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Abstract: The reactions of hydroxyl radicals with colloidal Q-CdS, Q-ZnS, and Q-Cd$_3$P$_2$ (materials of extremely small particle size showing optical size quantization effects) were studied pulse radiolytically. The radicals attack the particles at diffusion-controlled rates. In all three cases, a product with a broad absorption band in the visible (sulfides) or near-infrared (phosphide) is formed. This band shifts to shorter wavelengths with decreasing particle size (size quantization effect). It is attributed to surface trapped holes. These holes react with dissolved oxygen. The colloidal particles become a little smaller by OH attack. With use of a CdS sample with a structured absorption spectrum, it is shown that the product particles have their absorption maxima at slightly shorter wavelengths than the reactant particles (size quantization effect).

Radiation chemical studies on colloidal solutions of semiconductor materials allow one to investigate interfacial reactions of free radicals. The radicals are formed in bulk solution and transfer an electron to the colloidal particles. This electron transfer may lead to a cathodic dissolution of the colloid, such as in the case of silver halides. The transferred electrons may be stored for some time and produce a colored material, such as blue TiO$_2$, or reduce another solute in a two-electron-transfer process. Studies of this kind complement the studies on the photochemistry of such solutions. In the latter case, electrons and positive holes are generated by light absorption and the chemical reactions, which are initiated by these charge carriers, are investigated. The advantage of using radicals for the transfer of electrons is that excess electrons on small particles can be studied without positive holes being present simultaneously.

In the present studies, OH radicals are used to inject positive holes into semiconductor particles possessing anions such as S$^2-$ and P$^3-$ which are readily oxidized. The anodic corrosion is a disturbing problem in the electrochemistry and photoelectrochemistry of compact semiconductor electrodes. To generate OH radicals, colloidal solutions containing nitrous oxide were irradiated. Using the method of pulse radiolysis, one obtains information on the rate of OH attack and on the optical properties and lifetimes of the first intermediates of corrosion. The optical detection of intermediates at compact electrodes is not possible in most cases as the number of species produced in electrochemical experiments is too low. The experiments with colloidal particles

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of pulses were averaged. The solution slowly streamed through the irradiation vessel to avoid irradiation with more than one pulse. The base of the irradiation vessel was a 266; b, 94.

Therefore complement the corrosion studies in electrochemistry.

Special attention is paid in the present paper to the oxidation of "Q-materials". We use this term to designate materials of very small particle size which show size quantization effects due to the restrictions in space of the charge carriers. It has been shown that the optical properties of Q-materials strongly depend on particle size.\(^{8,11}\) Both the beginning of the light absorption and the fluorescence band are shifted toward shorter wavelengths with decreasing particle size. These materials represent a transition from bulk semiconductor properties to molecular properties. In some cases it was observed that the absorption spectrum contained several maxima spaced by 10 to 20 nm. This is explained by a structured size distribution of the colloids, i.e., the existence of preferential or "magic" agglomeration numbers.\(^{8,11}\) In the present work, it is shown that the size quantization effects can also be seen in the products of the reaction of hydroxyl radicals with very small colloidal particles.

**Experimental Section**

The pulse radiolysis apparatus with simultaneous detection of intermediates by optical absorption and conductivity measurements has already been described.\(^{12}\) In most of the experiments, radicals were generated in a low concentration of \(5 \times 10^{-7} \text{ M}\) in order to avoid multiple attack of the colloidal particles by the radicals. As the optical signals were very small under these conditions, the signals from a large number of pulses were averaged. The solution slowly streamed through the irradiation vessel to avoid irradiation with more than one pulse. The base line was recorded every other pulse and finally subtracted from the recorded signals.\(^{11}\)

The colloids were prepared, as recently described, by injecting hydrogen sulfide or phosphine into a deaerated solution of CdCl\(_2\) or ZnCl\(_2\).\(^{1,11}\) The solution also contained various amounts of sodium hexametaphosphate (Riedel de Haën). The solutions were always freshly prepared. They were bubbled for 30 min with purified nitrous oxide or oxygen as scavengers, the N\(_2\)O-O\(_2\) mixture was used in the experiments in which the stability of the trapped positive holes toward oxygen was to be investigated.

**Results**

**Cadmium Sulfide.** The absorption spectra of two CdS sols of different particle size are shown in the lower part of Figure 1. Note that the absorption coefficient \(e\) is expressed in \(M^{-1} \text{ cm}^{-1}\), where \(M\) is the molarity of colloidal particles. Sample a consisted of larger particles with a mean diameter of 3.3 nm, as determined by electron microscopy. It begins to absorb light slightly below 515 nm, the wavelengths at which macrocrystalline CdS starts to absorb. The absorption spectrum has a weak shoulder at 460 nm. Sample b consisted of smaller particles with a mean diameter of 1.6 nm. Its absorption begins at a much shorter wavelength than that of sample a. Two absorption maxima at 300 and 280 nm and a shoulder at 250 nm can be recognized. These maxima are attributed to exciton transitions in particles of preferential agglomeration numbers.\(^{8}\)

Parts a and b of Figure 2 show typical \(\Delta e\) vs. time curves obtained from pulse radiolysis experiments. \(\Delta e\) is defined as \((e_f - e_i) \times 10^6\), where \(e\) is the optical length of the cell, \(c\) the concentration of OH radicals produced in the pulse, and \(I_0\) and \(I_1\) the respective light intensities before and after the pulse.

Depending on the wavelength, one observes an increase or a decrease in absorbance after the pulse. A final plateau of the signal was always observed at times longer than 100 \(\mu\)s, and this plateau persisted for the time to which measurements could be extended. Several ms. \(\Delta e\) in the plateau represents the difference in specific absorbancies of the products of OH attack and the starting material. At longer wavelengths, where the starting material does not absorb, \(\Delta e\) is the absorption coefficient of the products. The OH radical practically does not absorb in the wavelength range investigated.

Note that wavelengths can be found (close to the beginning of light absorption) in the case of sol at which \(\Delta e\) first decreases and then increases at longer times after the pulse. This indicates
that the reaction first leads to a product which does not absorb and which is then transformed into an absorbing species. In Figure 3, the reciprocal half-life times of the increase in absorption at a longer wavelength and of the decrease at a shorter wavelength are plotted as functions of the overall concentration of colloid $a$. At very low concentrations, the two half-life times are almost equal. At higher concentrations, the decay at 460 nm becomes faster much more rapidly than the buildup at 650 nm. The latter strivers toward a limiting value of $3.2 \times 10^4$ s$^{-1}$. These effects are understood by a sequence of reactions

$$\text{OH} + \text{CdS} \rightarrow \text{P}_1 \rightarrow \text{P}_2$$

where $\text{P}_1$ is the first product of OH attack, which practically does not absorb, and $\text{P}_2$ is the absorbing second product. In the case of solution b, the life times of bleaching and buildup were always the same. The overall concentration of CdS in this solution was much lower than that in solution a, the consequence being that $\tau_2 \ll \tau_1$, i.e., the observed half-life time $\tau$ was always equal to $\tau_1$.

The upper part of Figure 1 shows $\Delta \varepsilon$ after 300 $\mu$s, i.e., after the reaction of OH + colloid was completed, as a function of the wavelength. A product $\text{P}_2$ is formed, which has a broad absorption band in the visible. This band is shifted toward shorter wavelengths with decreasing particle size. At wavelengths where this product has little or no absorption, $\Delta \varepsilon$ is negative in the case of sol a, as some of the absorbing CdS is consumed. However, in the case of sol b, one observes oscillations in $\Delta \varepsilon$. The wavelengths of the maxima of these oscillations roughly coincide with those of the minima in the spectrum of the starting material (lower part of Figure 1).

The molar conductivity of the solutions was found to be increased by 50 $\Omega^{-1}$ cm$^2$ with the same rate constant as the buildup of the absorbance of $\text{P}_2$. An increase would be expected if OH reacted via electron transfer to produce free OH$^-$.

Product $\text{P}_2$ was not stable in an oxygen-containing solution. Figure 4 shows a comparison of the time profiles of the 580-nm absorption for pulsed solutions containing $\text{N}_2\text{O}$ or the $\text{N}_2\text{O}/\text{O}_2$ (80:20%) mixture. It is seen that the absorption decays in the presence of oxygen. The decay followed pseudo-first-order kinetics. A rate constant of $1.3 \times 10^5$ M$^{-1}$ s$^{-1}$ was calculated for the reaction of product $\text{P}_2$ with oxygen. Experiments were also made at wavelengths in the range where $\Delta \varepsilon$ is negative (Figure 1). The signal was also practically constant in the presence of $\text{O}_2$. It is concluded that product $\text{P}_2$ does not significantly absorb in this wavelength range and that the negative $\Delta \varepsilon$'s in Figure 1 merely result from the decrease in CdS concentration by OH attack.

Zinc Sulfide and Cadmium Phosphide. In both cases, two solutions containing particles of different size were studied. The results are presented in Figures 5 and 6. A comparison with Figure 1 shows that the observed effects are quite similar to the effects observed for CdS. A long-lived product, with an absorption band in the visible (ZnS) or the transitory range between the visible and infrared (Cd$_3$P$_2$), is produced by OH attack. As for CdS, it is observed that this absorption band is blue shifted with decreasing particle size. In the case of ZnS, reaction of the absorbing particle with oxygen was found to also occur with $k = 1.3 \times 10^5$ M$^{-1}$ s$^{-1}$. In the case of Cd$_3$P$_2$, this experiment could not be carried out, since a thermal reaction of $\text{O}_2$ with the colloid...
size quantization effect would explain why the absorption band of S- is blue shifted with decreasing size of the colloidal particle. A similar explanation holds for the shift in the absorption of the P2- species produced in the oxidation of Cd3P2.

The attribution of the absorption band to a trapped hole or S- radical in the CdS particle, and the optical path length of a small particle size, the wavelength at which a transition to the exciton state takes place strongly decreases with decreasing particle size. As the particles become a little smaller by OH attack, their material had a structured absorption spectrum. In Q-CdS of very small particle size, the absorption maxima appear at shorter wavelengths. Before application of a pulse of radiation, the absorbance at the optical path length of 1 cm of the solution is

\[ E_0 = \varepsilon_1 c_1 \tag{4} \]

\( \varepsilon_1 \) being the absorption coefficient of the colloidal particles (expressed in \( M_p^{-1} \text{ cm}^{-1} \), where \( M_p \) is the molarity of the particles). After the pulse, the absorbance is

\[ E = \varepsilon_2 (c_1 - c_2) + \varepsilon_2 c_2 + \varepsilon_2 c_2 \tag{5} \]

where \( \varepsilon_2 \) is the concentration of radicals formed. \( c_1 \) was always smaller than \( c_1 \), i.e., one colloidal particle was attacked by no more than one radical. \( c_1 - c_2 \) is the concentration of undamaged CdS particles. \( \varepsilon_2 \) is the absorption coefficient of the intact (CdS) particles, part of the damaged particles (eq 3), and \( \varepsilon_2 \) the absorption coefficient of the trapped hole (or S- radical in the CdS particle, eq 3). The observed change in absorbance is

\[ \Delta E = c_2 (\varepsilon_2 + \varepsilon_3 - \varepsilon_1) = c_2 \Delta \varepsilon \tag{6} \]

from which \( \Delta \varepsilon \) is calculated as

\[ \Delta \varepsilon = \Delta E / c_2 \tag{7} \]

At long wavelengths \( \varepsilon_1 \) and \( \varepsilon_2 \) are zero and \( \Delta \varepsilon = \varepsilon_1 \), and at wavelengths where \( \Delta \varepsilon \) is negative or shows oscillatory behavior, \( \varepsilon_1 \) is, as pointed out above. In Figure 7, the full line represents the absorption spectrum of the colloid before the pulse and the dashed line the spectrum afterwards. We assumed here that the shift due to the size quantization effect was sufficient to move the maxima into positions where the minima were located before the pulse. If \( \Delta \varepsilon \) is measured at a wavelength \( \lambda \), it will be slightly positive, while in a measurement at wavelength \( \lambda_2 \) a strong negative change in absorbance will be found. This explains in principle the oscillatory behavior of \( \Delta \varepsilon \).

**Table I. Calculated and Observed Half-Life \( r^{650} \) for Various CdS Concentrations of Sol a**

<table>
<thead>
<tr>
<th>[CdS], M</th>
<th>( t^{650} ) obsd, ( \mu s )</th>
<th>( t^{650} ) calc, ( \mu s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 \times 10^{-3}</td>
<td>1.2</td>
<td>5</td>
</tr>
<tr>
<td>2 \times 10^{-3}</td>
<td>2.7</td>
<td>12</td>
</tr>
<tr>
<td>1 \times 10^{-3}</td>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td>5 \times 10^{-4}</td>
<td>10</td>
<td>18</td>
</tr>
</tbody>
</table>

\( t^{650} \) is the observed half-life of bleaching.

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**Registry**

- CdS, 1306-23-6; ZnS, 1314-98-3; Cd3P2, 12014-28-7; OH, 3352-57-6; H2O, 7732-18-5; O2, 7782-44-7; N2O, 109-95-5.