

Reactions On Colloidal Semiconductor Particles

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Colloides / Semiconductors

Inorganic colloids such as cadmium sulfide are often used as sensitizers and catalysts for photochemical reactions. In these reactions, which are described in terms of the concepts developed in electrode kinetics, electrons are transferred between the particles and molecules in the solution. Extremely small particles (Q-particles) often have optical and catalytic properties different from those of the macrocrystals. These effects are due to the restriction in space of the charge carriers produced by light absorption (size quantization). CdS particles carrying an excess electron strongly change their absorption at wavelengths near the absorption edge. This effect is attributed to the influence of the excess electron on the optical transition leading to the lowest excitonic state in these particles.

Introduction

In the photochemistry of inorganic colloids, which are typical semiconductors in the macrocrystalline state, there are three areas of interest:

1. Such colloids are used as sensitizers and catalysts for photochemical reactions. These reactions are initiated by the electrons and positive holes that are generated by light absorption in the semiconductor particles. The charge carriers rapidly move to the surface reducing or oxidizing solute or solvent molecules. These reactions are similar to reactions occurring on electrodes as electrons are exchanged between the colloidal particles and the solution, and the small particles, therefore, are often called "microelectrodes" although they do not constitute part of a closed electrical circuit.
2. A few years ago, it was discovered that extremely small colloidal particles have optical and catalytic properties differing to those of the macrocrystalline materials. These differences are due to size quantization as the particles gradually lose their semiconductor properties with decreasing size and a transition occurs to "molecular materials".
3. Even more recent are studies in which changes in the properties of the particles, occurring under illumination, are investigated. The charge carriers, produced by light absorption, may themselves change the optical properties of the particles, and these changes may result in non-linear optical effects.

Excess charge carriers can often be deposited onto the colloidal particles by free radicals produced in the bulk solution by irradiation. Strong reducing radicals or even hydrated electrons transfer an electron to the colloidal particles, and strong oxidizing radicals may inject positive holes. The advantage of this method of excess charge deposition consists of the fact that the effects of charge carriers of one sign can be investigated without being disturbed by recombination with carriers of opposite sign. Both chemical reactions of the deposited charge carriers and the influence of the carriers on the optical properties of the colloidal particles can be studied in this way.

For each of these three areas of interest we report here one example. Photoanodic dissolution and the mechanism of cadmium metal formation and H₂ evolution are examples of chemical reactions occurring between illuminated colloidal particles and the solution. The size quantization effects are demonstrated by CdS and Cd₃P₂. Finally, we describe the changes in optical absorption of CdS particles which carry one or two excess electrons deposited by hydrated electrons.

Results

Photoanodic Corrosion

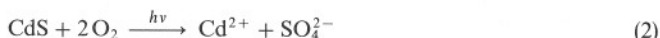
The photoanodic dissolution of compact electrodes of metal sulfides and selenides is an obstacle for the use of these materials in photoelectrochemical cells [1]. Cadmium sulfide, for example, decomposes according to the overall process:



The photoanodic dissolution is also encountered in the illumination of the colloidal solutions of these materials. In most cases disso-

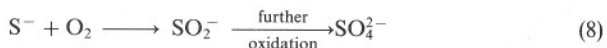
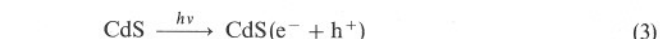
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lution occurs at an appreciable rate only in the presence of oxygen. In the first experiment of this kind [2], sulfate anions were found as the product, while it was later shown for ZnS [3] and CdS [3,4] that these ions were also the only oxidation products:



Recently, the formation of sulfate was also found in the photoanodic dissolution of compact CdS in the presence of oxygen [5].

Certain electron acceptors such as Ti^+ and MV^{2+} ions (MV^{2+} : methyl viologen, 1,1'-dimethyl-4,4'-bispyridinium dichloride) accelerate the dissolution of CdS [2,6]. In Fig. 1, the relative rate of dissolution is plotted as a function of the MV^{2+} concentration. The figure also shows the fluorescence intensity of the CdS sample. The symmetric behaviour of the two curves indicates that the two processes have a common intermediate which reacts with MV^{2+} . In the absence of methyl viologen, the mechanism of photoanodic dissolution is described by the following equations:



Light absorption produces electrons in the conduction band and positive holes in the valence band (Eq. (3)). The charge carriers mainly recombine (Eqs. (4) and (5)). A few electrons are scavenged by oxygen (Eq. (6)), and the holes can then semi-oxidize sulfide anions at the surface (Eq. (7)). Further oxidation of the radical anion S^- occurs by oxygen attack (Eq. (8)). In the presence of methyl viologen, which is strongly adsorbed on the colloidal particles [7], the electrons are more efficiently scavenged and the semi-oxidized methyl viologen, MV^+ , is reoxidized by oxygen:



MV^{2+} acts as an "electron relay". The positive holes can now more efficiently oxidize sulfide anions.

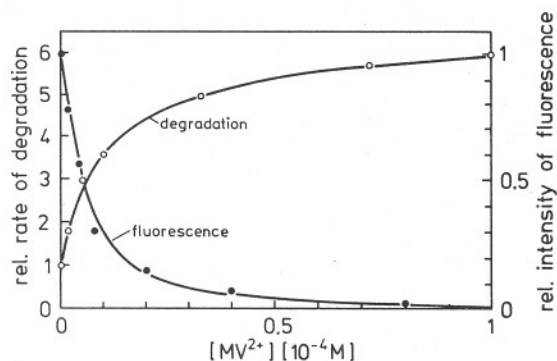


Fig. 1

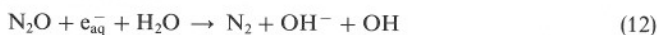
Relative rate of photo-anodic dissolution and intensity of fluorescence as functions of the concentration of methyl viologen, MV^{2+} , in a 2×10^{-4} M aerated CdS solution

A key reaction in the above scheme is Eq. (8). This reaction has also been studied by pulse radiolysis [8]. The CdS sol was exposed to a microsecond pulse of high energy electrons under an atmosphere of nitrous oxide, and the optical changes occurring in the

10^{-5} s range after the pulse were recorded. During the pulse, hydrated electrons, hydrogen ions, and hydroxyl radicals are formed by the radiolysis of the solvent:



The hydrated electrons react within the pulse with dissolved nitrous oxide to form additional hydroxyl radicals:



The OH radicals react with CdS particles and this reaction is accompanied by changes in the optical absorption of the solution:



Attack of OH on CdS resulted in the injection of positive holes, which, chemically speaking, are S^- radical anions at the surface of the particles. It was observed that these localized holes had a broad absorption band in the visible which shifted towards shorter wavelengths with decreasing particle size. In the presence of oxygen, this absorption decayed within a millisecond, and from this decay a rate constant of $1.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for reaction 8 was derived.

A few more details of the photoanodic dissolution of colloids will be only briefly mentioned. The rate of dissolution of CdS decreases with decreasing particle size and at the same time the quantum yield of fluorescence increases [9]. Using short illumination times and rapid analysis by ion-chromatography sulfite anions were found as product, the yield being comparable to that of sulfate (at longer illumination times, the sulfite anions are oxidized to sulfate) [10]. Not all the metal sulfides form sulfate or sulfite upon illumination in the presence of O_2 . Antimony sulfide, Sb_2S_3 , for example produces mainly sulfur [11]. Photoanodic dissolution in aerated solution has also been found for cadmium phosphide [12] and cadmium arsenide [13].

The initiation of the photodissolution occurs by electrons being scavenged by dissolved oxygen (Eq. (6)). However, oxygen cannot be substituted by other electron scavengers. For example, no dissolution occurs in a deaerated sol of CdS containing MV^{2+} or nitrobenzene although both additives react with electrons [2,6]. In aerated solution, the two additives accelerate the dissolution via the above relay effect (Eqs. (9) and (10)). In the absence of O_2 , a rapid re-oxidation of the species produced by electron scavenging, i.e. MV^+ and $\text{C}_6\text{H}_5\text{NO}_2^-$, by the positive holes takes place. This re-oxidation is prevented in the presence of O_2 as reactions 8 and 10 are faster.

Size Quantization Effects

The results of a typical photodissolution experiment with a CdS sol, in which a size quantization effect was encountered for the first time, are presented in Fig. 2, where the absorption spectrum of the sol before and after illumination with the intense light of a xenon lamp is shown. In the beginning, the onset of absorption was at 490 nm, i.e. slightly below the wavelength of 515 nm where macrocrystalline CdS starts to absorb. During photoanodic dissolution the particles became smaller. The spectrum of the fragment particles present after illumination was drastically different from that of the starting material. The onset was shifted to below 400 nm, i.e. these CdS particles were colorless, and a maximum appeared at about 30 nm below the onset.

After degradation experiments of this kind, methods were developed for the preparation of extremely small particles both in aqueous solution and in organic solvents [9]. In these methods, a rapid precipitation of CdS was achieved. Low temperature during precipitation and the presence of small amounts of polyphosphate in aqueous solution were found to be favorable for obtaining very small particles. Other semiconductor materials, such as cadmium phosphide [12], cadmium arsenide [13], cadmium selenide [14], zinc sulfide [14], zinc selenide [14], lead sulfide [15], lead selenide [16], and mercury selenide [16], were also made as "Q-materials" using these precipitation techniques. These materials are characterized with the prefix "Q" in order to point out that they differ

with respect to their optical and catalytic properties from the macrocrystalline materials. The Q stands for the quantum mechanical effect which is responsible for these changes. The shift in the onset of absorption was most drastic for semiconductors having a band gap of only a few 0.1 electron volts. Cd_3P_2 and Cd_3As_2 , for example, have band gaps of 0.5 and 0.1 eV, respectively. Usually these semiconductors are black and start to absorb in the infrared. However, they can be made in the form of small colloidal particles by precipitation with phosphine or arsine in an alkaline solution containing $\text{Cd}(\text{ClO}_4)_2$ and polyphosphate. Depending on the particle size, samples can be made which have all conceivable colors in the visible as the band gap is shifted from a few 0.1 eV's to about 3 eV. The 3 eV band gap particles are white with a yellow tinge. A method for removing the solvent from these colloidal solutions to recover the colloidal particles in the form of solid powders has also been described [9]. Fig. 3 is a colorphoto of Cd_3P_2 powders consisting of particles of different size. The particles do not touch each other in these powders as they are complexed with about 30 weight % of sodium polyphosphate. These powders can be redissolved in water to yield the original colloidal solutions.

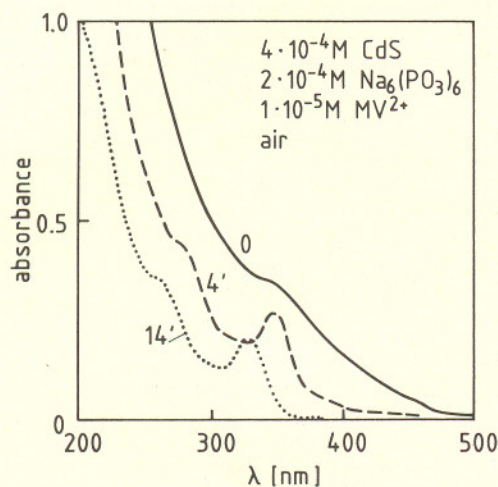


Fig. 2

Absorption spectrum of a 4×10^{-4} M CdS sol before and after different times of illumination. The aerated solution also contained 2×10^{-4} M $\text{Na}_6(\text{PO}_3)_6$ and 1×10^{-5} M MV^{2+}

Among the metal oxides, Q-colloids of ZnO [17], and more recently of CdO and In_2O_3 , have been prepared in our laboratory. The techniques applied here consisted of reacting alcoholic solutions of the corresponding cation with NaOH. Again, the materials could be recovered in the solid state. The size quantization effect in ZnO could be demonstrated as shown by Fig. 4. It was found that not only the onset of absorption was shifted to shorter wavelength with decreasing particle size but also the color of the fluorescence light [9, 12, 13]. When ZnO is precipitated, a solution is obtained which initially fluoresces blue but as the particles slowly grow upon aging, the color of the fluorescence light changes to blue-green and finally to yellow-green. This is shown by Fig. 4.

The size effects are generally described by the well-known quantum mechanics of a "particle in a box". The electron and the positive hole are confined to potential wells of small dimension and this leads to a quantization of the energy levels (which in the bulk material constitute virtual continua in the conduction and valence band, respectively). The phenomena arise when the size of the colloidal particle becomes comparable to the DeBroglie wavelength of the charge carriers. The quantization effects for an electron in an evacuated box become significant at box dimensions of some 0.1 nm. However, in colloidal particles the effects can already be seen at a much larger particle size. The reason for this lies in the fact that the effective mass of a charge carrier, which moves in the periodic array of the constituents of the crystal lattice, is generally much lower than the mass of an electron in free space. This results

in a larger DeBroglie wavelength. The smaller the effective mass of the charge carriers the more pronounced are the optical size effects. Most of the quantum mechanical calculations have been made for small CdS particles [9, 18–21]. A typical result of such calculations is shown by Fig. 5 in which the thirteen lowest electronic energy levels in CdS particles of different radii are given (only levels with a total angular momentum $L = 0$ are contained in the term schemes). The diagrams were obtained by an accurate quantum mechanical treatment of an electron and a positive hole in a box. However, a hard well potential had to be assumed, i.e. an infinite potential for $r > R$ ($R =$ radius of particle; $r =$ distance from the center of the particle). It can be seen that all levels are shifted to higher energies with decreasing particle size and the density of states is decreased. The shift of the lowest level would be slightly less for a finite potential above 4 eV (which is more realistic, but makes the quantum mechanical calculations drastically more difficult), while the higher levels would be influenced more strongly. However, despite the approximation of an infinite potential, the figure gives an instructive illustration of what happens to the electronic structure of a semiconductor during the transition from semiconductor to molecular properties.

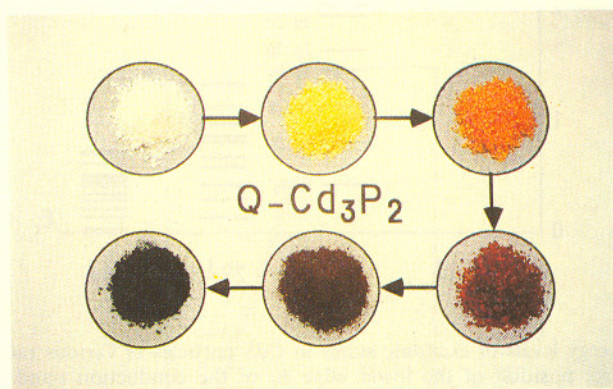


Fig. 3

$\text{Q-Cd}_3\text{P}_2$ samples of different particle size. (Mean diameter of the largest particles: about 10 nm. Mean diameter of the smaller particles: about 2 nm). Increasing particle size in the direction of arrows

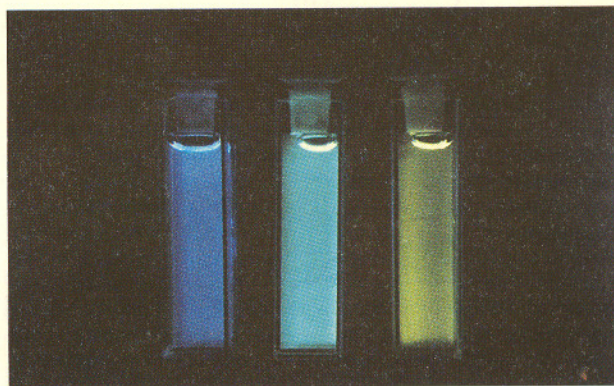


Fig. 4

Fluorescence of a ZnO sol in propanol-2. Increasing particle size from left to right

The maximum in the absorption spectrum of Q-particles (see Fig. 2) is attributed to optical transitions to the lowest electronic state. This state may be regarded as a strongly compressed exciton. In a macrocrystal, the exciton state is separated from the lower edge of the conduction band by only a few 0.01 eV. In this state, the electron has not escaped the Coulombic attraction of the positive hole. It moves around the hole in an orbital. In macrocrystalline CdS, this orbital has a diameter of about 5 nm. The optical transition to the

exciton state can only be resolved when the spectrum of a CdS crystal is recorded at liquid helium temperature. In Q-materials, the energy difference between the "exciton state" and the "lower edge of the conduction band" is strongly increased i.e. much greater than the thermal energy kT at room temperature, and the optical transition can, therefore, be resolved without cooling the sample.

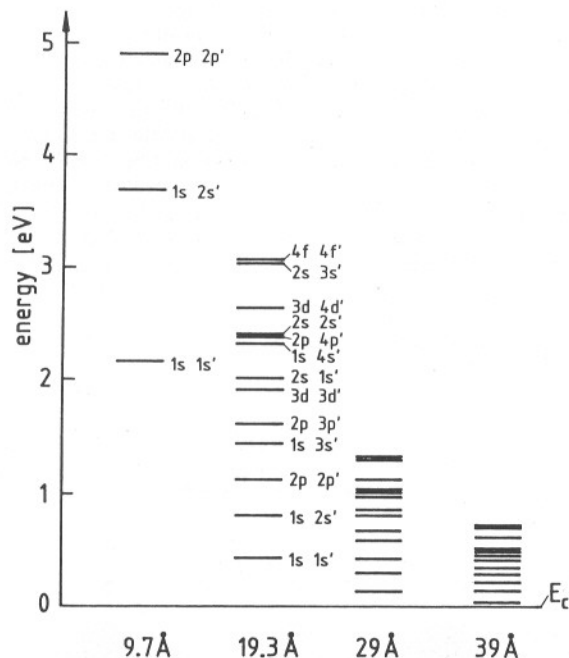


Fig. 5

Energy levels of excitonic states in CdS particles of various radii. Zero: position of the lower edge E_c of the conduction band in macrocrystalline CdS. Effective masses of electrons and holes 0.19 m_0 and 0.8 m_0 respectively. The letters with a prime designate the quantum state of the hole

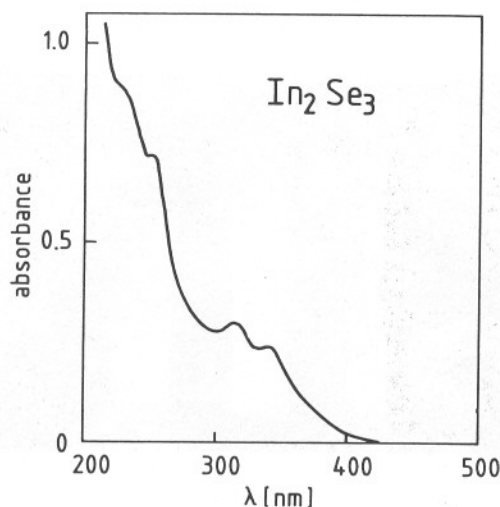


Fig. 6

Absorption spectrum of a Q- In_2Se_3 sol. The solution contained 2×10^{-4} M In_2Se_3 and 2×10^{-4} M $\text{Na}_6(\text{PO}_3)_6$, pH = 10

Sometimes the spectrum of a Q-material contains different maxima. A typical example is shown by Fig. 6 for Q- In_2Se_3 . Two effects can cause these maxima. In rather monodisperse samples the transition to different electronic states may be reflected by the maxima in the spectrum [14, 22]. On the other hand, Q-materials may possess a structured size distribution, in which certain agglomeration

numbers are a little more abundant than adjacent ones. The transition to the exciton state in particles of different size may then produce the various maxima [9, 23].

In Q-particles, the electron produced by light absorption should be on a more negative potential and the hole generated should be on a more positive potential than in the macrocrystalline materials. Chemical effects have been observed which can be explained by the stronger reducing properties of the electrons and the stronger oxidizing properties of the holes. For example, H_2 evolution was observed on illuminated PbSe and HgSe colloids and CO_2 reduction on CdSe when the particle size was less than 5 nm. These reactions did not occur on suspended larger particles [16]. Q-CdS particles catalyse the formation of the hydroperoxide $(\text{CH}_3)_2\text{C}(\text{OH})\text{OOH}$ when they are illuminated in aerated propanol-2 solution, while larger particles are not efficient in this respect [9].

Excess Electrons on CdS Particles

Albery et al. [24] have recently reported on flash photolysis experiments in which a hypsochromic shift of about 3 nm in the band edge of CdS was observed. They attributed the bleaching to excess electrons on the particles, although they could not identify the nature of these electrons and their mode of action. Electrons were also photo-emitted from CdS particles [25]. The photo-emitted electrons, which are hydrated in the aqueous solvent, may react with intact CdS particles and be stored on them.

The reaction of hydrated electrons with CdS particles has been studied using the method of pulse radiolysis [26]. The solution, which also contained 0.1 M t-butanol, was exposed to a microsecond pulse of 3.5 MeV electrons from a Van de Graaff generator. Equal concentrations of hydrated electrons, e_{aq}^- , hydrogen ions, and hydroxyl radicals were produced during the pulse. The OH radicals reacted with t-butanol during the pulse, the $\text{CH}_2(\text{OH})\text{C}(\text{CH}_3)_2$ radicals formed being unreactive towards the colloidal particles. The reaction of the hydrated electrons with the CdS particles was observed after the pulse by recording the optical absorption of e_{aq}^- at 700 nm (see inset in Fig. 7). At the wavelength of 470 nm, where the colloidal particles already absorbed, a strong bleaching occurred concomitantly with the disappearance of e_{aq}^- (see also inset of Fig. 7). The bleaching spectrum is shown by Fig. 7. It can be seen that bleaching occurs over a relatively narrow wavelength range below the beginning of light absorption of CdS at 510 nm.

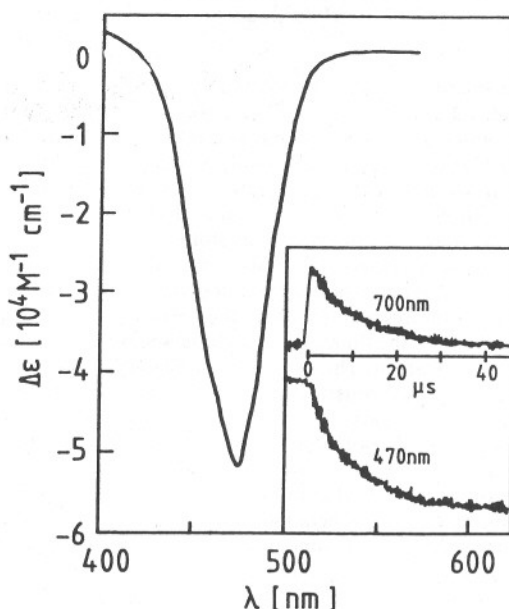


Fig. 7

Bleaching spectrum of a 2×10^{-3} M CdS solution. Inset: Decay of the 700 nm absorption of e_{aq}^- and time profile of bleaching at 470 nm

The same bleaching was observed when a solution containing excess Cd^{2+} ions was pulsed. The hydrated electrons reacted with Cd^{2+} ions to form Cd^+ ions which strongly absorb at 300 nm. This absorption decayed after the pulse simultaneously to the bleaching in the 400 to 500 nm range. This shows that Cd^+ ions can transfer an electron to CdS particles:



It also shows that Cd^+ ions are not stable in CdS because of the large negative potential of the $\text{Cd}^{2+}/\text{Cd}^+$ redox system.

Localization of an electron transferred to a CdS particle does not occur by a reaction with a Cd^{2+} ion but must take place in defect sites.

The huge decrease in the absorption coefficient in Fig. 7 indicates that the deposited excess electron influences an optical transition in the CdS particle as a whole. The bleaching was attributed to the influence of the excess electron on the excitonic state which is polarized in the field of the excess electron, is increased, the consequence being a blue shift in the absorption spectrum [26]. Fig. 8 shows the spectra of $(\text{CdS})_x$ and $(\text{CdS})_x^-$ as calculated from the data in Fig. 7.

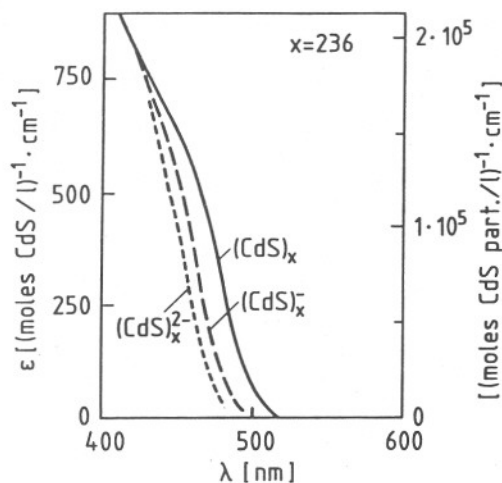


Fig. 8

Spectrum of the absorption edge of CdS particles carrying different numbers of excess electrons

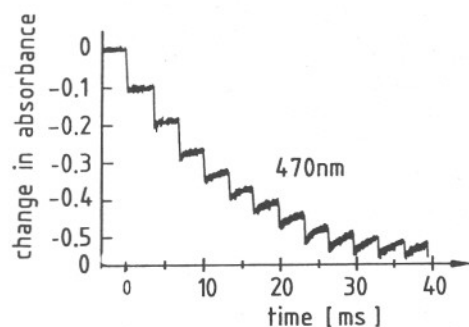


Fig. 9

Bleaching of the CdS solution by a train of pulses

Fig. 8 also shows the spectrum of CdS particles which have acquired two electrons. In these experiments, the CdS solution was irradiated with a train of pulses, the interval between the pulses being 3.8 ms. In each pulse 2×10^{-6} M electrons were produced while the concentration of the colloidal particles was 8×10^{-6} M. With increasing pulse number, the bleaching produced by a pulse recovered more and more during the following interval until a stationary state was reached. The recovery of bleaching between the

pulses was attributed to mutual annihilation of electrons deposited on the same colloidal particle, the product of this annihilation being a Cd atom [26]:



The first electron deposited is trapped and long-lived in this trap. The second electron reacts with the $\text{Cd}^{2+} e^-$ pair. As already mentioned above, the formation of Cd cannot occur through an intermediate Cd^+ ion.

When the number of deposited electrons is increased further, more and more Cd atoms are formed on the surface of the colloidal particles and the electrons then start to reduce the aqueous solvent to form hydrogen. This can also be demonstrated in an experiment with continuous illumination. Fig. 10 shows the Cd formation and H_2 evolution for a suspension of CdS containing 1 M Na_2SO_3 . The sulfite anions react with positive holes to form sulfate and a smaller amount of dithionite, the remaining excess electrons first produce cadmium metal, and after an induction period H_2 is generated [27].

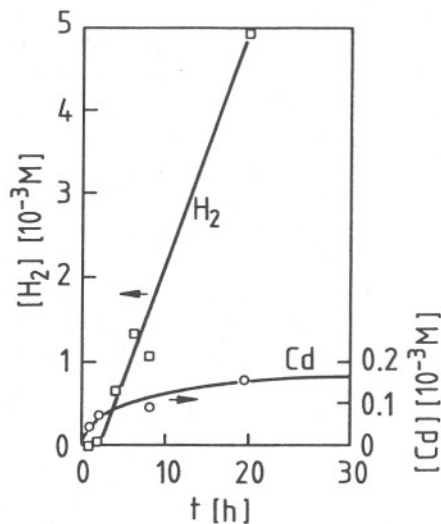


Fig. 10

Cd metal formation and H_2 evolution as functions of illumination time. CdS suspension in 1 M Na_2SO_3 solution

Discussion

The heterogeneous photochemistry occurring on colloidal semiconductor particles differs from the photo-electrochemistry of compact semiconductors, or even metal electrodes. First, band bending, which is very important for the charge separation in illuminated macroelectrodes, does not play a role in the case of small particles, as the size of the particles is much smaller than the thickness of the depletion layer. In the second place, the problem of storage of charge carriers exists. Many of the chemical reactions, such as H_2 formation from water, Cd metal formation at the surface of CdS, and oxidation of SO_3^{2-} anions, require two electrons or two positive holes, i.e. the absorption of two photons. However, one can easily calculate that the time interval between the absorption of two photons in one colloidal particle is some 100 μs or even longer depending on the light intensity. The first charge carrier, therefore, has to be stored until the next one arrives. This phenomenon is not encountered in the photoelectrochemistry or electrochemistry of compact sem-

iconductor electrodes where the second electron can rapidly be supplied by the external battery. The consequences with regard to the kinetics of the reaction on microelectrodes have recently been discussed by us [28]. We could not deal with this problem in detail in the present paper, although the mechanism depicted by Eqs. (15) and (16) is a typical example for the course of a two-electron transfer reaction.

Flash photolysis and pulse radiolysis experiments with colloidal particles often complete the studies in the electrochemistry of a semiconductor. The existence of surface states is derived in electrochemistry in a rather indirect way by electrical current measurements and capacity determinations. In the case of colloidal particles, electrons and holes localized at the surface can often be recognized by their optical absorption. Typical examples are the positive holes in CdS and Cd₃P₂ [8], and in TiO₂ [29]. After the absorption of such a surface species has been recognized, one can measure the rate constants of its reactions with dissolved substances [30].

The studies on the photocorrosion of CdS described above are another example for the use of colloidal particles for the understanding of important electrochemical reactions. They have for the first time revealed the importance of oxygen, if this corrosion is carried out in aerated solution.

The observations of quantum mechanical size effects in extremely small colloidal particles have added a new dimension to the chemistry and physics of colloids. The small particles represent the case where the quantum mechanical effect due to size restriction acts in all three dimensions. Solid state physicists would call this case the zero dimensional one as they count the number of dimensions where quantization does not take place. The two-dimensional case is already of practical importance in microelectronics where new chips with "superlattices" are being developed. These structures consist of alternating thin layers of two semiconductors with two different band gaps, the small band gap semiconductor forming a series of square-well potentials and the large gap semiconductor forming a series of potential barriers. In the case of very thin layers of a few nanometers, the electrons and holes form extended bands and the positions of these bands can be regulated by the thickness of the layers. Such superlattices also possess interesting properties as photoelectrodes in photoelectrochemistry [31]. As the quantization occurs only in one dimension, the shifts of the electronic levels are only of the order of a few 0.1 eV in most cases, while the shifts in colloidal particles, where quantization is operative in all three dimensions, can readily amount to several eV.

Electrons which are produced in colloidal CdS particles cause the absorption of the particles to change at the wavelength close to the absorption edge. The effect is astonishingly strong and makes it interesting to investigate small particles with respect to their non-linear optical properties.

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