
TiO_2, generates electrons and positive holes which may react with the
aqueous solvent or dissolved substances. In ZnS and CdS, recombination
of the charge carriers is often accompanied by emission of light.

The absorption spectra of very small CdS or ZnS particles (1 - 3 nm) show
changes which indicate a transition from semiconductor to polymolecular
material. The conduction band energy is shifted, and the exciton transit-
ion band becomes more pronounced. The fluorescence spectra of small CdS
particles contain a band at the onset of absorption and two bands at lon-
ger wavelengths. They are attributed to emission from the short-lived ex-
citon state and from longer-lived states of trapped electrons and holes.
The chemical reactions described include the photo-anodic and the photo-
cathodic dissolution of colloidal sulfides, the reduction of water and car-
bon dioxide, and the oxidation of alcohols and sulfite anions. Two-electron
(two-hole) and one-electron (one-hole) transfer mechanisms are discussed.

Flash photolysis studies of colloidal TiO_2 gave the absorption spectra of
long-lived electrons and positive holes which are trapped in surface states
of different energies. Chemical reactions of these charge carriers are also
described, including the reduction of tetranitromethane, the oxidation of
SCN^- and OH^- anions, and of various organic compounds. The electrochemi-
cal nature of all these photo-reactions is emphasized.

INTRODUCTION

The first studies on the photochemistry of inorganic particles in aqueous suspension were
made with zinc sulfide some fifty years ago (Ref. 1,2). Zinc sulfide, a component of the
white pigment lithophone, was shown not only to photolyse but also to catalyse redox pro-
cesses including the photo-decomposition of water. The catalysis of redox reactions has also
been observed in colloid chemistry some 70 years ago. At that time, the chemistry of free
radicals in solution had just started, i.e. radicals were recognized as intermediates of redox
processes. The theory of the solid state – inorganic colloids are typical solids – had also not
yet been developed. Today these two fields are well understood, and this provides the right
background for investigating the mechanism of reactions at the interface between semiconduc-
tor colloids and aqueous solutions.

We already face a vast number of papers describing photo-chemical effects in suspensions of
semiconductors. These studies were initiated by A.J.Bard and his coworkers who, for ex-
ample, observed the decomposition of carbonic acids into CO_2 and alkyl radicals (Kolbe decar-
boxilation) (Ref.3), the reduction of precious metal ions (Ref.4) and the formation of amino
acids (Ref.5) in illuminated TiO_2 suspensions. Studies of this kind are often carried out
from the point of view of using solar energy for chemical purposes. We will briefly discuss this
point and focus on fundamental mechanistic studies of catalysed photo-reactions. Such stu-
dies are best carried out using colloidal particles with a diameter smaller than 10 nm. Solut-
ions of these particles are optically transparent, and therefore optical methods can be applied
which have proven to be so powerful in kinetic analysis of homogeneous systems. The elec-
tron transfer reactions occurring at interfaces are understood in terms of electrode kinetics;
the small particles therefore are often referred to as micro-electrodes, although they are not
part of an electrical circuit in the usual sense.

Interesting photo-physical investigations can also be carried out with the small colloidal part
icles. As the attenuation of light by scattering is negligible, one could detect their molecular
fluorescence (Ref.6,7) (in contrast to the scattering fluorescence which is known from many
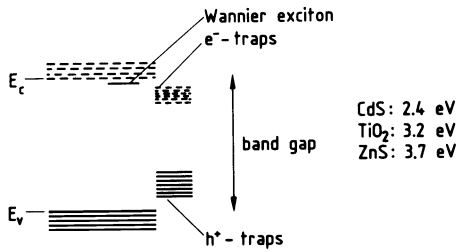older studies in colloid chemistry). Furthermore, interesting changes in the absorption and

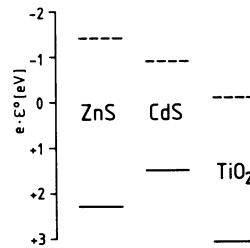Fig.1 Scheme of energy levels in a semi-conductor

Fig.2 Position of the energies E_v and E_c for CdS, ZnS, and TiO_2 on the electrochemical standard energy scale
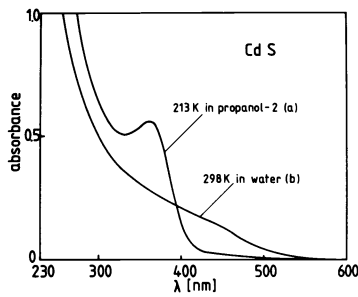

Fig.3 Spectra of colloidal CdS at different particle size. The particles in water were produced by precipitation of CdS in the presence of $6 \times 10^{-3}M$ colloidal SiO_2 (Ludox HS30 from Dupont; particle size: 13 nm). They have a diameter of about 3 nm. The smaller particles in propanol-2 were produced without a carrier
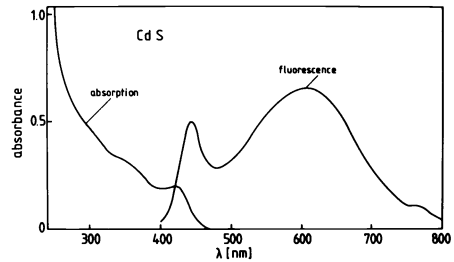

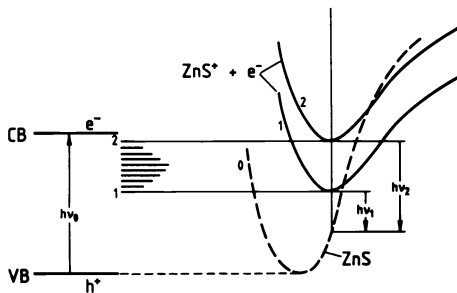Fig.4 Spectra of a CdS sol in water on silicon dioxide (Ludox HS-SM)

Fig.5 Energetics of fluorescence in colloidal ZnS particles

fluorescence of the colloids were observed when the size was decreased down to 1 to 3 nm, i.e. a size where the colloids start to loose their semiconductor properties.

Figure 1 is to remind the reader of the important features of semiconductors. E_V is the energy of the upper edge of the valence band, E_c the energy of the lower edge of the conduction band, while the level of the exciton lies very slightly below E_c. Various traps for electrons and positive holes may exist at the surface. Absorption of a photon leads to an electron in the conduction band and a positive hole in the valence band. The onset of light absorption occurs at a photon energy which practically coincides with the band gap energy. This energy is given in the figure for CdS, ZnS, and TiO$_2$, materials which are most commonly studied. Fig.2 shows the energies E_c and E_V on the standard electrochemical energy scale which relates to the inner energy scale of a semiconductor by the formula

$$e \cdot \varepsilon^o \; = \; IE - 4.5 \tag{1}$$

(e = elementary charge, ε^o = standard potential, IE = ionization potential of an electron in the level under consideration; 4.5 eV is the free energy required to move an electron from a standard hydrogen electrode into vacuum). It is recognized that positive holes in TiO$_2$ have especially strong oxidizing power while electrons in ZnS are strongly reducing. The chemical effects are explained as reactions of the charge carriers with the solvent or dissolved substances, and the fluorescence is attributed to the recombination of the charge carriers.

ABSORPTION SPECTRA OF EXTREMELY SMALL CdS AND ZnS PARTICLES

Figure 3 shows the absorption spectra of CdS particles of different size, the total CdS concentration being kept constant at 2×10^{-4}M. CdS sols generally have a yellow-orange color. Solution b is yellow-green, and solution a is colorless. The particle size of colloid b was determined as 3 nm by electron microscopy, which corresponds to an agglomeration number of about 300; solution a contained smaller particles. The onset of light absorption of colloid b takes place at a photon energy of 2.4 eV which coincides with the band gap energy of macrocrystalline CdS. However, the increase in absorption at shorter wavelengths occurs more slowly, and a weak shoulder is present at about 460 nm which is absent in the spectrum of a macrocrystal. The onset of the absorption of solution a occurs at 410 nm and the shoulder has now grown into a distinct maximum. When the yellow-green colloid was first prepared, it was thought that it had an amorphous structure (Ref. 6,7). In the meantime, it has been shown by high resolution electron microscopy that it is crystalline (Ref.8) and there is little doubt that the unusual spectral properties of the green and colorless CdS are caused by quantum mechanical effects due to the small sizes of the particles (Ref.9,10,11). Similar effects have been found for colloidal ZnS.

In rough terms, the energy of an electron in the conduction band of a small particle should be increased by about $h^2/8m^* R^2$ where m^* is the effective mass of the electron and R the radius of the colloidal particle. This effect becomes noticible in CdS at $R < 5$ nm (Ref.9,10). As a consequence, the density of the levels in the conduction band is decreased, and this,in turn, causes a decrease in the absorption coefficient at shorter wavelengths. The exciton state is not so drastically affected at larger particle sizes (spectrum b) as the wave function of this state is not so expanded as that of an electron in the conduction band. The onset of light absorption therefore remains close to the photon energy of 2.4 eV, although the absorption coefficient in the UV is already strongly decreased. The shoulder in the absorption spectrum is caused mainly by transitions to the exciton state. As the particle size is further decreased, the energy of the exciton state is noticibly shifted upwards, and the onset of absorption shifted to shorter wavelengths. With the very small particles of solution a, the semiconductor properties are already markedly changed, i.e. a transition from semiconductor CdS to polymolecular CdS can be seen.

FLUORESCENCE OF CdS AND ZnS

After the first observations of a fluorescence band in CdS (580 to 650 nm) (Ref.6) and in ZnS (428 nm) (Ref.7), several papers have appeared (Ref.13-17), in which additional bands at 510 nm and 760 nm for CdS were reported. Depending on the method of preparation of colloidal CdS, the 510 nm band is sometimes not present at all. The intensity of the fluorescence in both colloids is increased in the presence of up to 50% excess metal ions; the fluorescence centers therefore have been thought to be anion vacancies (Ref.11). In the case of CdS, the intensity is drastically increased by Ag$^+$ and Cu^{2+} ions provided that they are present during the precipitation of the colloid (Ref.6). When these ions are added after the formation of the colloid they quench the fluorescence. Aging of ZnS and CdS sols in the absence of air is accompanied by an increase in fluorescence intensity. The most dramatic increase, however, was observed when these sols were illuminated for some time in the presence of air (Ref.11). Under these circumstances, a photo-anodic dissolution partly takes place:

$$CdS + 2O_2 \xrightarrow{\text{light}} Cd^{2+} + SO_4^{2-} \tag{2}$$

which is described in more detail below. The largest quantum yields of fluorescence which could be achieved were 13% for ZnS and 2% for CdS (Ref.11,12).

Figure 4 shows spectra of a CdS colloid in water where the particle size again was rather small as can be recognized from the onset of the absorption well below 510 nm. All three fluorescence bands mentioned above are present, the first one appearing at 480 nm, i.e. at the onset of the absorption. This band is attributed to the fluorescence from the exciton state. The strong band at 600 nm is attributed to the recombination of charge carriers trapped in surface states of different energy. The band at 760 nm is also attributed to charge recombinations although the type of recombination sites may not be anion vacancies but another kind of lattice distortion. These suggestions were made on the basis of observations on the quenching of these emission bands by methyl viologen (MV^{2+}, 1,1'dimethyl-4,4'bispyridylium chloride) and on the decay of the fluorescence as measured by single photon counting. MV^{2+} was found to efficiently quench the 600 nm band and to have almost no affect on the 480 nm band. The decay at 480 nm (< 1 ns) was much faster than at 600 nm (~ 15 ns). It therefore seems that the exciton is very short-lived in these small colloidal particles. Rapidly decaying fluorescences, which could not be quenched by added solutes, have also been found for colloidal silver halides (Ref.7).

Colloidal ZnS has a broad fluorescence band with λ_{max} = 428 nm. The decay at various wavelengths in this band has been measured (Ref.11). The decay was of multi-exponential order. The fraction of long-lived fluorescence was found to increase with increasing wavelength. These effects are explained by the energy diagram of Fig.5.

On the left side, the upper edge of the valence band and the lower edge of the conduction band are shown as well as a distribution of surface states of the electron. Let us regard states 2 and 1 at the higher and lower energy ends of this distribution. The right side shows the potential curves anticipated for the ground state of ZnS (dashed lower curve), and for the positive hole $ZnS^+ + e^-$ (full, upper curves; curves 2 and 1 were drawn in a parallel manner, adjusting the minima to the electronic energies 2 and 1 on the left side). In these potential curves, a representative coordinate on the abscissa could be the $Zn^{2+} \text{——} S^{2-}$ distance (ground state) and the $Zn^{2+} \text{——} S^-$ distance (hole), the latter is expected to be larger due to smaller Coulomb attraction between the ions. Tunnelling of the electron from the shallow trap 2 should be faster than from the deeper trap 1. In the first case, a photon of relatively large energy $h\nu_2$ would be emitted by the intermediate excited state; in the second case, a photon of lower energy would be produced. This mechanism explains why the long-lived fraction of the fluorescence is stronger at longer wavelengths. We have not yet considered the fact that various distances of trapped electrons and holes are possible. Electrons in a trap of given energy will therefore return to the holes with different life-times depending on the distances involved. This means that the decay of the fluorescence at a given wavelength will not follow first order kinetics but be composed of many first order components.

CHEMICAL REACTIONS AT CdS AND ZnS PARTICLES

The photo-anodic dissolution of CdS, eqn.2, can be promoted by dissolved substances such as methyl viologen. Fig.6 shows the relative rate of decomposition and the fluorescence intensity as functions of the concentration of added methyl viologen. The two curves run symmetrical to each other. This indicates that the fluorescence of CdS and its photo-anodic dissolution occur through a common intermediate which can react with MV^{2+}.

The mechanism is described in Fig.7. The electron in the conduction band reacts with adsorbed oxygen, the positive hole semioxidizes a sulfide anion at the surface. Further oxidation of the semioxidized sulfide anion takes place by oxygen. As oxygen is only weakly adsorbed at the colloidal particles, the quantum yield is only 0.04 molecules consumed per absorbed photon. In the presence of MV^{2+}, the electrons are more efficiently removed; the positive holes can now oxidize sulfide anions at a greater rate. In CdS solutions containing MV^{2+} as an electron scavenger and excess sulfide anions as a hole scavenger, MV^+ and sulfur are produced with a large quantum yield of 0.6.

The photo-cathodic dissolution of colloidal CdS according to

$$H^+ + CdS \xrightarrow{\text{light}} Cd + SH^- + 2h^+ \tag{3}$$

is brought about in the presence of a solute which reacts with the holes h^+ such as sodium sulfite, and chemically reactive cadmium metal is deposited on the CdS particles. Its amount
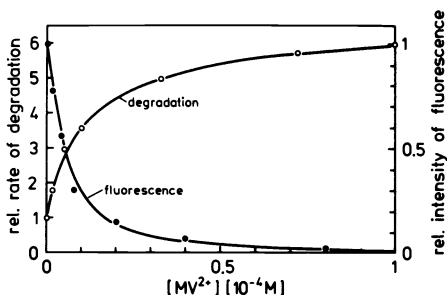
Fig.6 Relative rate of photo-anodic dissolut-
ion and intensity of the fluorescence of
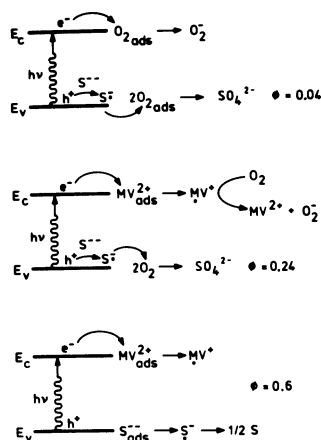CdS as functions of the concentration
of added methylviologen

Fig.7 Mechanism of the photo-anodic dissolut-
ion (upper), the promotion of the dis-
solution by methylviologen (middle), and
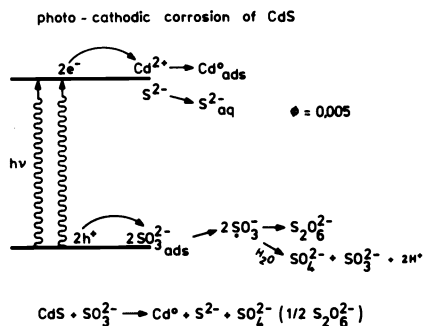the MV$^+$ plus sulfur formation in the
absence of oxygen (lower)

Fig.8 Mechanism of the photo-cathodic disso-
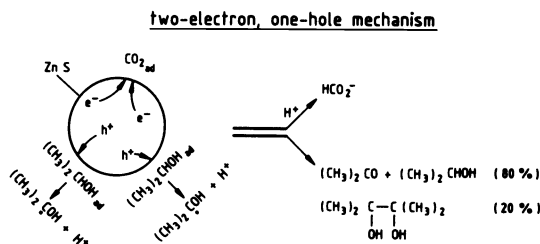lution of CdS in the presence of sulfite
anions

Fig.9 Illustration of the two-electron plus
one-hole redox mechanism. (The two
propanol-2 molecules generally are semi-
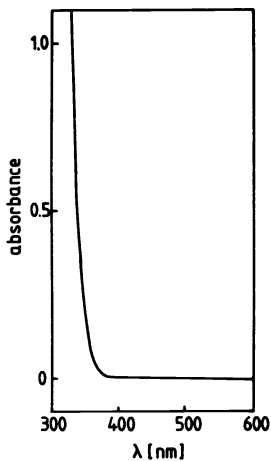oxidized at different colloidal particles)

Fig.10 Absorption spectrum of a solution containing
6.3×10^{-3}M TiO$_2$ at pH = 3

can be determined by adding methyl viologen after the illumination. The solution immediately turns blue due to the MV^+ radical, which is formed by the reoxidation of Cd by methyl viologen: $Cd + 2MV^{2+} \longrightarrow Cd^{2+} + 2MV^+$. As the spectrum of MV^+ is well-known, the amount of Cd formed during the illumination can be determined in this way (Ref.18).

Figure 8 shows the mechanism of the photo-cathodic dissolution in the presence of sulfite. An adsorbed sulfite anion picks up only one positive hole to form a SO_3^- radical which subsequently undergoes combination or disproportionation with another radical in the bulk solution to form dithionate and sulfate, respectively. The quantum yield, however, is only 0.005. In the presence of excess Cd^{2+} ions, the formation of cadmium metal occurs with a ten times greater yield.

The electrons in the conduction band of CdS have sufficient negative potential to reduce water to form hydrogen. Hydrogen evolution from water generally requires a large overpotential unless a catalytically active surface for the intermediate storage of H atoms is present. It seems that a CdS particle is not active in this respect. However, when the illumination of a CdS solution containing sulfite is continued, the metal deposition ceases and hydrogen is produced with a quantum yield of about 0.05. This effect is explained by an improvement of the catalytic properties of the CdS surface by the cadmium atoms deposited in the early stages of illumination (Ref.18).

Similarly, the formation of zinc metal was observed in the illumination of ZnS solutions containing sulfite and excess zinc ions (Ref.19). ZnS was also found to catalyse the simultaneous reduction of CO_2 to yield formic acid and the oxidation of sulfite to yield sulfate. The quantum efficiency for these processes was 80%. The mechanism of CO_2 reduction is discussed further below. Other reactions observed at ZnS particles include the oxidation of alcohols and formic acid and the reduction of chloro-organic compounds (Ref.19).

TWO-ELECTRON(HOLE) VERSUS ONE-ELECTRON(HOLE) MECHANISM

In the preceding section it was mentioned that CO_2 is reduced to H_2CO_2 and SO_3^{2-} oxidized to SO_4^{2-} at illuminated ZnS particles with a large quantum efficiency of 0.8. Two questions may be asked: 1) How can these reactions occur so efficiently, although the anodic and cathodic sites are so close together, i.e. the intermediates of the SO_3^{2-} oxidation should undergo a rapid back reaction with the intermediates of the CO_2 reduction. 2) In order to reduce CO_2 to H_2CO_2, two electrons have to be picked up. Do these two electrons originate from the same colloidal particle? In this respect it is interesting to note that the time between two successive photon absorptions in a colloidal particle is about 100 µs under the conditions of illumination with the filtered light of a xenon lamp. Or do the two electrons originate from different colloidal particles? Obviously, in the first case, the intermediate CO_2^- radical formed after the first electron picked-up, is strongly adsorbed at the colloidal particle and resides there until the next photon arrives. In the second case, the CO_2^- radical is detached and disproportionates with a CO_2^- radical from another colloidal particle. Similar questions can be asked for oxidation processes in which two holes are involved. We will speak of a two-electron(hole) mechanism, if the two electrons (holes) originate from the same colloidal particle, otherwise we will speak of a one-electron(hole) mechanism (Ref.20).

In order to distinguish between these two mechanisms, an analysis has to be made for the products formed in the crossed combination of intermediate radicals from the anodic and cathodic reactions sites. The absence of the crossed combination product is then taken as proof for at least one of the processes being of the two-electron (or hole) nature. Let us regard the following example: It was found that alcohols are oxidized at illuminated ZnS particles (the reduction product found being H_2 from water). If this oxidation occurred through the two-hole mechanism, only one product would be expected, such as acetone from propanol-2. However, pinacol and acetone were found, and the ratio between these products was the same as in the homogeneous oxidation of propanol-2 in water by OH radicals. It therefore can be said that the oxidation of alcohols at ZnS particles exclusively occurs via the one-hole mechanism, 1-hydroxy alkyl radicals being the intermediates which form the final products by reactions among themselves in the bulk solution. Regard now a solution containing both an alcohol and CO_2 where formic acid is the reduction product. If CO_2^- radicals which freely diffuse into the solution were formed as intermediates, the crossed combination product from these radicals with the 2-hydroxy alkyl radicals from the alcohol oxidation should be found. It was shown that this was not the case and it was concluded that the reduction of CO_2 at ZnS particles occurs via the two-electron mechanism. The two-electron/one-hole redox mechanism in this system is illustrated again by Fig.9. It seems that the least interference between the anodic and cathodic reactions takes place in those cases where these reactions are ruled by different e^- and h^+ transfer mechanisms, i.e. under these circumstances large yields of the final products become possible (Ref.20).

LASER FLASH PHOTOLYSIS OF TiO$_2$ SOLS

Figure 10 shows the absorption spectrum of a TiO2 solution. The absorption steeply increases at wavelengths below 380 nm which corresponds to the band gap energy of 3.2 eV in macrocrystalline TiO$_2$. On the standard electrochemical energy scale the upper edge of the valence band in macrocrystalline TiO2 is located at 3.1 V, and the lower edge of the conduction band at -0.1 V. Positive holes created in TiO2 are very strong oxidizing agents while the electrons have only moderate reducing power.

When a TiO2 sol is flashed in the absence of an adsorbed reactant for either electrons or holes, no absorption signal can be detected, i.e. a very fast recombination of the charge carriers takes place. However, the absorption of long-lived excess electrons is observed when polyvinyl alcohol is present as scavenger for positive holes, and the absorption of relatively long-lived trapped holes is seen in the presence of an adsorbed reactant for electrons (Ref.21,22). The absorption spectra of these intermediates are shown in Fig.11 and 12. The insets of the figures show the time profile of the absorption. The excess electrons live for minutes or even hours depending on the kind of the TiO$_2$ sol. The trapped holes disappear according to a multi-exponential decay, which indicates that states of different energies participate. In acidic solutions, trapped holes can still be detected after several milliseconds.

Electron deficient surface states are well-known from many studies in the electrochemistry and photo-electrochemistry of semiconductor electrodes. Their existence is deduced from electrical current measurements. The studies on colloids complement these findings in electrochemistry by observing trapped holes by their optical absorption. The trapped holes can now be dealt with as are the intermediates of photo-reactions in homogeneous solution. Their chemical reactions with dissolved substances can be followed by fast absorption measurements.

Figure 13 shows the results obtained in experiments where the TiO2-Pt sol contained various organic additives. The right side shows the 475 nm absorption of the holes immediately after the laser flash as a function of the concentration of the additive. It is recognized that citrate is most efficient in reacting with the holes during the flash, ethanol being the least efficient reactant. The left side of the figure shows the time required for a drop of the residual absorption at 475 nm after the flash by 25%. It is recognized that ethanol is now the most efficient reactant while citrate has rather little effect. Reaction with the holes during the laser flash requires the adsorption of the reactant at the colloidal particles. Citrate is more strongly adsorbed than ethanol. On the other hand, it is by far less readily oxidized in homogeneous solution than ethanol. The holes which react during the flash are on such a high positive potential that they can react with practically all adsorbed organic molecules regardless of their structure. However, when the reaction after the flash is concerned, the holes are already trapped (i.e. they are on a less positive potential) and now the particular ability of the organic compound to be oxidized determines the rate of reaction (Ref.22).

In the experiments of Fig.14, a TiO2 sol at pH = 10 was used, where the colloidal particles were negatively charged. The solution also contained methyl viologen, MV^{2+}, which is strongly adsorbed at the colloidal particles in alkaline solution. The 392 nm absorption of the radical cation $MV^{+\cdot}$ (which is a stable radical in the absence of air) was present immediately after the laser flash (curve a). The conductivity of the solution was also recorded (curve b). It decreased after the flash according to first order kinetics, the half life time being 8.5µs. With increasing OH$^-$ concentration, the pseudo-first order rate constant of this decrease became greater. The decrease in conductivity is attributed to the oxidation of OH$^-$ ions by positive holes after the flash, i.e. to the first step of the evolution of oxygen or hydrogen peroxide at the TiO2 particles. As expected, the decrease in conductivity was not observed in the absence of methyl viologen. Methyl viologen was the scavenger which interfered with the e$^-$ - h$^+$ recombination, leaving excess positive holes on the colloidal particles which finally oxidized OH$^-$ (Ref. 21,22).

An interesting side reaction was observed in the TiO$_2$-MV^{2+}-system in alkaline solution. The solution became strongly fluorescent after some illumination, λ_{max} of the fluorescence band lying at 517 nm. This effect became less pronounced when a solution was used which contained polyvinyl alcohol in addition. As this polymer is a hole scavenger, it is concluded that methyl viologen not only scavenges electrons but also holes, although to a much lesser degree, the product having fluorescent properties. As will be described elsewhere, fluorescing products are also found in the oxidation of methyl viologen in homogeneous solution by ·OH radicals. The oxidation product in the heterogeneous photo-oxidation at TiO$_2$ was found to be 1'2'-dihydro-1,1'dimethyl-2'-oxo-4,4'-bipyridylium chloride.
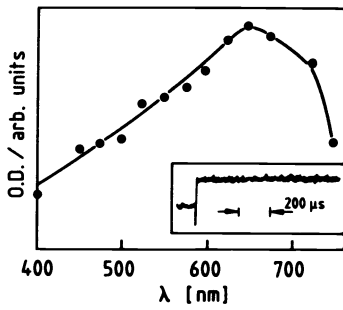
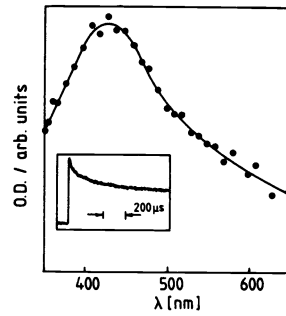Fig.11 Absorption spectrum of excess elec-
trons on TiO$_2$

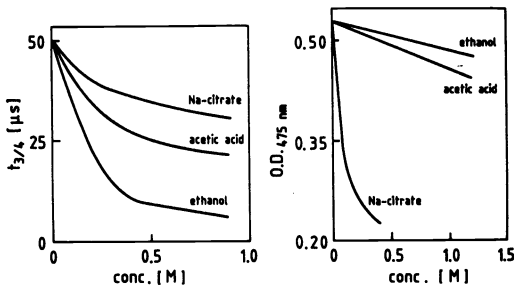Fig.12 Absorption spectrum of trapped holes
in TiO$_2$

Fig.13 right: 475 nm absorbance of the holes
immediately after the laser flash
as a function of the concentrat-
ion of added organic compounds
       left: reaction of the remaining holes:
time for 25% decrease as a funct-
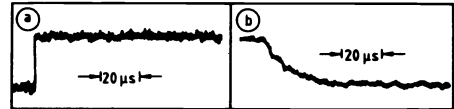ion of the concentration of the
organic compound

Fig.14 Time profile of the 392 nm absorption
(a) and the conductivity (b) of a
flashed TiO$_2$ sol containing 5×10^{-5}M
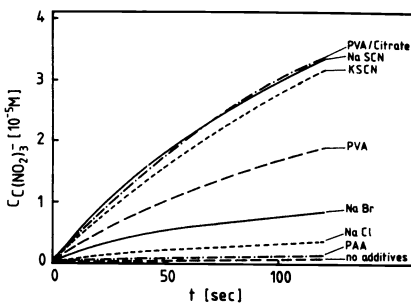methyl viologen. pH = 10

Fig.15 Concentration of the nitroform anion
as a function of the illumination time.
The TiO$_2$ sol contained various addi-
tives (salts at 0.1M or polymers at
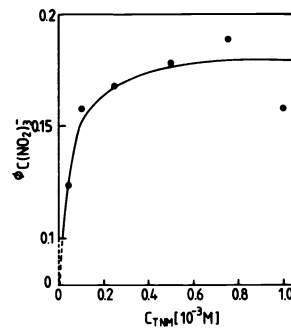5×10^{-3}M). pH = 2

Fig.16 Quantum yield of the nitroform anion
as a function of the concentration of
tetranitromethane. 0.1M SCN$^-$ was pre-
sent as hole scavenger. pH = 2

REDUCTION OF TETRANITROMETHANE AT TiO_2 PARTICLES

An efficient reduction of dissolved compounds, which are not adsorbed at the colloidal TiO_2 particles, occurs only in the presence of an adsorbed scavenger for positive holes. Tetranitromethane was used as reactant for electrons:

$$e^- + C(NO_2)_4 \longrightarrow C(NO_2)_3^- + NO_2 \tag{4}$$
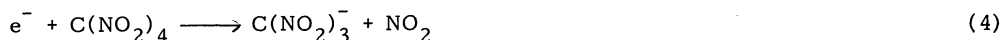
This reaction can readily be followed by recording the light intensity at 350 nm where the stable product $C(NO_2)_3$ strongly absorbs. In Fig. 15 the concentration of this anion is shown as a function of the illumination time for solutions containing various sodium salts and polymers (PVA: polyvinylalcohol; PAA: polyacrylamide). It is recognized that thiocyanate and citrate most efficiently promote the reduction of tetranitromethane. Of the polymers, PVA is more active than PAA. The efficiency of the hole scavenger is determined by both its ability to be adsorbed and to be oxidized. At short illumination times, the concentration of $C(NO_2)_3^-$ formed is proportionate to the time; at longer times the curves bend towards the horizontal axis, which is due to photo decomposition of $C(NO_2)_3^-$ at the colloidal TiO_2 particles (Ref.23).

The reaction of eqn.4 requires the diffusion of tetranitromethane to the colloidal particles as tetranitromethane is not adsorbed. In fact, laser flash experiments have shown that the reduction of tetranitromethane occurs after the flash (Ref.21). Under continuous illumination conditions, a stationary concentration of excess electrons will be built-up on the colloidal particles. An excess electron may either react with tetranitromethane or recombine with the positive hole created by the next photon absorbed in the colloidal particle. At sufficiently high concentrations of tetranitromethane, all the electrons will react with it (or, more precisely, as many electrons will react as there are positive holes scavenged by the adsorbed hole scavenger). The yield will then become independent of the concentration of tetranitromethane. Fig.16 shows the quantum yield of the formation of $C(NO_2)_3^-$ as a function of the concentration of tetranitromethane; thiocyanate was used as scavenger for positive holes. Above about 4×10^{-4}M, the yield is constant at 0.17 $C(NO_2)_3^-$ anions per photon absorbed. When the SCN^- concentration is varied, the $C(NO_2)_3^-$ yield initially increases linearly and levels off at concentrations above 0.3M as the Langmuir adsorption limit of SCN^- is gradually reached. These experiments show how the yield of the reaction of the non-adsorbed scavenger for electrons (i.e. $C(NO_2)_4$) is determined by that of the oxidation of the adsorbed scavenger for positive holes (i.e. SCN^-). This interplay of the scavengers for e^- and h^+ strongly determines the kinetics of the reactions at microelectrodes (Ref.20).

THE QUESTION OF CYCLIC WATER SPLITTING

In the preceding chapters examples have been given of the simultaneous reduction and oxidation of dissolved substances at colloidal semiconductors, some of these redox processes occurring with appreciable quantum yields. It would be intriguing to find a system, in which the electrons from the conduction band reduce water to form H_2 and the positive holes from the valence band oxidize water to form O_2. In fact, suspended strontium titanate particles carrying a rhodium deposit generate H_2 plus O_2 upon illumination with UV light (Ref.24). During the last few years, a number of systems which split water into H_2 and O_2 have been described (Ref. 25,26). However, an obscure situation arose as these results could not be reproduced in other laboratories. As a number of demonstrations by the authors have recently failed to prove the simultaneous formation of H_2 and O_2 it must be concluded that no acknowledged colloidal or suspended particle system exists at the present time in which visible light is used to split water in a cyclic manner. In the systems reported, H_2 is always formed but an anodic corrosion of the catalyst occurs or some other oxidation takes place instead that of water.

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