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Photochemistry and Radiation Chemistry of Colloidal Semiconductors. 23. Electron Storage on ZnO Particles and Size Quantization

Markus Haase, Horst Weller, and Arnim Henglein*

Hahn-Meitner-Institut Berlin, Bereich Strahlenchemie, 1000 Berlin 39, Federal Republic of Germany
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Improved methods for the preparation of colloidal ZnO solutions of different particle size are described, and the relation between absorption threshold and particle size is reported. CH_2OH radicals, radiolytically generated, transfer electrons to ZnO particles. The electrons are long-lived and cause a substantial blue shift of the absorption spectrum of ZnO in a wavelength range of 60 nm below the threshold. The wavelength of maximum bleaching is shifted to shorter wavelengths with decreasing particle size (size quantization effect). Maximum bleaching occurs with a negative absorption coefficient of $1.1 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$. Electrons are also stored upon UV illumination of colloidal ZnO. The stored electrons react rather slowly with oxygen, the rate constant becoming lower with increasing particle size, and more rapidly with peroxy radicals.

Introduction

Zinc oxide is a semiconductor which has often been investigated in photoelectrochemistry¹ and photocatalysis.^{2,3} After the preparation of ZnO as transparent colloidal solution became possible,^{4,5} the photochemical studies on this material could be extended by the application of the fast kinetic methods of flash photolysis and pulse radiolysis. The previous studies have shown that electrons deposited on small particles of ZnO influence their optical absorption and fluorescence.⁴⁻⁶ Excess electrons can be generated either by UV light absorption in the colloidal particles or by electron transfer from reducing free radicals produced radiolytically in the bulk solution. Both methods are described in the present paper. Experiments of this type are of fundamental importance for the understanding of the mechanism of interfacial electron transfer in heterogeneous photocatalysis and of the mechanism of electron storage on semiconductor microelectrodes.

The preparation of ZnO sols has previously been described.⁴ In principle, Zn^{2+} ions are reacted with NaOH in alcohol solution, making use of the dehydrating properties of this solvent to prevent the formation of zinc hydroxide. However, it is crucial to use an alcohol having a certain water content that controls the rate of growth of the colloidal particles. The mechanism of ZnO formation is rather complex and poorly understood. Some improved methods of preparation are also described in the present paper.

Small ZnO particles show typical size quantization effects,^{4,5,7} the onset of light absorption and position of the fluorescence band being shifted to shorter wavelengths with decreasing particle size. This effect has now been investigated in more detail to obtain the relationship between particle size and the wavelength of the absorption threshold.

Experimental Section

Preparation of Colloidal Solutions. ZnO forms stable colloids in methanol if either Zn^{2+} or OH^- ions are present in excess. For the preparations described below, two stock solutions were made: (A) 0.2 M NaOH in CH_3OH by dissolving 2.0 g of NaOH in 250 mL of methanol and (B) 0.2 M $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ by dissolving

7.448 g of this salt (Alfa-Ventron) in 100 mL of methanol p.a. (Merck, water content <0.05%).

ZnO Sols with Excess Zn^{2+} Ions. A 20-mL sample of solution A was diluted with 800 mL of methanol. A 5-mL sample of solution B was added by means of a pipet under strong stirring. At the spot where the drops fell into the solution local turbidity was produced as $\text{Zn}(\text{OH})_2$ precipitated. This turbidity rapidly disappeared as tetrahydroxozincate was formed. The solution finally became transparent after 5 min of additional stirring. A mixture consisting of 7 mL of solution B, 5 mL of water, and 100 mL of methanol was then added under vigorous stirring within about 10 s and methanol was added to bring the solution to a volume of 1 L. The opalescing solution was then stirred overnight at 20 °C. The opalescence disappeared, and a transparent $2 \times 10^{-3} \text{ M}$ ZnO solution with $4 \times 10^{-4} \text{ M}$ excess Zn^{2+} was obtained. This solution was stable for about 1 week and contained relatively small particles (mean diameter $\sim 20 \text{ \AA}$). Using 1:1 dilution with methanol led to a substantial increase in stability (stable for weeks). Figure 1 shows how the spectrum of the colloid developed after the addition of the stock solution B–water–methanol mixture. As reported previously,⁴ the absorption threshold moved toward longer wavelengths as the particles grew, which is explained by the quantization of the electronic energy levels in the small particles.

The mean size of the ZnO particles in the diluted methanol solution was about 20 Å. The solution had an absorption of only a few percent at 347 nm, the wavelength of the frequency-doubled ruby laser with which the flash photolysis experiments were performed. A solution with a stronger absorption at 347 nm was obtained by mixing the diluted methanol solution with water (60% water, 40% solution) under argon. The particles grew in the mixture to about 40 Å. This water-containing solution was stable for about 2 days.

ZnO Sols with Excess OH^- Ions. Two procedures were applied where first a tetrahydroxozincate solution was made in which ZnO developed in the presence of a small amount of water.

In the first procedure, 75 mL of stock solution A was diluted with 600 mL of methanol. A mixture of 15 mL of solution B and 70 mL of methanol was added under vigorous stirring. The zincate solution formed was transparent and stable. ZnO formation was started by adding a mixture of 5 mL of water and 95 mL of methanol under strong shaking. Methanol was added to bring the solution to a volume of 1 L and stirred for 24 h at 20 °C. The transparent ZnO sol, which was stable at 20 °C for weeks, contained $3 \times 10^{-3} \text{ M}$ ZnO and $9 \times 10^{-3} \text{ M}$ excess OH^- . Lower OH^- concentrations led to less stable sols. Figure 2 shows the absorption spectrum during the development of the colloid. Again, one observes a shift of the absorption threshold to longer wavelengths. Note that the threshold after long ripening of the colloid is still far below 372 nm, i.e., the threshold of macrocrystalline ZnO.

In the second procedure, a very concentrated ZnO sol was obtained which then was diluted with methanol. It could also be

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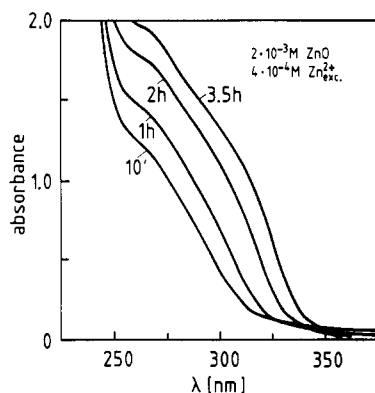


Figure 1. Development of the absorption spectrum of ZnO in methanol at 20 °C and in the presence of 20% excess Zn^{2+} ions. Note that the long wavelength tail is due to scattering which becomes smaller with increasing reaction time.

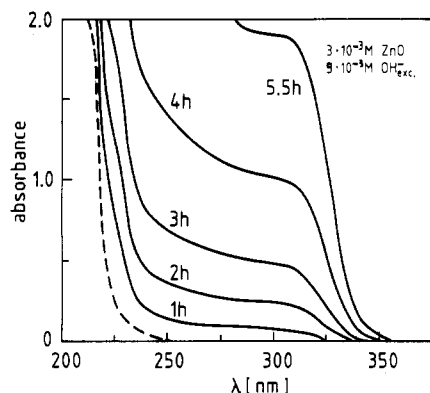


Figure 2. Development of the absorption spectrum of ZnO in methanol at 20 °C and in the presence of 300% excess OH^- ions. The dashed line is the spectrum of the zincate solution.

diluted with 2-propanol or 2-methyl-2-propanol to obtain sols where these diluents were the main solvents (>95%). A 10-mL sample of stock solution B was added dropwise to 50 mL of stock solution A. The transparent zincate solution obtained was stored in a closed vessel at 20 °C. ZnO formed over 2 days, the reaction of zincate being initiated by the water content of solution B (due to the water in $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$). The sol finally obtained contained 3.3×10^{-2} M ZnO, 0.2 M water, and 0.1 M excess OH^- . As it was stable for only a few days, it was diluted with 940 mL of methanol, giving a solution containing 2×10^{-3} M ZnO and 6×10^{-3} M excess OH^- which was stable at 20 °C for weeks. When the concentrated sol was diluted with 2-methyl-2-propanol or 2-propanol, the resulting solution was stable for only a few days.

Apparatus. Particle sizes were determined by transmission electron microscopy. To prepare the samples, a drop of the colloid solution was applied to a copper mesh covered with a carbon film for 30 s and subsequently removed with a paper tip. Adhesion of the particles was promoted by exposing the carbon film to a glow discharge prior to this procedure. The granulation contrast originating from the amorphous carbon film was suppressed by an opodization technique.⁸

Irradiations were carried out with a pulsed laser or a 4-MeV Van de Graff generator. The radicals were produced in a low concentration of less than 10^{-6} M to avoid radical-radical deactivation. In some experiments a train of pulses with long intervals between the pulses was applied. The signals for eight pulses (or trains of pulses) were averaged. The base line was recorded every other pulse and finally subtracted from the recorded signals. γ -Irradiations were carried out with a ^{60}Co source.

The flash photolysis experiments were performed with a frequency-doubled ruby laser ($\lambda = 347.1$ nm, 15-ns pulse width). The data from several flashes were digitized and transferred to

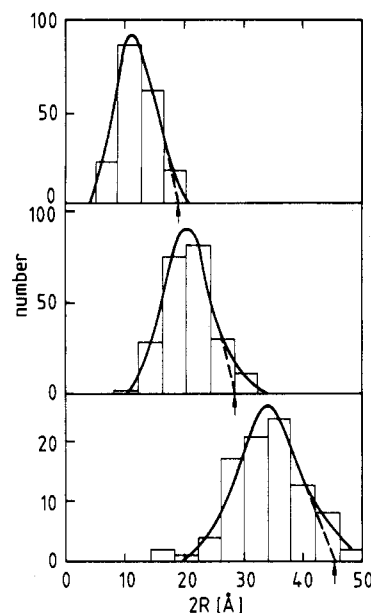


Figure 3. Electron microscopic histograms of various ZnO samples. The arrows point to the extrapolated values of the particle size.

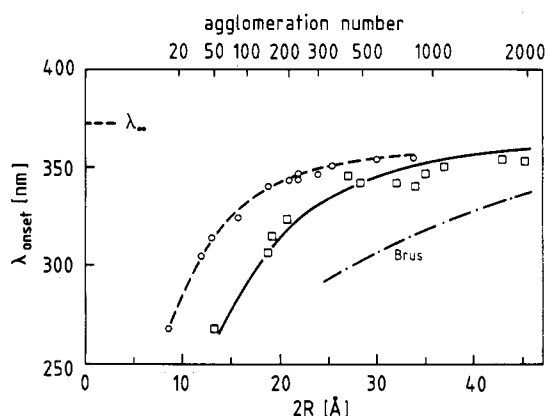


Figure 4. Wavelength of absorption onset as a function of particle size: (\square) experimental points obtained by extrapolation (see Figure 3); (\circ) mean size of the samples used; (—) quantum mechanical calculation. The results of a quantum mechanical calculation by Brus¹⁴ are also included (---).

a PDP 11/40 computer. The digitized signals were analyzed on-line by using a Tektronix 4010 interactive graphic display.

Colloidal ZnO is very sensitive toward UV light. It was therefore necessary to carry out the laser flash and electron pulse experiments with a low-intensity analyzing light beam.

Results

Particle Size and Absorption. Figure 3 shows histograms of various ZnO colloids as determined by electron microscopy. The solution was investigated at different times after precipitation, i.e., at different phases of particle growth. As has already been described for cadmium sulfide,⁹ the particle size, which can be related to the onset of absorption, was obtained by extrapolating the steep part of the size distribution curve. The onset of light absorption was obtained by extrapolating the steep part of the rising absorption curve. In Figure 4, the wavelength of the absorption threshold is plotted versus the particle diameter. Above 40 Å, the particles absorb close to 372 nm, where macrocrystalline ZnO starts to absorb. With decreasing size, the onset is more and more rapidly shifted toward shorter wavelengths. Figure 4 also contains a curve which relates λ_{onset} with the mean particle size of the samples as determined by electron microscopy. This curve is of practical interest, when one wishes to obtain the mean

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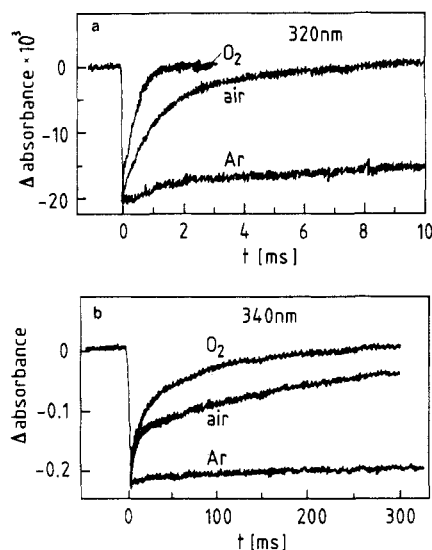


Figure 5. (a) Change in absorbance as a function of time after a laser flash. 1×10^{-3} M ZnO and 2×10^{-4} M excess Zn^{2+} in methanol. Concentration of absorbed photons: 4×10^{-5} M. Mean ZnO particle size: 17 Å. (b) Change in absorbance as a function of time after a laser flash. 8×10^{-4} M ZnO and 1.6×10^{-4} M Zn^{2+} in methanol-water (40:60 vol %). Concentration of absorbed photons: 3×10^{-4} M. Mean ZnO particle size: 40 Å.

agglomeration number or the concentration of the particles from the absorption spectrum.

Laser Flash Photolysis. Figure 5a,b shows the time profiles of the absorbance changes which were recorded after application of a single 347-nm flash of the ruby laser. Immediately after the flash, a negative signal was observed at 320 and 340 nm, respectively. The higher the concentration of oxygen in the solution, the more rapidly it decayed after the flash. In the case of the small particles (Figure 5a) the decay was much faster than for the larger ones (Figure 5b).

The spectra of the absorbance change are shown in the upper part of Figure 6a,b. The lower part of the figures contains the absorption spectra of the solutions. It is seen that the signal is negative in a wavelength range of about 60 nm below the onset of absorption. In the previous studies on the continuous illumination of deaerated ZnO solutions long-lived bleaching had been observed in this wavelength range.^{4,5} The dashed curve in the lower part of Figure 6b is the absorption spectrum of the solution after the laser flash as calculated from the original absorption spectrum and the changes in absorption. Note that the absorbance at the laser wavelength of 347 nm was much lower in the experiments of Figures 5a and 6a than in those of Figures 5b and 6b.

γ -Radiolysis. A deaerated solution of 1×10^{-3} M ZnO containing 3×10^{-3} M excess NaOH and 0.1 M formaldehyde as electron scavenger was γ -irradiated at a dose rate of 2.45×10^4 rad/h. Figure 7 shows the absorption spectrum at different times of irradiation. It is seen that the onset of absorption was shifted to shorter wavelengths, this effect becoming less and less pronounced with increasing irradiation time until a final shift was reached after about 7 min. γ -Ray absorption produces reducing organic radicals, CH_2OH , with a radiation chemical yield of 6.6 radicals per 100 eV of absorbed radiation energy,¹⁰ which are, to a certain degree, dissociated in the presence of NaOH: $\text{CH}_2\text{OH} + \text{OH}^- \rightleftharpoons \text{CH}_2\text{O}^- + \text{H}_2\text{O}$.¹¹ The reaction of these radicals with the colloidal particles produced the same shift in absorption as the direct illumination with UV light.^{4,5}

The shifts persisted after the irradiation for about 20 min and then very slowly disappeared. Exposure of the irradiated solution to air led to an immediate recovery of the absorption spectrum.

In Figure 8, the change in absorbance at various wavelengths is plotted as a function of the radiation dose. The latter is given

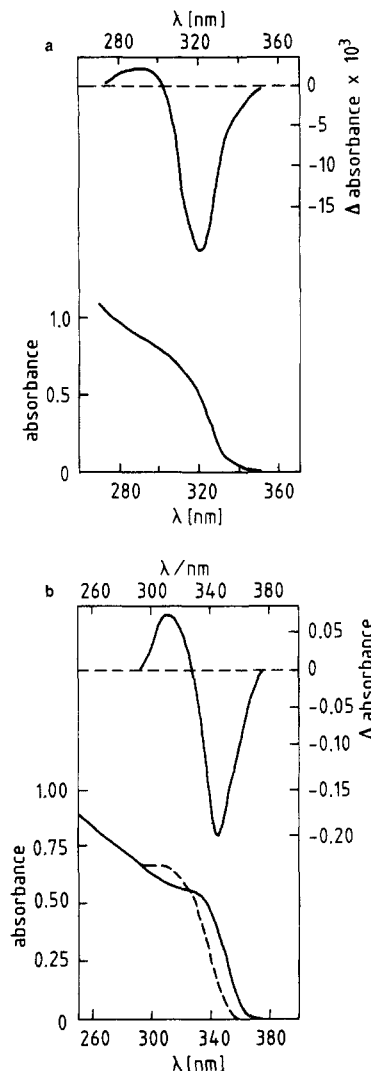


Figure 6. (a) Upper part: Change in absorbance immediately after the laser flash as a function of wavelength. Lower part: Absorption spectrum of the ZnO sol. Solution as in Figure 5a. (b) Upper part: Change in absorbance immediately after the laser flash as a function of wavelength. Lower part: full line, absorption spectrum of the ZnO sol; dashed line, spectrum of the solution after the laser flash. Solution as in Figure 5b.

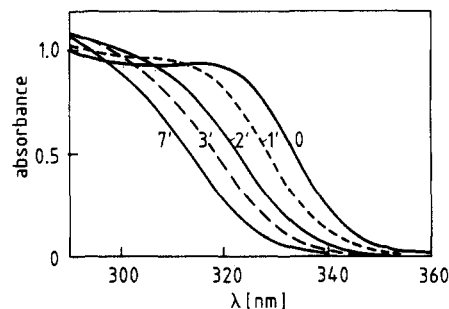


Figure 7. γ -Irradiation of a deaerated 1×10^{-3} M ZnO sol in methanol containing 0.1 M formaldehyde and 3×10^{-3} M NaOH. Absorption spectrum at different times of irradiation. Dose rate: 2.45×10^4 rad/h.

in terms of the concentration of CH_2OH radicals produced. It is recognized that a decrease in absorbance was observed at wavelengths above about 315 nm. At shorter wavelengths an increase occurred in the early stages of irradiation, followed by a decrease at higher doses.

Pulse Radiolysis. Two sols of different particle size were used in the pulse radiolysis experiments. Sol A contained particles of mean size 30 Å in water-methanol (60:40 vol %); sol B contained 20-Å particles in methanol. The absorption spectra of both solutions are shown in the lower part of Figure 9.

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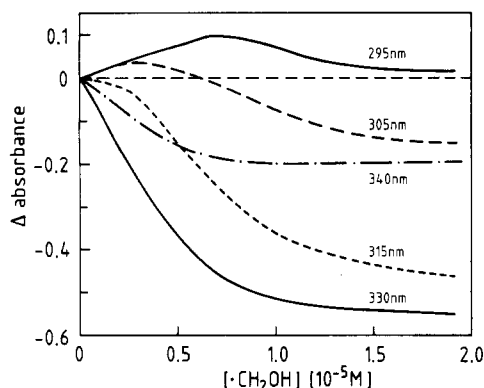


Figure 8. Change in absorbance at various wavelengths as a function of irradiation dose (dose expressed as concentration of radicals generated). Solution as in Figure 7.

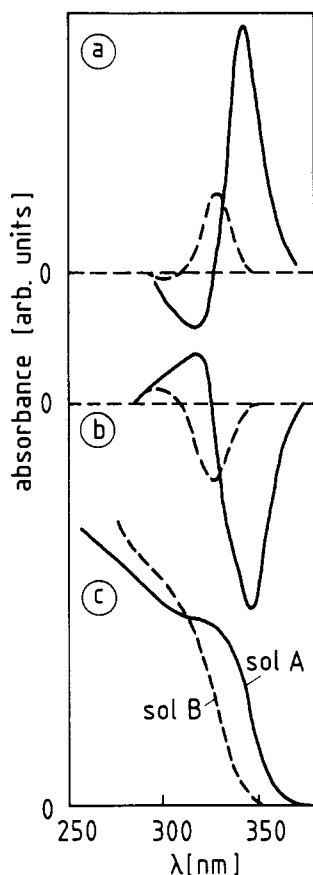


Figure 9. Absorption spectrum of the two colloids used in the pulse radiolysis experiments (c) and difference spectra in the irradiation of the solutions under N_2O (b) and air (a). In the experiments with N_2O -saturated solutions, the intensity of the analyzing light beam was very low; in the experiments with air-containing solutions, a high light intensity was used. Particles in sol A were larger than in sol B.

Two kinds of experiments were performed with these sols.

In the first experiment, the solution was saturated with nitrous oxide and the intensity of the analyzing light beam kept very low. Under these conditions, CH_2OH radicals were generated which attacked the colloidal particles after the pulse. In most of the experiments, a train of eight pulses were used, the duration of a pulse being $1.5 \mu s$ and the interval between the pulses 50 ms. Typical kinetic traces are shown in Figure 10 for sol A. It can be seen that the absorption at 340 nm decreased within a few milliseconds after each pulse, the decrease after the first pulse being noticeably smaller than after the following ones. At 320 nm, however, an increase after each pulse was observed. Similar observations were made with sol B. The absorbance changes after the third pulse were used to construct the difference spectra shown in part b of Figure 9. They are quite similar to the spectrum

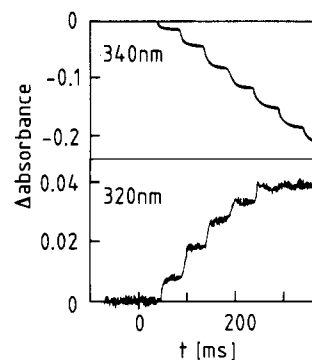


Figure 10. Changes in absorbance of sol A (30-Å particles) upon irradiation with a train of pulses (irradiation under N_2O , low intensity of analyzing light beam).

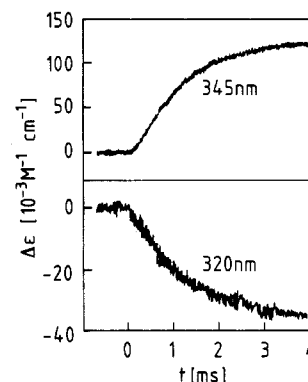


Figure 11. Changes in absorption of sol A in a single pulse experiment (irradiation under air, high intensity of analyzing light beam).

obtained after laser illumination (Figure 6); i.e., bleaching occurred in a certain wavelength range below the absorption threshold, followed by an increase in absorption at shorter wavelengths. The difference spectrum was more intense for sol A ($\Delta\epsilon_{\max} = -1.1 \times 10^5 M^{-1} cm^{-1}$). Note that the observed changes in absorbance were independent of the analyzing light intensity provided that low intensities were applied.

In the second experiment, the solutions contained air and the intensity of the analyzing beam was high. Under these circumstances oxidizing free radicals, such as O_2^- and O_2CH_2OH , were formed which reacted with the colloidal particles during the interval between the pulses. Figure 11 shows kinetic traces obtained with sol A in single-pulse experiments. Depending on the wavelength, bleaching or absorption signals were observed. Note that the half-life time of the buildup of these changes was independent of the wavelength of absorption. It amounted to 0.84 ms. The difference spectra for the two sols are shown in part a of Figure 9. It is seen that these spectra are mirror images of the spectra shown in part b. In other words, where bleaching occurred in the experiments of part b absorption signals were observed in the experiment of part a, and vice versa. Note that in these experiments the change in absorption became stronger with increasing intensity of the analyzing light.

Experiments under N_2O were also carried out with solutions in which 2-propanol or 2-methyl-2-propanol were the solvents (besides a small amount of methanol; see Experimental Section). It was found that the $(CH_3)_2COH$ radicals, which were generated in 2-propanol, reacted as fast with the colloidal particles as the CH_2OH radicals produced in methanol solution. The $CH_2(C-H_3)_2COH$ radicals which were generated in 2-methyl-2-propanol did not react with the ZnO particles.

Discussion

Formation of Colloidal ZnO. ZnO cannot be made as a colloid by reaction of Zn^{2+} ions with NaOH as the hydroxide which is formed does not dehydrate: $Zn(OH)_2 \rightarrow ZnO + H_2O$. In fact, it can be calculated from the thermodynamic data of the substances involved that the dehydration reaction is practically

thermoneutral at room temperature. That ZnO is formed in alcoholic solution must be due to a substantially lower free enthalpy of the products of hydration. Kinetically, the process is very complex. It was observed that ZnO is formed in alcoholic solutions only in the presence of small amounts of water. Further, in our preparations, first a stable solution of tetrahydroxozincate was made, and the formation of ZnO was initiated by the addition of water to this solution. It thus seems that water exerts a catalyzing effect on the transformation of zincate into ZnO in methanol solution. No detailed mechanism of this catalysis can be given at the present time.

Particle Size and Absorption Threshold. Quantum mechanical calculations of the shift of the band gap in small semiconductor particles were first carried out by Efros and Efros¹² and by Brus.^{13,14} In Brus' treatment, the lowest eigenstate of an exciton was calculated by solving Schrödinger's equation at the same level of approximation as is generally used in the analysis of bulk crystalline electron-hole states. Both the electron and the hole were considered as particles in a spherical box, and the usual values of the effective masses of the charge carriers were used. More recently, it was shown that the experimental observations on small CdS particles could be well described by wave mechanical one-body calculations using a wave function of the form $\exp(-\gamma r)\psi_1(r)$, where the hydrogen-like factor takes account of the Coulomb attraction and $\psi_1(r) = 1/r \sin(\pi(r/R))$ is the lowest particle-in-a-spherical-box orbital (γ = variational parameter, R = radius of the particle, r = distance from center of particle). For $r \gg R$, a potential increase of 3.8 eV was used.^{9,15}

The curve in Figure 4 was calculated by using the above wave function, expressing r and R in units of $\epsilon_\infty \hbar^2 / \mu^* e^2$, where the reduced effective mass, μ^* , was 0.1775 and the dielectric constant of ZnO (ϵ_∞) was 3.82, and again using a potential jump of 3.8 eV. Taking into consideration that certain unknowns exist in these calculations such as the exact shape of the particles and the applicability of the bulk values of μ^* and ϵ_∞ , one may conclude that there is good agreement between the experimental observations and the theoretical calculations on small ZnO particles. The results of calculations by Brus are also included in Figure 4. They overestimate the size quantization effect.

Blue Shift of Absorption upon Illumination. In the laser flash photolysis experiments (Figures 5 and 6) similar observations were made as in the previous studies on the continuous illumination of ZnO sols.⁴⁻⁶ The onset of absorption was shifted to shorter wavelengths; i.e., an effect was observed as if the particles had become smaller under illumination. In fact, in our first explanation of the phenomenon, a mechanism of dissolution of illuminated ZnO was discussed and the absorption shift attributed to the decrease in size of the colloidal particles. However, after it was found later in the case of small CdS particles that storage of an electron affected the absorption spectrum in the same way, it was proposed that illumination of ZnO particles also produces excess electrons.⁶ The shift is explained by an increase in the energy of the exciton formed by light absorption due to the strong electric field caused by the excess electron. Perhaps, it could also be explained as the first step of "band filling", whereby the excess electron fills the lowest state so that subsequent absorption requires higher photon energies in order to access empty states. The conclusion that the shift is caused in ZnO by excess electrons is corroborated by the fact that the shift in aqueous ZnO sols was much stronger when alcohol was present. The alcohol acts as a scavenger of the positive holes, simultaneously formed upon light absorption, and thus prevents the electrons from recombining with holes.

The excess electrons are long-lived in the absence of oxygen. In the presence of O₂, they are removed from the colloidal particles which explains the decay of the bleaching signal after the laser

flash (Figure 5). However, this reaction is relatively slow. From the half-life time of 0.8 ms in air-saturated solution (Figure 5a), one calculates a rate constant of $3.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for the reaction of O₂ with electrons stored on 17-Å ZnO particles. In the case of 40-Å particles (Figure 5b) the specific rate is about 50 times lower. It thus seems that the electrons are present in traps of less negative potential in the case of large particles as is expected from the theory of size quantization.

In the laser experiments, where the wavelength of the exciting light was not far from the onset of absorption, smaller particles in the solution were less excited, or even not at all, than the larger particles which possibly absorbed more than one photon. Under these conditions, a more detailed analysis of the data, such as a correlation between the amount of bleaching and the number of excess electrons, did not seem promising. Clearer conditions prevailed in the γ -radiolysis experiments where the number of stored electrons was known and no loss of electrons due to recombination with holes had to be feared.

γ -Radiolysis: Electron Injection from Free Radicals. When reducing radicals, which are formed in the γ -irradiation of methanol or 2-propanol solutions, react with ZnO particles, similar changes in the absorption spectrum were observed as in the UV illumination of such solution. The effects are explained in terms of electron injection from the organic radicals onto ZnO particles. In fact, CH₂OH and (CH₃)₂COH radicals have reduction potentials (-1.0 and -1.5 V, respectively¹⁶) which are much more negative than the lower edge of the conduction band in ZnO (-0.2 V). On the other hand, the CH₂(CCH₃)₂OH radicals, formed in 2-methyl-2-propanol solution, did not react with ZnO which is understood in terms of the lower reducing power of such radicals.

From the initial slope of the curve for 330 nm, where maximum bleaching occurred in the experiments of Figure 8, a negative absorption coefficient of $9 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ is calculated. The mean agglomeration number of the colloidal particles was 230. At an overall concentration of $8 \times 10^{-4} \text{ M}$ ZnO, the particle concentration was $3.5 \times 10^{-6} \text{ M}$. The solution had an absorbance of 0.6 at 330 nm (curve 0 in Figure 7), the absorption coefficient of the colloidal particles being $0.6 / 3.5 \times 10^{-6} = 1.7 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$. We thus find that deposition of an electron on a small colloidal ZnO particle is accompanied by a decrease in its 330-nm absorption by almost a factor of 2. This indicates that the excess electron influences not just one ZnO molecule in the colloidal particle but an optical transition in which practically all the ZnO molecules in the particle are involved. We have made similar arguments in our previous study on electron deposition on small CdS particles.⁶

When more than one electron is deposited per ZnO particle, i.e., when more than about $3.5 \times 10^{-5} \text{ M}$ free radicals were generated in the experiments of Figure 8, the changes in absorbance no longer increased in a linear manner. At 330 and 340 nm, the absorbance decreased less and less strongly. At 315 nm, little absorption changes occurred during deposition of just one electron, but significant bleaching took place upon the storage of additional electrons. At still shorter wavelengths in Figure 8, a slight increase occurred upon deposition of the first electron, which was followed by a slight decrease upon further electron injection. The nature of the stored electrons is not known yet. They could be present in traps or in the form of monovalent zinc ions, Zn⁺. The latter possibility does not seem very plausible because of the very negative redox potential of Zn⁺ (<-2 V). On the other hand, Zn⁺ is known to absorb close to 300 nm,¹⁷ i.e., the wavelength where the absorption increased upon deposition of one electron. When more than one electron is present, isolated Zn atoms may be formed.

Pulse Radiolysis: Reactions of Reducing and Oxidizing Radicals. As in the continuous irradiation experiments (Figure 7), the reaction of pulse radiolytically generated CH₂OH radicals with ZnO particles caused bleaching at longer and absorption at

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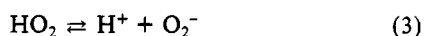
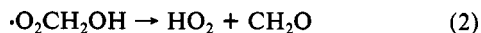
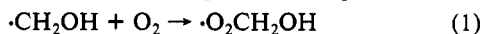
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shorter wavelengths (Figures 9 and 10). Upon application of the first pulse (Figure 10) the changes in absorbance were smaller than in the subsequent ones. This is attributed to traces of oxygen adsorbed on the colloidal particles which cannot be removed by bubbling the solution with another gas. The small radiation dose applied in the first pulse was sufficient to remove this residual oxygen. The rate constant of reaction of the radicals with ZnO particles was determined in a single-pulse experiment using a solution which had been preirradiated with two pulses. At a concentration of ZnO particles of 3.5×10^{-6} M the half-lifetime of the 340-nm bleaching, which obeyed pseudo-first-order kinetics, was about 2 ms. A rate constant of $1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ is calculated. This value is more than 10 times smaller than expected for a diffusion-controlled reaction.

It has already been mentioned that the intensity of the analyzing light beam had to be kept low in the laser flash and electron pulse experiments using N_2O -saturated solutions in order to avoid storage of electrons on the ZnO particles before the laser flash or electron pulse arrived. In experiments with aerated solutions (Figures 9a and 11) the intensity of the analyzing light beam was as strong as in ordinary pulse radiolysis experiments with chemical systems that do not photolyze. The reaction of oxygen with stored electrons being rather slow as described above, illumination with the analyzing light beam led to a certain stationary concentration of stored electrons on the colloidal particles. The oxidizing radicals which were formed in the electron pulse via the processes



thus reacted with ZnO particles already carrying electrons. Removal of an electron by an oxidizing radical was accompanied by the recovery of the bleaching (at 345 nm) and of the absorption (at 320 nm) which were originally caused by this electron. The result being that an absorption signal at 345 nm and a bleaching signal at 320 nm were now observed (Figure 11). The mirror images of the difference spectra obtained after the attack of reducing and oxidizing radicals (Figure 9) are thus readily understood. From the data in Figure 11 it was calculated that the oxidizing radicals reacted with a specific rate of $3.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ with the colloidal particles.

The changes in absorbance were smaller when ZnO particles of smaller size were used in the experiments of Figure 9. When

an excess electron is deposited on a smaller ZnO particle, the number of ZnO molecules affected is smaller, this effect leading to a smaller change in absorbance. On the other hand, one would expect that the optical changes should also become smaller in the case of very large particles (larger than used in the present work) as the electric field produced by the excess electron would be rather weak in parts of the particle. These two opposing effects make us believe that there might exist a definite particle size where the absorbance changes that accompany the deposition of one electron are most pronounced. The large bleaching coefficient of $1.1 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$, observed for 40–50 Å particles, may be taken as an indication that this particle size is close to 40 Å. However, further experiments with particles of different size are required to check the validity of this supposition.

It has recently been proposed that the fluorescence of colloidal ZnO in aerated solution is brought about by a "shuttle" mechanism.⁵ An electron generated by light absorption transfers to adsorbed O_2 to form O_2^- . The latter transfers the electron into a deeper trap on the surface. Recombination with a preexisting hole is accompanied by light emission. In the course of the present studies on solutions in which O_2^- is formed a few experiments were carried out to check this mechanism. In an experiment with the analyzing light beam shut off, fluorescence light should have been emitted, if O_2^- transferred an electron to ZnO and if recombination with a preexisting hole took place. No fluorescence was observed. We have to conclude that the more direct kinetic method of pulse radiolysis does not confirm the above mechanism. A shuttle mechanism in solutions containing methylviologen, MV^{2+} , as additive has also been proposed, MV^+ acting as the shuttle agent which is formed by electron transfer to MV^{2+} and then transfers its electron into a lower surface state of ZnO.⁵ More recent pulse radiolysis experiments in our laboratory showed that MV^+ does not react with ZnO particles. Again, it must be concluded that a shuttle mechanism is not operative.

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Registry No. ZnO, 1314-13-2; CH_2OH , 2597-43-5; O_2 , 7782-44-7; formaldehyde, 50-00-0.

Thermodynamic Properties of Liquid Toluene

L. Ter Minassian,* K. Bouzar, and C. Alba

Laboratoire de Chimie Physique, 11 rue P. et M. Curie, 75231 Paris, France (Received: May 13, 1987; In Final Form: July 29, 1987)

Expansivity and compressibility measurements have been made for toluene in the temperature range 200–450 K up to 4 kbar. The experiments were performed by a modified piezothermal technique bringing out a self-consistent set of data for these quantities. An anomaly is observed in the behavior of the heat capacities at low temperature in the high-density region. This has been interpreted as a progressive conversion from one type of molecular motion to another as volume increases. The qualitative aspects of this phenomenon are discussed.

Introduction

In a previous study,¹ we have reported a set of empirical equations of the thermodynamic properties of the liquid phase based on a direct measurement of the expansivity α as a function

of pressure and temperature. Derived from such molecules as CO_2 and *n*-butane, these equations exhibit simple forms:

(i) As a function of pressure, the expansivity follows a square root law

$$\alpha = A/(p - p_\lambda)^{1/2} \quad (1)$$

where A and p_λ are pressure-independent coefficients. In spite

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