Particle Size and Surface Chemistry in Photoelectrochemical Reactions at Semiconductor Particles

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In the present paper reactions at small and large ZnS particles have been investigated. It has been shown that ethanol is selectively oxidized at large (micrometer) particles to acetaldehyde without side products by a "two hole" process. In the case of nanometer particles the primarily formed α-hydroxyethyl radicals in a "one hole" process undergo a secondary reaction, i.e., the dimerization and disproportionation of the free radicals. It has been shown that a two hole process on nanometer particles becomes impossible because the time interval between two successive photon absorption incidents which lead to a successful hole transfer process in a 1-nm particle is much longer than the maximum lifetime of the α-hydroxyethyl radicals formed in the first step. The different mechanisms of ethanol oxidation and the influence of surface chemistry are discussed in detail.

1. Introduction

Since the pioneering work of Gerischer in the field of semiconductor electrochemistry (see, e.g., ref 1) many electrochemical processes at extended semiconductor electrodes as well as reactions at small semiconductor particles have extensively been studied. Essential results especially obtained with nanometer particles are summarized in various review articles.[2−8] The methods of determining reaction rates and products are quite different for semiconductor electrodes and particles. In the first case the charge transfer processes are mainly characterized by measurements of current voltage curves and of the interfacial impedance. The properties of semiconductor particles, i.e., mainly of colloidal solutions, are investigated by absorption and fluorescence measurements, by time resolved laser flash studies and by analyzing reaction products.

In principle, the same electrochemical reactions should occur at semiconductor electrodes and particles. However, it has to be considered that a spatial separation of the cathodic and anodic processes at particles is only possible in specially designed devices.[8a] In all experiments involving suspensions or dispersions of particles one cannot exclude reactions between intermediates being formed in a first step and the formation of corresponding products which would not occur at polarized electrodes. One example is the light induced oxidation of acetate (Photo Kolbe reaction) at TiO_2, according to which the observed CH_4/C_2H_6 product ratio is smaller at TiO_2 electrodes compared to the ratio observed at platinized TiO_2 particles.[9,10] Gerischer[11] analyzed theoretically the influence of the rate of oxygen reduction and the oxidative decomposition of organic molecules on different sized TiO_2 particles and demonstrated that the kinetics of the reactions at the semiconductor/electrolyte interface and the quantum yield will differ dramatically if the particle size is varied in the nanometer- to micrometer-size regime. Besides these calculations, however, not much research has systematically been done in this field.

While the partial currents at extended electrodes are rather small under open circuit conditions, high overall reaction rates at semiconductor particles can be reached because of their extremely large total surface area. This can be of advantage, e.g., if the reactants are adsorbed at their surface.[12] However, always the slowest partial reaction determines the overall rate. In every case the question arises whether the particle size is of any importance.[13] In this context it has to be realized that the recombination of electron/hole pairs created by light excitation competes with a charge transfer process. Accordingly, the quantum efficiency of the reaction depends on the transfer rate at the interface, on the recombination rate, and on the transit time within the particle.[11] For small particles of a radius of some nanometers the average transit time is less than 1 ps.[14] This value is much smaller than the speed of recombination, which usually needs more than 1 ns. Accordingly, high quantum yields are expected for small particles.

In addition, the time interval between the absorption of two photons incident on one particle can be important for reactions where two or more electrons are involved, such as, for instance, in the reduction of CO_2 or in the oxidation of alcohols or water. This time interval depends strongly on the particle size, which may have an influence on the reaction mechanism. Taking a suspension of about 10^8 particles (1-μm diameter) in 1 cm^3 so that the incident light is just completely adsorbed, it takes about 1 ns between the absorption of two photons in one particle for an incident photon flux of typically 10^{17} cm^{-2} s^{-1}. Using a suspension of particles of 3-nm size, this time interval is longer by 6 orders of magnitude. This would mean that a radical formed in the first reaction step may undergo another reaction before a second electron or hole is available in the same particle. This phenomenon will be shown in the present paper.

2. Selection of Semiconductor Material

The easiest way of studying the size effect described above is the investigation of the oxidation of an alcohol such as ethanol. This compound is oxidized to a α-hydroxyethyl radical in a "one hole" process and can further be oxidized by a second

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hole transfer to acetaldehyde, which is a stable compound. On the other hand, if the time interval for a production of a second hole by light excitation within the same semiconductor particle is too long, then the initially formed α-hydroxyethyl radicals can undergo other reactions such as dimerization typically found for reactions of free radicals in solution.

However, the selection of a suitable semiconductor material is of importance. In most applications particles consisting of oxide semiconductors, such as TiO_2 and ZnO, are used, because these are very stable materials. Unfortunately, however, the conduction bands of these semiconductors at the water interface are located at rather positive values. Investigations with both semiconductor electrodes have shown a current doubling effect upon addition of methanol or ethanol to the electrolyte.[15-18] Accordingly, the radical formed in the primary oxidation step via a one hole transfer from the valence band of such an oxide semiconductor particle to the alcohol is further oxidized to the corresponding aldehyde by electron injection from the radical into the conduction band of the same particle. In order to prove the particle size effect, it is necessary, however, to use a semiconductor with which no current doubling occurs. This can be achieved by a semiconductor, the conduction band of which has a rather high position energetically. The candidate chosen here is ZnS.[19]

3. Experimental Procedure

The ZnS colloids were prepared by modifying a method developed by the Henglein group.[20] The colloids were produced under argon by adding quickly a solution of oxygen free $Zn(ClO_4)_2$ (Alfa Products) to an oxygen free solution of Na_2S (purity grade p.a., Merck) in water/ethanol (volume ratio 5:1) containing 16 mM colloidal SiO_2 (Ludox HS 40, Du Pont, particle size ≈15 nm) as a stabilizer. The purity grade of ethanol was "for chromatography" and the water was purified by a Millipore-Q/RO system. The specific conductivity of the purified water was less than 5×10^{-8} siemens. All chemicals for ZnS preparations were stored under nitrogen in a glovebox (MBraun, Type 150-GI). The stoichiometric ratio of the original components determined the composition of the surface of the ZnS particles. The following ZnS particles with different surface compositions were prepared: 0.17 mM ZnS with an excess of 17 mol % SH^-, prepared by quick addition (within about 0.5 s) of 1 mL of 17 mM $Zn(ClO_4)_2$ solution to 99 mL of 0.2 mM Na_2S solution; 0.2 mM ZnS with an excess of 4 mol % Zn^{2+} (1 mL of 20.8 mM Zn^{2+} solution to 99 mL of 0.2 mM Na_2S solution); 0.15 mM ZnS with an excess of 45 mol % Zn^{2+} (1 mL of 21.8 mM Zn^{2+} solution to 99 mL of 0.15 mM Na_2S solution).

Dunstan et al. have shown that all excess ions are specifically adsorbed on the ZnS surface.[21] Oxygen was removed from all solutions by purging argon through them before use. In order to get reproducible results, it was important that all parameters in this procedure were carefully kept constant. Under these conditions a particle size of 3 nm was obtained for ZnS particles with 17 mol % SH^- excess, which was determined by transmission electron microscopy (TEM). Photoelectrochemical measurements were always performed with particles being aged for 1 day.

Particles with diameters in the range of micrometers have been produced by using a method described by Williams et al.[22] Here 120 mL of a 0.88 M thioacetamide solution, 148 mL of a 0.081 M $Zn(ClO_4)_2$ solution, and 2 mL of concentrated H_2SO_4, all solutions being preheated to 80 °C, were mixed, leading to a slow hydrolysis. Since the reaction is diffusion controlled very uniform spherically shaped particles were formed. During

a reaction time of 60 min the particles reach a diameter of around 4 μm with a rough surface (porous surface) as proven by STM and SEM investigations. According to an X-ray analysis the ZnS particles mainly consist of β-ZnS (cubic modification, 93%) with a small amount of α-ZnS (hexagonal modification, 7%). The specific surface area of the micrometer particles was determined by using the BET method with a "flow sorb 2300" from Micromeritics. The measured surface was 20 ± 2 m^2 g^{-1}, therefore 50 times larger than expected for particles with a smooth surface.

The photochemical investigations were performed by using a temperature controlled quartz vessel (volume, 95 mL) with a flat window on one side. It was sealed with a double septum for taking gas samples and another one for liquid samples by using corresponding syringes. In every experiment the cell was filled with a 70-mL suspension containing 100 mg of micrometer ZnS particles or colloidal solutions and stirred with a magnetic stirrer. Before starting the illumination the solution was deaerated by flushing argon through it for at least 1 h. In addition, an external argon flushing was used through the interstice of the double septum in order to avoid any penetration of oxygen through the punctured septums. The cell was kept at 25 °C. The light source was a 150-W xenon lamp. A quartz cell filled with water was used as an IR filter.

The reaction products were analyzed by gas chromatography. The gases H_2, O_2, and N_2 present in the gas phase in the quartz vessel were determined by using a gas chromatograph (GC-8A, Shimadzu, Sehnde) at 80 °C equipped with a stainless steel column (length, 2 m; diameter, 4 mm) filled with a molecular sieve (0.5 nm, 60/80 mesh from Chrompack) and a heat conduction detector. The carrier gas was argon with a flow rate of 45 mL/min. The composition of the liquids was analyzed by using a gas chromatograph (HR GC 5300, Carlo Erba, Hofheim) which was supplied with a flame ionization detector (FID). Here we used a fused silica capillary column (DB-Wax ID 320 from J & W Scientific, ASS, Bad Homburg) with a length of 30 m and an inner diameter of 0.32 mm combined with a deactivated precolumn. Hydrogen was used as a carrier gas with a flow rate of 71 cm/s. The pressure in front of the precolumn was 60 kPa. An on-column system was used as an injection and 5 μL of the illuminated suspension was injected via the on-column system into the precolumn. In order to obtain good reproducibility in the determination of acetaldehyde and of 2,3-butanediol, different temperatures were used in the detection system. In the case of 2,3-butanediol the liquid was injected at a temperature of 100 °C and the column was heated up to 145 °C at a rate of 15 °C/min. Under these conditions the retention times for 2,3-butanediol were 3.51 and 3.73 min for the meso form and the racemate. For the acetaldehyde analysis the GC was kept constant at a temperature at 50 °C. The retention time was 1.24 min. Elemental zinc deposited on the particle surface after illumination was determined by reaction with viologen MV^{2+} which gives the blue $MV^{\bullet}$ radical. The photon flux of the xenon lamp into the cell was determined by chemical actinometry using iron(III) oxalate for calibration.[22a]

4. Results

The ZnS colloids synthesized in the presence of a stabilizer SiO_2 are stable over months and their solutions are transparent up to a concentration of 5×10^{-4} M. The stabilizer SiO_2 acts also as a buffer so that the pH of the Na_2S/SiO_2 solution only varies very little upon the addition of the Zn^{2+} ions. All illumination experiments with semiconductor particles were carried out at pH = 10 and the pH did not change during illumination in the presence of SiO_2. ZnS colloids without SiO_2

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were transparent immediately after their synthesis, but they coagulated how within about 3−24 h, even for low concentrations.

The size of the colloidal particles was mainly determined from absorption measurements by using a finite depth potential well model derived by Nosaka et al.,[23] which takes into account a finite energy well at the particle surface. For nanometer ZnS particles a finite energy well of $V_o = 1.5$ eV was used and with this assumption the particle size of the nanometer ZnS colloids can be calculated from the onset of the absorption spectrum very well. Further details of our calculations are given elsewhere.[30] According to this evaluation the bandgap decreased (e.g., from 4.07 to 3.82 eV for ZnS particles with an excess of 17 mol % SH⁻) within 24 h after synthesis and the size of the same particles increased from 1.9 to 3.0 nm within this time. The final average size of 3.0 nm was also found in TEM measurements. Although the aged ZnS colloids with an excess of 4 and 45 mol % Zn^{2+} were prepared under equal conditions, their sizes were slightly different after 24 h, i.e. 26 nm and 1.9 nm, respectively. The size of the large micrometer ZnS particle was carefully controlled by the synthesis. We used here particles with an average diameter of 4 μm.

The colloids with a Zn^{2+} excess exhibited a pronounced fluorescence peaking around 430 nm, whereas colloids with an excess of SH⁻ ions did not show any fluorescence. The dependence of the fluorescence on the Zn^{2+} concentration on the surface of the colloids was not studied in further detail. According to quantitative investigations by Yanagida et al.[24] the fluorescence intensity increases over a considerably large range of the Zn^{2+} concentration.

Figure 1a represents the reaction products formed during illumination of ZnS colloids with an excess of 17 mol SH⁻ in ethanol/water solutions. Here hydrogen, acetaldehyde, and 2,3-butanediol were formed. The molar ratio of butanediol and acetaldehyde was 1:2.51 ± 0.48 (±19%) and remained constant through the whole illumination experiment. In a second experiment (not shown here) higher concentrations of all three products were obtained, probably due to slightly different absorption conditions of the synthesized ZnS colloids. In the latter experiment the ratio of butanediol to acetaldehyde was 1:2.60 ± 0.13 (±5%). The relative error in the measurements of the acetaldehyde and butanediol concentration by GC was 10−15% and of their concentration ratio around 20%. The solutions were investigated with respect to elementary zinc. This was proven by adding methylviologen (MV^{2+}) to the solution. Any Zn^0 formed during the illumination would have reduced the MV^{2+} to MV^+ radicals, which can easily be identified because of their characteristic blue color. However, no Zn^0 was found after illumination of the ZnS colloids. In order to check whether this negative result is due to oxygen in the solution because O_2 may have reoxidized the MV^+ radicals to the colorless MV^{2+}, a very small amount of Zn^0 was added to the illuminated colloidal solution after this test with viologen. After addition of Zn^0, the blue color appears immediately. The latter test has proven that the solution was really free from any O_2.

In the case of colloids with an excess of 4 mol % Zn^{2+}, the distribution of products compared with the products formed on ZnS colloids with SH⁻ excess (Figure 1a) is completely different as shown in Figure 1b. According to the analysis of the final products, only a very small amount of butanediol was formed here (after 130 min of illumination only 2 μmol compared to 35 μmol of acetaldehyde). The viologen test at the end of the experiment led to a faint blue color of the solution. Accordingly, some Zn^0 was deposited on the colloids during illumination. A quantitative analysis of Zn^0 by absorption measurements was
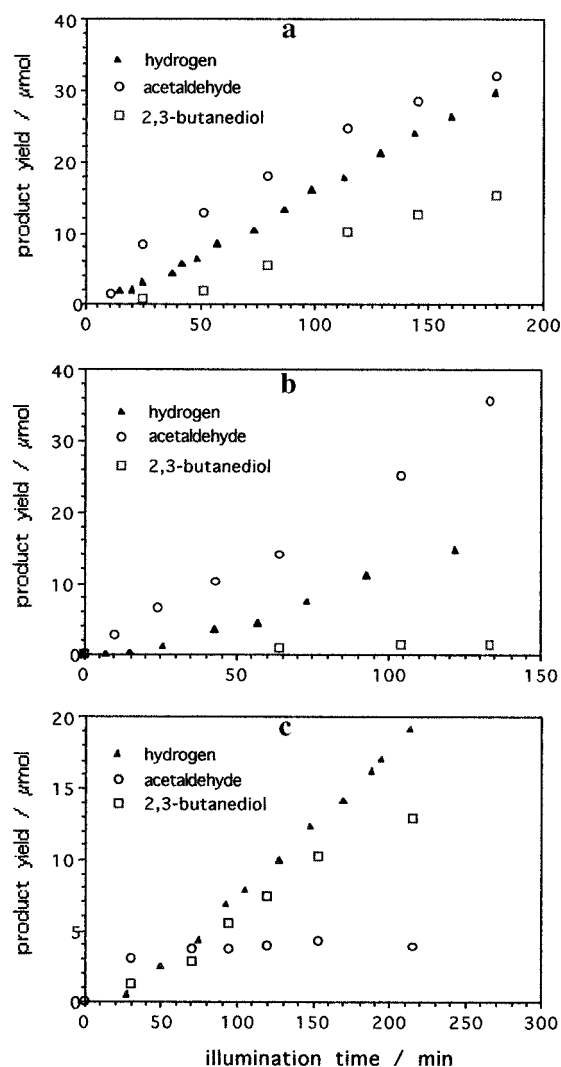

Figure 1. Formation of hydrogen, acetaldehyde, and 2,3-butanediol at ZnS colloids in an ethanol/water solution (ratio 1:5) at pH 10 in the presence of 16 mM SiO_2 vs illumination time: (a) 3-nm ZnS colloids with 17 mol % SH⁻ excess, cutoff filter WG 320; (b) 2.6-nm ZnS colloids with 4 mol % Zn^{2+} excess, WG 320; (c) 1.9-nm ZnS colloids with 45 mol % Zn^{2+} excess, WG 280.

not performed because in our experimental setup it was impossible to guarantee a transfer of the solution into a corresponding cell suitable for the spectrometer without getting oxygen into the solution.

In the case of ZnS colloids with even higher excess of Zn^{2+} (45 mol %), surprisingly a considerable amount of butanediol was formed as shown in Figure 1c. It is also remarkable that the concentration of acetaldehyde increasing during the first period of illumination but then saturated after a relatively short illumination time. Also elementary Zn^0 was found here, its concentration being higher than in the 4 mol % case. The amount of hydrogen produced at these colloidal particles was considerably smaller than at colloids with 4 mol % excess in Zn^{2+}. It should further be mentioned that the experiments with ZnS (45 mol % Zn^{2+} excess) were performed by using the cutoff filter at 280 nm instead of at 320 nm, because these very small particles (diameter 1.9 nm) absorb light only below $\lambda = 305$ nm. Accordingly, we did not observe any reaction products when using a 320-nm cutoff filter (see also below).

The same type of photoreactions were studied with ZnS suspensions consisting of particles with a diameter in the micrometer range. Since these investigations were mainly performed in order to test whether different reaction products
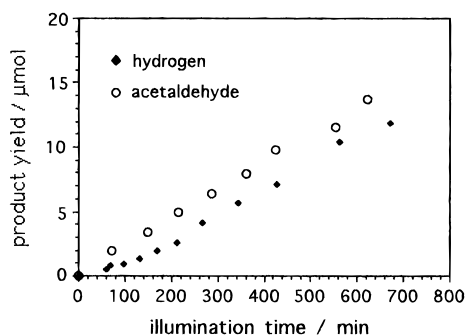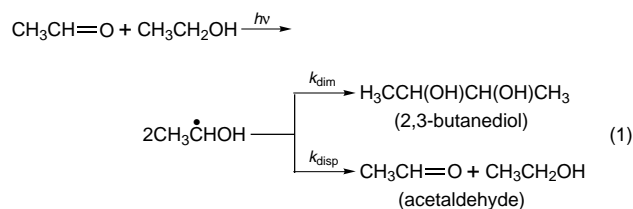
Figure 2. Formation of hydrogen and acetaldehyde at 4 μm ZnS particles in an ethanol/water solution (ratio 1:5) at pH 10 vs illumination time. The solution contains 7.4 μmol of SH$^-$ ions and 16 mM SiO$_2$ colloids; cutoff filter, WG 280.

are formed at large particles, special care was taken that the experiments were performed under the same conditions as in the case of nanometer particles. We restricted our investigations to the formation of reaction products at large particles in the presence of HS$^-$, because only in the case of nm particles prepared with an excess of 17 mol % SH$^-$ the concentrations of butanediol and acetaldehyde increased linearly with illumination time, which means that the butanediol/acetaldehyde ratio was constant during the whole illumination experiment (Figure 1a). In order to provide the same experimental conditions we added SH$^-$ ions on the order of some micromoles to the suspension. This concentration corresponds to the 17 mol % SH$^-$ excess on 3-nm particles mentioned above, considering the rough surface of the micrometer particles of 20 m^2 g^{-1} found by BET measurements. In addition, 16 mM colloidal SiO$_2$ was added to the suspension in order to reach the same pH (i.e., pH = 10) as for the colloidal solutions. The course of the products formation during illumination of the suspension is given in Figure 2. No butanediol was found here. The smallest amount of butanediol detectable according to the sensitivity of our GC was 0.5 μmol per 70 mL. Therefore, the ratio of acetaldehyde to butanediol is here larger than 34:1 compared with the concentration ratio of 2.5:1 found for the nanometer particles with SH$^-$ excess (Figure 1a). According to the viologen test, which we performed after the illumination, no Zn^0 was deposited on the surface of the particles. A further experiment had shown that the hydrogen formation increased with increasing SH$^-$ concentration, an observation also reported by Reber et al.[25]

Since ZnS colloids absorb light only in the UV region because of their large bandgap, we also checked whether any photochemical reactions already occur without the semiconductor but with molecules formed on this. A well-known photoreaction is the formation of 2,3-butanediol upon excitation of acetaldehyde in ethanol solutions as given by[26,27]

$$CH_3CH\!\!=\!\!O + CH_3CH_2OH \xrightarrow{h\nu}$$

$$2CH_3\overset{\bullet}{C}HOH \begin{cases} \xrightarrow{k_{dim}} H_3CCH(OH)CH(OH)CH_3 \\ \quad \text{(2,3-butanediol)} \\ \xrightarrow{k_{disp}} CH_3CH\!\!=\!\!O + CH_3CH_2OH \\ \quad \text{(acetaldehyde)} \end{cases} \quad (1)$$
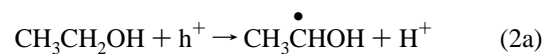
Since this reaction occurs at a high quantum yield we illuminated a solution (free from ZnS) containing a relatively large acetaldehyde concentration (11.3 mM) using a 280-nm cutoff filter. Indeed, we then found considerable concentrations of butanediol. If instead a lower acetaldehyde concentration of 0.3 mM is used (this corresponds to the amount of acetaldehyde formed on the ZnS colloids after a 100-min illumination by using a 320-nm

cutoff filter, Figure 1a), then no butanediol could be detected even after a 1-h illumination by using a 280 nm-cutoff filter. This result is due to the low extinction coefficient of acetaldehyde at λ_{max} = 280 nm. Hydrogen was not found in these photochemical reactions. Thus, acetaldehyde formed on the ZnS colloids does not photochemically react in a detactable amount to 2,3-butanediol under our illumination conditions. This photochemical reaction can be neglected here and the formation of 2,3-butanediol is exclusively contributed to the photoinduced reactions occurring on the ZnS particles (compare, e.g., Figure 1a).
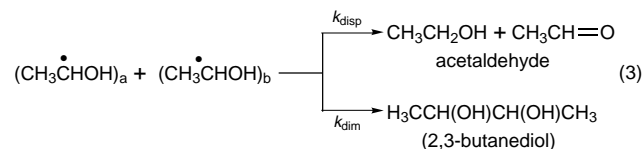
5. Discussion

According to the results presented in the previous chapter the reaction properties of small and large ZnS particles are very complex. The formation of products depends not only on the particle size but also on the chemical composition and possibly even the structure of the particle surface. As already mentioned in the introduction ethanol is expected to be oxidized at large particles by the transfer of two holes being created successively by light absorption within the particle according to the reaction

$$CH_3CH_2OH + h^+ \rightarrow CH_3\overset{\bullet}{C}HOH + H^+ \qquad (2a)$$

$$CH_3\overset{\bullet}{C}HOH + h^+ \rightarrow CH_3CH\!\!=\!\!OH + H^+ \qquad (2b)$$

Both of these reactions can occur at the surface of one particle without side reactions forming byproducts only if the time interval $\Delta t_{transfer}$ between two successive hole transfer processes at one particle is sufficiently short and the residence time of the initially produced α-hydroxyethyl radicals on or near the surface of the particle is longer than $\Delta t_{transfer}$. Under our illumination conditions the time interval between two absorption incidences within one particle is about 20 ps (Table 1), and considering the relative low quantum yield of about 0.01% for the formation of acetaldehyde and hydrogen the time interval between two successive hole transfer processes is about 200 ns (see also Table 1, eqs 5 and 7, and also the following discussion).

During this time the initially formed α-hydroxyethyl radical could in principle diffuse about 35 nm as was calculated from the equation $l = (6D\Delta t_{transfer})^{0.5}$ with $D = 10^{-5}$ cm^2 s^{-1}. Thereby this diffusion length of the α-hydroxyethyl radical is smaller than the depth of micropores located on the rough surface of the particles. They have been determined by STM, BET, and SEM measurements. Therefore we assume that the time interval of 200 ns is too short for the initially formed radical to diffuse from the porous surface into the electrolyte. Therefore it is further oxidized by a second hole according to eq 2b to form acetaldehyde. We call this oxidation process a "two hole" process.

On the other hand, if the time interval between two successive hole transfer processes is much longer (e.g., several seconds), then the radicals can undergo subsequent reactions such as dimerization and disproportionation to form stable products as given by

$$(CH_3\overset{\bullet}{C}HOH)_a + (CH_3\overset{\bullet}{C}HOH)_b \begin{cases} \xrightarrow{k_{disp}} CH_3CH_2OH + CH_3CH\!\!=\!\!O \\ \quad \text{acetaldehyde} \\ \xrightarrow{k_{dim}} H_3CCH(OH)CH(OH)CH_3 \\ \quad \text{(2,3-butanediol)} \end{cases} \quad (3)$$

in which the subscripts a and b indicate that the radicals are formed at different colloidal particles. In reaction 3 2,3-

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TABLE 1: Comparison of Generation Rates of Charge Carriers, Quantum Efficiencies, and Time Intervals between Two Successive Charge Transfer Processes for Nanometer and Micrometer ZnS Particles

	particle diameter	
	3 nm	4 μm
absorption cross section σ	5.4×10^{-16} cm^2 at 320 nm	1.25×10^{-7} cm^2
photon flux, N_{ph}	3.4×10^{16} cm^{-2} s^{-1}	4.1×10^{17} cm^{-2} s^{-1}
time interval between two absorptions incidences within one particle, $\Delta t = g^{-1}$	54 ms	20 ps
no. of generated electron/hole pairs per particle and second, g	18 s^{-1}	5×10^{10} s^{-1}
quantum efficiency with respect to H$_2$ formation, ϕ	1.6%	0.01%
time interval between two successive hole transfer processes within one particle, $\Delta t_{transfer}$	3.4 s	200 ns
av lifetime of α-hydroxyethyl radicals in the electrolyte produced on 3-nm ZnS particles with 17 mol % SH$^-$ excess, τ	60 ms	

butanediol is formed together with acetaldehyde. In principle, the secondary reactions of radicals can occur either on the surface of the particles or in the bulk of the electrolyte. We assume the latter process to be dominant for two reasons:

(a) The ratio of acetaldehyde to 2,3-butanediol found in our experiments is about 2.5 (see Figure 1a), which is close to the ratio found for the well-investigated free α-hydroxyisopropyl radicals in solution.[31] This radical reacts completely analogous to our system, forming acetone and pinacol in a ratio of $\gamma = 3.4$. This slightly larger value for this radical is probably due to the higher steric hindrance for the dimerization reaction in the case of the very bulky α-hydroxyisopropyl radical compared with the α-hydroxyethyl radical.

(b) The ratio 1:2.5 is constant throughout the hole illumination experiment as is typical for reactions of free radicals in homogeneous solution. On the other hand, if the secondary reaction of the radicals would occur on the surface of the particles, γ would probably increase above 2.5 because the probability for a direct second oxidation step would also increase when the radical concentration rises with time on the surfaces.

Independent of all assumptions concerning the reaction sites, it is clear from our experiments that only in the case of small particles butanediol is formed (Figure 1a) whereas in the case of large micrometer ZnS particles this product is missing (Figure 2). Also it seems clear to us that acetaldehyde can only be formed selectively by a second hole transfer if the time interval between two successive hole transfer processes at one particle is short compared to the residence time of a primarily produced radical.

Generation rates of electron/hole pairs in nanometer particles and average lifetimes of produced radicals required for a second charge transfer can be calculated in a more general way as follows: In order to determine the generation rate g of electron/hole pairs in 1-nm semiconductor particles, one has to calculate first the absorption cross section for photons for nanometer particles. According to the Mie theory this is given for $R_o \ll \lambda_{gap}$ by[28,29]

$$\sigma(\lambda) = \frac{8\pi^2 n_1}{\lambda} R_0^3 \, \text{Im}\left(\frac{m^2 - 1}{m^2 + 2}\right) \qquad (4)$$

with

$$R_o < \frac{\lambda}{2\pi n_1} \qquad (4a)$$

and

$$m = \frac{n_2 + i\frac{\alpha\lambda}{4\pi}}{n_1} \qquad (4b)$$

in which n_1 and n_2 are the refractive indices of the liquid and

the semiconductor, respectively, R_o is the particle radius, and α is the absorption coefficient of the semiconductor. On the other hand, if $R_o \gg \lambda_{gap}$ as for 4-μm ZnS particles we have to use[29]

$$\sigma_{(\lambda)} \approx \pi R_o^2 [1 - \exp(-\alpha 2R_o)] \qquad (5)$$

In the case of 3-nm ZnS particles one obtains from eq 4 an absorption cross section of $\sigma = 3.1 \times 10^{-16}$ cm^2 for $\lambda = 320$ nm using an absorption coefficient of $\alpha = 3.7 \times 10^4$ cm^{-1} as typical for this direct band gap semiconductor. For this calculation the refractive indices $n_1 = 1.33$ for water and $n_2 = 2.37$ for cubic ZnS[29a] were used. Nearly the same cross section for photons as derived from the Mie theory can also be taken from the absorption spectra of the 3.0-nm ZnS colloids prepared with 17 mol SH$^-$ excess. Here we found a cross section of 5.4×10^{-16} cm^2.[30] The cross section for the 4-μm particles can be calculated by using eq 5, and one obtains a cross section of $\sigma = 1.25 \times 10^{-7}$ cm^2 for $\lambda = 320$ nm using the same absorption coefficient as above.

In the case of nanometer particles with an excess of SH$^-$ a 320-nm cutoff filter was used for the illumination experiments. Our light source generates 1.07×10^{17} photons per second between 320 and 325 nm (the absorption onset of the colloids) on a spot 20 mm in diameter. So we used $N_{ph} = 3.4 \times 10^{16}$ photons cm^{-2} s^{-1}. For the illumination experiments with 4-μm ZnS particles a 280-nm cutoff filter was used. The photon flux to excite the micrometer particles was here 4.1×10^{17} photons cm^{-2} s^{-1} or 1.3×10^{18} photons s^{-1}. From this the generation rate g of electron/hole pairs in one particle can be calculated according to

$$g = N_{ph}\sigma \qquad (6)$$

and we obtain $g = 18$ for the 3-nm particles and $g = 5 \times 10^{10}$ per particle and second for the 4-μm particles. The corresponding time intervals between two absorptions incidences within one particle, which can be obtained from $\Delta t = g^{-1}$, are then 54 ms and 20 ps for the 3-nm and 4-μm particles, respectively. These data are summarized in Table 1.

According to Figure 1a about 30 μmol of H$_2$ was formed by the 3-nm particles during 180 min. On the basis of the photon flux determined by actinometry (assuming that also in the semiconductor suspension all ligt absorbed) the quantum efficiencies of hydrogen formation are 1.6% and 0.01% for the small and large particles, respectively. The small quantum yield indicates that most of the generated electron/hole pairs recombine, so that not all charge carriers created by light excitation are available for a transfer across the interface. The time interval between two successive successful charge transfer processes can be calculated considering the quantum efficiency on the basis of the equation

$$\Delta t_{transfer} = (N_{ph}\sigma\phi)^{-1} \tag{7}$$

in which ϕ is the quantum yield. Using the experimental data given above, one obtains $\Delta t_{transfer} = 3.4$ s and 200 ns for the small and large particles, respectively, as also given in Table 1. Already here it becomes clear that the time interval between successive charge transfer processes at 3-nm colloidal particles is on the order of seconds making it very improbable that a second hole becomes available for a second oxidation step of the alcohol to directly form the aldehyde.

On the other hand, applying the kinetics as given by eqs 2a and 3 and using the experimental data on the formation of butanediol (Figure 1a) in a bimolecular (second-order) reaction of two radicals, one can determine the average lifetime of the free hydroxyethyl radicals in solution. From the kinetics observed and considering the generation rate of α-hydroxyethyl radicals on the nanometer particles g_{rad} and the dimerization/disproportionation reactions in the electrolyte according to eq 3 as discussed above, one can derive the stationary radical concentration c_{rad} in the electrolyte as given by

$$c_{rad} = \left(\frac{g_{rad}}{2(k_{disp} + k_{dim})}\right)^{1/2} \tag{8}$$

in which the generation rate of radicals g_{rad} is given by

$$\frac{dc_{rad}}{dt} = g_{rad} = 2\left[g_{but}\left(\frac{k_{disp}}{k_{dim}} + 1\right)\right] \tag{9}$$

with $g_{but} = dc_{but}/dt$ being the generation rate of butanediol.

From the results given in Figure 1a one can calculate $g_{but} = 2.6 \times 10^{-8}$ mol L^{-1} s^{-1} and with the ratio $\gamma = k_{disp}/k_{dim} = 2.5$ and with $2(k_{disp} + k_{dim}) = 1.4 \times 10^{9}$ M^{-1} s^{-1} [27] one obtains from eq 9 $g_{rad} = 1.8 \times 10^{-7}$ mol L^{-1} s^{-1}. According to eq 8 the stationary radical concentration in the electrolyte is $c_{rad} = 1.1 \times 10^{-8}$ mol L^{-1}.

From these data the average lifetime of the free radicals in the electrolyte is then given by

$$\tau = \frac{1}{2(k_{disp} + k_{dim})c_{rad}} \tag{10}$$

Using the above calculated data one obtains $\tau = 60$ ms (see also Table 1). This time is much shorter than the time interval of two successive charge transfer processes in a single 3-nm particle which is on the order of some seconds (Table 1).

This indicates that the further oxidation of initially produced α-hydroxyethyl radicals to acetaldehyde cannot occur on nanometer ZnS particles under our reaction conditions and this is consistent with our model as mentioned above. Furthermore it is interesting to note that the free α-hydroxyethyl radicals within its lifetime of 60 ms can diffuse about $l = 19$ μm ($l = (6D\tau)^{1/2}$, with $D_{radical} = 10^{-5}$ cm^2 s^{-1}) before it reacts in the electrolyte with a second radical to butanediol or acetaldehyde. This diffusion length is much longer than the average distance of about 0.15 μm between two 3-nm ZnS colloids.

Influence of Surface Chemistry. Surprisingly, almost no butanediol was formed at colloidal ZnS particles with a 4 mol % of Zn^{2+} excess (Figure 1b). In addition these particles exhibit fluorescence ($\lambda_{max} = 430$ nm) as already published by other authors.[24,32,33] Since this fluorescence can be quenched by methylviologen (MV^{2+}) and SH$^-$ ions it has been concluded that the fluorescence is due to a transition via surface states (anion vacancy), as illustrated in the energy scheme of Figure 3. The position of the energy bands is derived from measure-
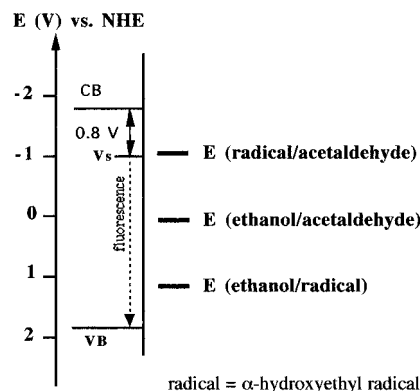

Figure 3. Energy scheme of ZnS particles and redox potentials of the ethanol/α-hydroxyethyl radical, ethanol/acetaldehyde, and α-hydroxyethyl radical/acetaldehyde systems at pH 10.

ments performed with extended ZnS electrodes.[19] The redox potential of the α-hydroxyethyl radical/acetaldehyde couple is $E_2 = -0.94$ V (NHE) at pH 7.[27] Since this value varies with 59 mV per pH one obtains $E_2 = -1.10$ V at pH 10 as also indicated in Figure 3. At this pH, the radical mainly exists (98%) in its protonated form because of its p$K_s = 11.6$.[27] The redox potential E_1 of the ethanol/radical couple, corresponding to the first oxidation step (one hole process), has been calculated from theoretical data.[37] The redox potential E^0 of the couple ethanol/acetaldehyde (two hole process) has been calculated as the mean value of the two others. Here, only the E_2 value is of interest, which is located below the conduction band but above the surface state. Since the position of the energy bands,[19] the surface states, and the redox potential E_2 all depend on the pH in the same way, the relative position of E_2 and the surface state remain constant. According to this energy scheme (Figure 3) an electron can be injected from the radical formed by hole transfer in the first reaction step (one hole process) into the surface state of the same particle. This means that the radical is further oxidized in this second step at the surface of the colloid, which would almost explain the absence of butanediol in this experiment. The electron stored in this surface state may be used for the reduction of H$_2$O or for excess Zn^{2+} to Zn^0 on the particle surface. Since very little Zn^0 was experimentally found, this should be a less important reaction route. It should be mentioned that also other authors have found that Zn^0 is only formed with colloids prepared with an excess of Zn^{2+}.[2,34] A direct reduction of Zn^{2+} by an electron transfer from the radical to Zn^{2+} in the solution can be excluded.[35]

On first sight one would expect the same result for particles with 45% excess in Zn^{2+} because the fluorescence intensity and accordingly the density of surface states is further increased. According to the experimental result, however, butanediol was found again, but compared with experiments with ZnS colloids with SH$^-$ excess (Figure 1a) the production of acetaldehyde saturated here (Figure 1C). The latter result indicates that the acetaldehyde formed by an oxidation reaction by electron injection into the surface states as described above undergoes a subsequent further reaction, i.e., it is then reduced again via a different route. Since in this case considerably more Zn^0 was formed during illumination than with the particles of 4 mol % Zn^{2+} excess, it may be possible that the reduction of aldehyde occurs at small Zn^0 clusters, which may lead to the formation of butanediol. Yanagida et al. have reported that acetaldehyde is reduced at stoichiometric ZnS colloids by using propylamine as a hole scavenger.[24] They did not find butanediol. The formation of Zn^0 was not investigated here.

Some research groups have also investigated light induced reactions at ZnS colloids with an excess of Zn^{2+} using

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isopropanol as a hole scavanger and CO_2 as an electron acceptor.[20,36] Henglein et al. found pinacol after illumination of ZnS (11 mol % Zn^{2+} excess).[20] On the other hand, Inoue et al. studied reactions at ZnS colloids with different excess of Zn^{2+} (25, 50, and 200 mol %) but did not observe any pinacol formation.[36] They only found acetate, formate, and hydrogen. These differences may be due to slight differences in the preparation of the ZnS colloids, which seem to be extremely critical.[37]

6. Conclusions

The very different generation rates of electron/hole pairs in nanometer and particles lead to different reaction mechanisms for the light induced oxidation of ethanol. To our best knowledge it is the first time that this phenomenon has been studied systematically on semiconductor particles in the nanometer to micrometer size regime. It is concluded that on ZnS particles radicals are formed in a primary photoinduced oxidation step via a one hole process. The secondary reactions of these intermediates now depends strongly on the chemical composition of the particle surface as well as on the availability of a second hole. In the case of defect free nanometer ZnS particles it takes more than 50 ms before the next photon is absorbed by the same particle and even a few seconds before the next successful charge transfer occurs at this particle. Here therefore the radicals have plenty of time to diffuse into the electrolyte where disproportionation and recombination of radicals can take place. However, in the case of a semiconductor with surface states (anion vacancies) the radicals can inject electrons into these surface states, which are located energetically in the band gap of the semiconductor.

On micrometer ZnS the formation of long-lived radicals plays a much less important role and the oxidation of ethanol can proceed here via a two hole process without forming dimerization products. We cannot exclude that the very porous surface of the self-synthesized micrometer ZnS particles also supports the two hole process, because the initially produced short-lived radicals may here be trapped within nanopores leading to a second oxidation step. In order to investigate this, particles with different porosities, including such with a smooth surface, should be studied.

In order to compare reactions on nanometer and micrometer particles it was found necessary to control precisely the reaction conditions for the differently sized particles including their surface chemistry. Both surface chemistry and size strongly control the formation of products on the particles. The surface to volume ratio of small particles is by orders of magnitude larger than for large particles and therefore any surface effects will control the reactions on these particles, which play a less important role in the case of large particles.

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