



**PHOTOCHEMISTRY OF SEMICONDUCTOR COLLOIDS.
PREPARATION OF EXTREMELY SMALL ZnO PARTICLES,
FLUORESCENCE PHENOMENA AND SIZE QUANTIZATION EFFECTS** ^{*}

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Extremely small ZnO particles (< 2.5 nm) are formed in the precipitation of Zn^{2+} by OH^- in alcoholic solution. The absorption threshold and fluorescence band shift towards longer wavelengths upon growth of the colloidal particles. These shifts are typical for the transition from molecular to semiconductor material. The colloidal ZnO could be separated in the form of a powder with a specific surface of 108 m²/g. A Cu^{2+} -doped colloid was also prepared. Colloidal ZnO has a strong fluorescence, $\lambda_{max} = 540$ nm, which decays with $\tau = 10$ ns, and a weak one, $\lambda_{max} = 370$ nm, $\tau < 1$ ns. Intense illumination in the absence of O_2 results in the disappearance of the 540 nm fluorescence and a blue-shift of the absorption spectrum. Both changes are immediately reversed upon admission of air. The results are explained on the basis of the Hauffe mechanism for the dissolution of ZnO, in which intermediate Zn^+ plays a role. Prolonged illumination of a propanolic sol leads to precipitation of zinc metal. In the presence of 1×10^{-4} M methylviologen, MV^+ is formed with a quantum yield of 60%.

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1. Introduction

When semiconductors are made in the form of small particles, for example as colloids in solution, they experience large changes in the position of their electronic energy levels. This was recently shown for CdS [1,2], ZnS [3], Cd_3P_2 [4], and Cd_3As_2 [5]. The perturbations are due to charge carrier confinement resulting in an increase in the energies of the exciton and the band gap. In this "Q state", where a gradual transition from semiconductor to molecular material takes place, the optical and photocatalytic properties change. In many cases, the colloidal particles, which are formed by chemical precipitation, can be recovered in the solid state by careful evaporation of the solvent, and the solid materials can be redissolved without significant changes in size.

In the present paper, the preparation of colloidal zinc oxide, ZnO, is reported. When zinc ions are precipitated by OH^- ions in aqueous solution, zinc hydroxide is formed, which cannot be dehydrated in the colloidal state. However, by carrying out the precipitation in alcoholic solution, making use of the dehydrating properties of the alcohols, one obtains photo-active ZnO in the form of very small particles. A stabilization of the particles is achieved when the precipitation is carried out in the presence of small amounts of polyphosphate. Particles produced in this way can be separated from the solution in the form of a powder. This method has recently been applied to prepare small solid particles of other semiconductors [2,4,5]. Zinc oxide is a standard material in semiconductor electrochemistry and photoelectrochemistry, and also in conventional catalysis [6]. Further, ZnO dispersions have often been used to photo-catalyze chemical reactions [7,8]. The possibility of preparing ultra-fine colloidal ZnO in solution and solid state should therefore be of interest to various fields of research.

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2. Experimental

Preparation of colloidal ZnO in methanol. 50 ml of a 10^{-2} M $\text{Zn}(\text{ClO}_4)_2$ solution is added to 442 ml methanol plus 8 ml 5 M NaOH. The solution is vigorously shaken for 10 min and left overnight. After about 24 h a transparent solution of stable colloid is obtained, the light absorption of which starts at 350 nm. The development of the spectrum of the colloid can be followed during the reaction time. Note that small amounts of water in the solution change the rate of formation of ZnO.

Preparation of colloidal ZnO in propanol-2. 50 μl 10 M NaOH is added to 90 ml dried propanol-2, and the solution stirred until the phase separation has disappeared. 10 ml of a 1×10^{-2} M $\text{Zn}(\text{ClO}_4)_2$ solution in propanol (containing 1% water) is added. Fig. 1 shows the absorption spectrum of the ZnO after various times.

Preparation of solid ZnO. 0.8 g $\text{Zn}(\text{ClO}_4)_2$ is dissolved in 1.2 l methanol p.A., and the solution is bubbled with nitrogen. 0.2 ml of a 0.1 M sodium hexametaphosphate solution is added to obtain a slightly opalescent solution. After further bubbling with nitrogen for 10 min the opalescence is weaker. 3 ml 10 M NaOH is added and the solution left for 30 min. It still is slightly opalescent. The solution is now concentrated to 150 ml in a rotor-evaporator at 30°C . The solid is separated by centrifugation. Washing and drying of the solid with the following solutions: (1) mixture of 70% methanol + 30% water, (2) 100% methanol, (3) acetone or ethanol, (4) diethyl ether leads to a white powder. This ZnO powder contains 3 weight% phosphate, 4% water and 3% excess oxygen. One can therefore assume that the surface of the particles contains a lot of hydroxyl groups. The excess O_2 content indicates that the particles very strongly chemisorb oxygen. The specific surface as determined by single point BET after vacuum drying of the powder at 60°C for one hour was $108 \text{ m}^2/\text{g}$. This value is about one order of magnitude higher than those reported for ordinary ZnO used in catalytic studies.

Preparation of ZnO in water. 15 mg of the above powder is dissolved in 100 ml water with the aid of ultrasound. A small insoluble residue is removed by centrifugation. The transparent ZnO solution has a *pH* between 9.2 and 9.8. Its absorption starts at 350 nm.

The colloid in alcoholic solution starts to dissolve

upon addition of HCl already at a formal *pH* = 11.3. However, the aqueous solution of ZnO can be brought to *pH* = 7 without any changes in the intensity of the absorption spectrum of ZnO. Addition of small amounts of water (1 ml to 1 l) to the propanol-2 solution leads to precipitation of the colloid. However, when 70% water is rapidly mixed with the propanol-2 solution, no precipitation occurs, and the specific absorption is not changed. The ZnO in all these solutions is photoactive.

The size of the particles in the propanol-2 sol was determined by electron microscopy. A drop of the solution was evaporated on a thin carbon film on copper mesh as carrier. The film had prior to this procedure been cleaned by exposing it to a glow discharge. ZnO particles with a mean diameter of 2.5 nm were seen.

3. Results and discussion

Fig. 1 shows the absorption spectrum (a–d) and fluorescence spectrum (a'–d') of a ZnO sol in propanol-2 at various times after preparation. In the beginning, the sol starts to absorb at 310 nm, a wavelength substantially lower than the wavelength of 360 nm (photon energy 3.4 eV) of the absorption threshold of macrocrystalline ZnO. Upon aging, the absorption spectrum is shifted to longer wavelengths until the colloid absorbs like a macrocrystal. The spectra have a shoulder at about 30 nm below the threshold. Initially, the colloid fluoresces blue-green, the maximum of the fluorescence band lying at 460 nm. Upon aging, the fluorescence color becomes green, and finally yellow-green, and the maximum is then positioned at 540 nm. The fluorescence quantum yield is 4.3% in the beginning and decreases upon aging. The rate of aging is increased by small amounts of water in the alcoholic solution.

All the effects in fig. 1 correspond to what has been observed for the aging of extremely small particles of the other colloids mentioned in the introduction. The very small ZnO particles thus show the typical behavior of a Q material, i.e. of a material in which the charge carriers produced by light absorption feel the restriction in space [1,2]. The shoulder in the absorption spectrum is attributed to optical transitions to the exciton state, the energy of which strongly increases with decreasing size of the particles [2].

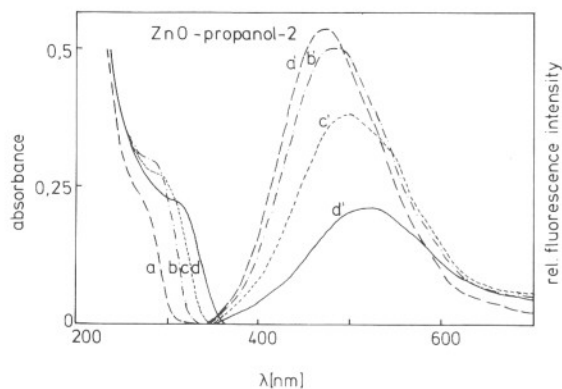


Fig. 1. Absorption and fluorescence spectra of an aerated 3×10^{-4} M ZnO sol in propanol-2 at various times of aging. $pH = 12$. (a) 1 min; (b) 5 min; (c) 20 min; (d) 60 min.

The intensity of the fluorescence band is increased up to 20% by adding excess Zn^{2+} ions to the solution. This indicates that anion vacancies are the fluorescence centers. Doping of the colloid with 0.1% Cu^{2+} ions leads to an increase in the fluorescence by 30%. This doping was performed by adding $Cu(ClO_4)_2$ to the propanol-2 solution prior to precipitation. The maximum of the 540 nm fluorescence band was shifted by 5 nm to shorter wavelengths in the presence of Cu^{2+} . This action of Cu^{2+} in the colloid probably consists of creating additional anion vacancies in the colloid. On the other hand, when Cu^{2+} was added to the colloid after preparation, the fluorescence was quenched. 5×10^{-6} M Cu^{2+} were sufficient to quench the intensity

of fluorescence by 50%. We thus encounter a phenomenon which had already been observed for small CdS particles, i.e. Cu^{2+} promoting the fluorescence when being present inside, and quenching the fluorescence when being adsorbed on the colloidal particles [9]. The quenching action is attributed to the scavenging of photo-generated electrons by adsorbed Cu^{2+} ions before these electrons undergo radiative recombination with positive holes.

The aqueous ZnO sol also fluoresces at 540 nm. However, as can be seen from fig. 2, a weak fluorescence with $\lambda_{max} = 370$ nm also occurs close to the wavelength where the sol starts to absorb. The two fluorescences decay with quite different lifetimes: $\tau = 10$ ns at 500 nm, and $\tau < 1$ ns at 370 nm. The 540 nm fluorescence is quenched by Cu^{2+} as in the above propanol-2 sol, while the 370 nm fluorescence is not influenced by Cu^{2+} . Similar observations have previously been made for CdS colloids [2,10]. As in those studies, we attribute the fluorescence close to the absorption threshold to exciton fluorescence.

Fig. 2 also shows the fluorescence spectra after a 1 min illumination of the deaerated aqueous sol with the intense 330 nm light of a xenon lamp (light selected by a monochromator). The band at 540 nm has disappeared and that at 370 nm is slightly increased. After the solution stood for 30 min, the 540 nm band was present again. Immediate recovery of this band occurred upon the admission of air to the illuminated solution. It is also seen from fig. 2 that the absorption spectrum of ZnO is shifted to shorter wavelengths

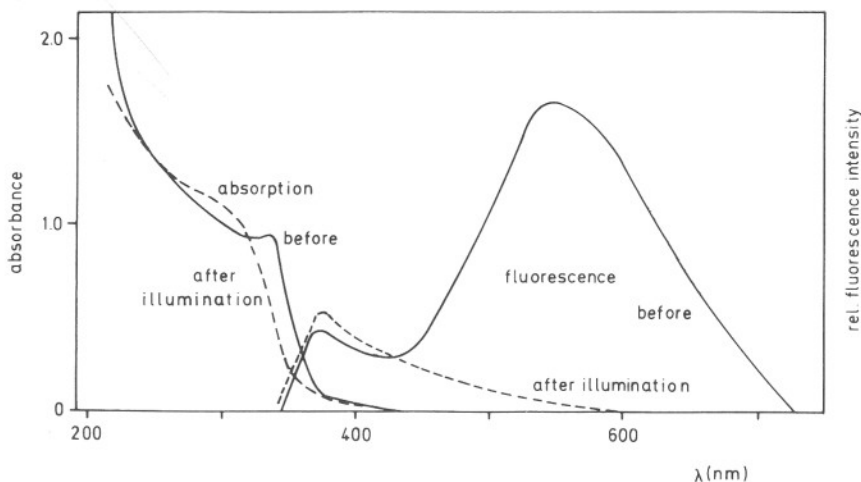
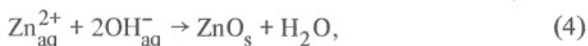
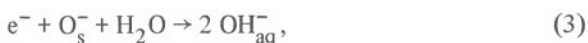


Fig. 2. Absorption spectrum and fluorescence spectrum of a ZnO sol in water, $pH = 11.7$, before and after 330 nm illumination.

after the illumination. This shift is recovered upon standing for 30 min or the admission of air.

We explain these effects on the basis of the Hauffe mechanism for the dissolution of ZnO [11]:



where the subscript "s" indicates surface species.

Illumination leads to the destruction of ZnO (eq. (1)). The decrease in size of the undamaged ZnO causes the blue-shift in the absorption (size quantization effect, see above). After illumination, reactions (2)–(4) take place, reaction (2) being rate determining. These reactions lead to a restoration of the original ZnO particle, i.e. to a restoration of its original optical properties. The Zn_s^+ centers quench the fluorescence at 540 nm by reacting with positive holes: $\text{Zn}^+ + h^+ \rightarrow \text{Zn}^{2+}$, the electrons simultaneously formed by light absorption producing new Zn^+ centers. When oxygen is admitted after illumination, the restoration of ZnO (eq. (7)) rapidly occurs via the reactions:



When deaerated propanol-2 solutions were irradiated for longer times, a black precipitate of Zn metal was formed. In the presence of the alcohol, reaction (1) also occurs. However, a fraction of the positive holes generated by light absorption oxidizes the alcohol. Reducing equivalents are then accumulated on the colloidal particles, the consequence being a complete reduction of the Zn^{2+} ions.

The removal of positive holes by the alcohol is especially efficient when a scavenger for electrons is present simultaneously. In the presence of 1×10^{-4} M methylviologen, MV^{2+} , as e^- scavenger in the methanolic sol, the quantum yield for MV^+ formation was 60%. The corresponding amount of formaldehyde as product of oxidation was also detected.

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