Influence of Adsorbed Oxygen on the Emission Properties of Nanocrystalline ZnO Particles

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This paper discusses the influence of electron scavengers (such as oxygen) on the emission properties of colloidal suspensions of nanocrystalline ZnO particles. Emission measurements are performed on deaerated suspensions of ZnO particles in alcohols (2-propanol and ethanol) and other organic solvents (DMF and propylene carbonate). Upon UV irradiation the visible emission quenches while the intensity of the exciton emission increases. Admission of oxygen into the colloidal suspension restores the initial emission properties. The role of oxygen in the quenching of the visible emission is accounted for by assuming that oxygen scavenges photogenerated electrons. In the absence of oxygen, excess photogenerated electrons are present resulting in a passivation of $V_O^\bullet/V_O^{\bullet\bullet}$ centers, which are involved in the visible emission process in ZnO.

1. Introduction

Owing to the high surface-to-volume ratio of nanocrystalline semiconductor particles, the nature of the surface is very important when considering the properties of such particles. The surface is a strong perturbation of the lattice where a high concentration of both shallow and deep levels provides pathways for nonradiative recombination of photogenerated charge carriers.[1] This explains why the quantum efficiency of the emission of nanocrystalline semiconductor particles is generally far below unity and is strongly dependent on surface passivation.[2−4] However, surface states can also be of importance for radiative transitions, as we have demonstrated for ZnO particles.[5]

Next to these intrinsic surface properties, it is known that surface adsorbates—such as reaction byproducts, solvent molecules, or dissolved gases—can influence various properties of a colloidal suspension of semiconductor particles. For instance, using zinc perchlorate instead of zinc acetate yields a less stable ZnO suspension.[6] It was suggested that weakly bound acetic acid plays the role of a stabilizer.[7] Surface adsorbates can also influence the optical properties of a suspension of semiconductor particles, viz., by scavenging charge carriers that are created upon photoexcitation.[8] The photogenerated holes can be removed by oxidation of solvent molecules, while adsorbed oxygen molecules can scavenge photogenerated electrons. The influence of surface adsorbates, more particularly solvent molecules and oxygen, on the optical properties of suspensions of ZnO particles will be the main topic of this paper.

It has been observed that a deaerated suspension of ZnO particles in methanol or 2-propanol exhibits remarkable emission properties. A freshly prepared sample shows two types of emissions under UV irradiation. One is a relatively weak and narrow emission band in the UV due to exciton recombination, while the other is a strong and broad emission band in the visible part of the spectrum. The visible emission is due to recombination of an electron from a level close to the conduction band edge with a deeply trapped hole.[9] UV irradiation (using photons with an energy higher than the band gap) of a deaerated

suspension of ZnO particles quenches the trap emission while the intensity of the exciton emission slightly increases. Simultaneously, a shift of the absorption onset to higher energies was observed.[10] The initial emission and absorption properties are restored some time after the UV irradiation is stopped or after the admission of air.

First, these observations were explained by assuming a photodissolution of the ZnO particles.[10] In this model, Zn^+ is formed at the particle surface, which quenches the trap emission by reacting with photogenerated holes to form Zn^{2+}. Furthermore, the shift of the absorption onset was thought to be a quantum size effect as a result of the decrease in size of the ZnO particles. In the meantime, comparable photodissolution mechanisms have been described mainly for sulfidic semiconductor particles.[11−15] However, in the case of the observed behavior for ZnO particles, the explanation of the shift of the absorption onset and the quenching of the visible emission by a photodissolution mechanism was rejected after it was recognized that the presence of even a single excess electron on a semiconductor particle causes a shift of the absorption onset to higher energies.[16] This was explained by a model based on the Stark effect in semiconductors. The excess electron is treated as a localized point charge producing a strong electric field in the semiconductor particle. In this way, the energy for the lowest exciton state is increased. The blue-shift of the absorption onset can also be explained by the Burstein−Moss effect, in which the excess electrons fill the lowest states of the conduction band.[17−19] In this way, subsequent absorption requires photons of higher energies in order to access the lowest empty states.

An alternative model for the quenching of the trap emission of ZnO particles was proposed, which was based on an oxygen-mediated shuttle mechanism.[6] In this mechanism, photogenerated electrons are scavenged by adsorbed oxygen molecules that subsequently transfer these electrons to deep traps. Recombination of the deeply trapped electron with trapped holes gives the visible emission. Additional experiments were performed on colloidal suspensions of ZnO in which O_2^- was formed by pulse radiolysis.[20] If the shuttle mechanism is correct, an emission should be observed when O_2^- transfers an electron to a ZnO particle. However, no emission was observed.

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In this paper, the results of studies on the influence of oxygen (as electron scavenger) on the emission properties of nanocrystalline ZnO particles are presented. Emission measurements are performed before and after saturating a suspension with nitrogen, and the influence of UV irradiation is studied. Second, the influence of adsorbed hole scavengers on the emission properties is investigated by using different organic solvents. To explain the quenching of the visible emission upon UV irradiation, a model is presented that is based on the experimental results as described in this paper in combination with experimental results that were previously reported.[5] The key feature of this model is charging of the ZnO particles with electrons.

2. Experimental Section

Sample Preparation. Suspensions of nanocrystalline ZnO particles can be prepared in organic solvents such as ethanol or 2-propanol. For the preparation in 2-propanol,[6] 25 mL of a 0.02 M NaOH solution was slowly added while stirring to 225 mL of a 0.001 M $Zn(CH_3COO)_2 \cdot 2H_2O$ solution, after both solutions were first cooled to 0 °C. The preparation in ethanol is very similar.[21,22] In this case, 50 mL of a 0.14 M $LiOH \cdot H_2O$ solution (prepared using an ultrasonic bath) was added to 50 mL of a 0.1 M $Zn(CH_3COO)_2 \cdot 2H_2O$ solution. Again, both solutions were first cooled to 0 °C before the hydroxide solution was added slowly to the zinc solution while stirring. For the preparation in 2-propanol, TEM measurements have shown that the mean particle diameter of the fully grown particles is about 60 Å.[15] This corresponds to particles that contain approximately 5000 molecular ZnO units. The preparation in ethanol yields particles of a similar size, but the concentration of ZnO is about 2 orders of magnitude higher than that for the preparation in 2-propanol. Upon addition of hexane to the suspension in ethanol (volume ratio hexane to ZnO solution of 2:1) the ZnO particles precipitate.[22] The ZnO particles can be separated from the mixture by centrifuging followed by decantation of the supernatant. The precipitated ZnO particles can be resuspended in another solvent. To make sure that none of the initial solvent was still present in the new suspension, the ZnO particles were carefully dried in a nitrogen atmosphere. In this way, suspensions of ZnO particles were prepared in propylene carbonate (anhydrous 99.7%) and *N,N*-dimethylformamide (DMF, 99.8%).

Optical Measurements. The photoluminescence measurements were performed on a SPEX Fluorolog spectrofluorometer model F2002 equipped with two double-grating 0.22 m SPEX 1680 monochromators and a 450 W xenon lamp as the excitation source. The emission spectra were corrected for the spectral response of the emission monochromator and the PM tube. It took about 2 min to record a full emission spectrum. UV irradiation of the suspensions was carried out inside the spectrofluorometer using the excitation beam. The suspension was measured in a quartz cuvette of dimensions 1 cm:1 cm:4 cm (width:depth:height). The excitation beam had a rectangular shape with a height of about 1 cm and a width of approximately 1 mm. The penetration depth of the UV radiation was such that absorption took place over the entire width of the cuvette.

3. Results

In Figure 1, the emission spectrum of a colloidal suspension of nanocrystalline ZnO particles is shown before (a) and after (b) saturating the suspension with nitrogen. It is clear that the emission spectrum does not change significantly. In both spectra two emission bands are observed. The relatively weak and narrow emission band at 3.4 eV is due to the radiative
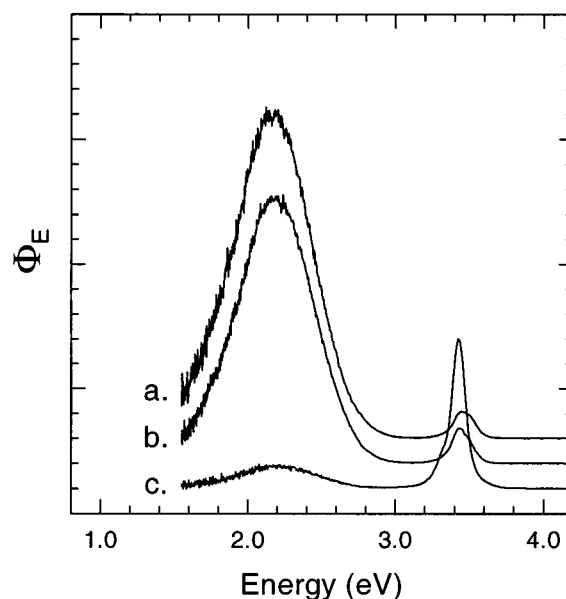

Figure 1. Room-temperature emission spectra of a suspension of nanocrystalline ZnO particles in 2-propanol upon excitation with photons of 4.3 eV. Φ_E denotes the photon flux per constant energy interval. The emission spectra are plotted with an offset relative to each other. Spectrum a is taken before and spectrum b after saturating the suspension with nitrogen. Spectrum c is taken after the nitrogen-saturated suspension has been illuminated with UV radiation (4.3 eV) for 75 min.

annihilation of excitons (exciton emission). The intense broad emission band at 2.2 eV is assigned to a transition of a photogenerated electron from a shallow level close to the conduction band to a deeply trapped hole (trap emission).[9] However, the emission properties change drastically when the nitrogen-saturated suspension is illuminated with UV radiation. From Figure 1 it can be seen that upon UV irradiation for 75 min the trap emission band has been quenched while the intensity of the exciton emission band has increased. Furthermore, the exciton emission band has shifted to lower energies and the trap emission to higher energies, both by about 30 meV. The fwhm of the exciton emission band has decreased to about 60% of the initial value, while the width of the trap emission band did not change significantly. Turning off the radiation or adding oxygen restores the initial luminescence properties. This behavior does not occur upon UV irradiation of a suspension in which oxygen is present.

To investigate the quenching of the trap emission in more detail, we have measured the intensity of the emission at 2.2 eV as a function of time while illuminating with UV radiation. The results of this measurement are shown in Figure 2. After about half an hour the intensity of the trap emission has reached a constant value of about 10% of the initial value. When the UV irradiation is interrupted for a period of time by using a shutter, the emission intensity recovers. The degree of recovery depends on the time that the suspension is kept in the dark. From Figure 2 it can be seen that keeping the suspension in the dark for about 5 min results in a full recovery of the intensity of the trap emission. Following such a recovery, the intensity decreases much faster upon UV irradiation than for the freshly prepared sample. Within 10 s the intensity of the trap emission decreases to 25%, and a constant intensity (~10%) is reached in less than a minute. For the exciton emission the opposite behavior is observed. Figure 3 shows in more detail the fast quenching of the trap emission and the fast increase of the intensity of the exciton emission upon UV irradiation.
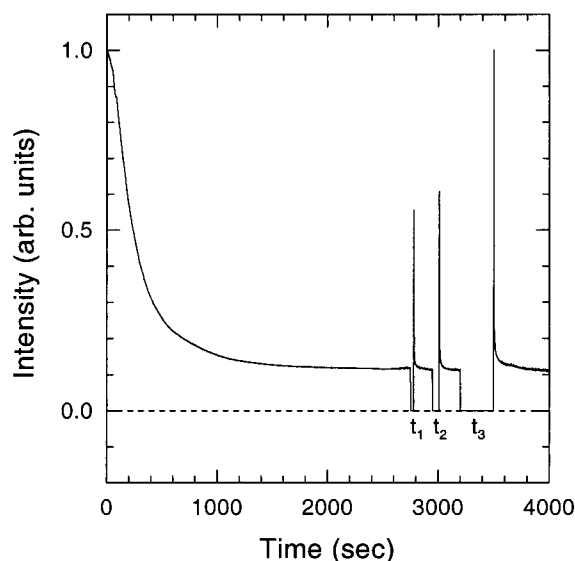
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Figure 2. Intensity of the trap emission at 2.2 eV as a function of time while illuminating with UV radiation (4.3 eV). The measurement is performed at room temperature on a suspension of nanocrystalline ZnO particles in 2-propanol that has first been saturated with nitrogen. During the periods t_1 (30 s), t_2 (60 s), and t_3 (300 s), the suspension is kept in the dark.
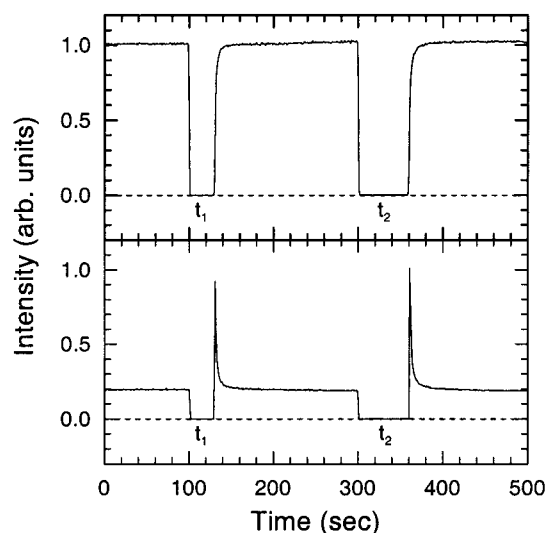

Figure 3. Intensity of the exciton emission band at 3.4 eV (upper graph) and of the trap emission band at 2.2 eV (lower graph) as a function of time while illuminating with UV radiation (4.3 eV). The measurement is performed at room temperature on a suspension of nanocrystalline ZnO particles in 2-propanol that has first been saturated with nitrogen and illuminated with UV radiation for 45 min. During the periods t_1 (30 s) and t_2 (60 s) the suspension is kept in the dark.

The influence of the intensity of the UV beam on the quenching rate of the trap emission was studied by using filters with a known transmission at the UV wavelength. Before the measurements were performed, the suspension was first saturated with nitrogen and illuminated with UV radiation until the trap emission intensity had reached its minimum intensity, after which it was kept in the dark for a few minutes to allow the trap emission to recover. Figure 4 shows the results of these measurements.

Similar experiments as those described above were performed on suspensions of nanocrystalline ZnO particles in ethanol, propylene carbonate, and DMF. The suspension in ethanol behaved identically to the suspension in 2-propanol. For the
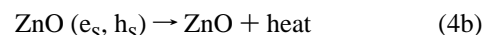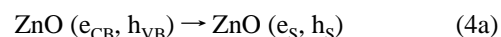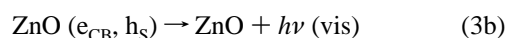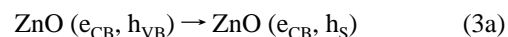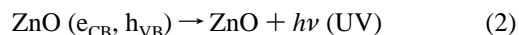
other two suspensions, the intensity of the visible emission during UV irradiation is shown in Figure 5. In general, the visible emission intensity decreases to a constant value after a certain time. For propylene carbonate and DMF, this constant value is 75% and 40% of the initial intensity, respectively. Before this constant value is reached, the change of the visible emission intensity with time shows a different behavior for each of the solvents. It has to be remarked that the suspensions in propylene carbonate and DMF showed some light scattering. In Figure 6 the absorption spectra for ZnO in ethanol and DMF are shown. The tail on the low-energy side in the absorption spectrum of redispersed ZnO in DMF is due to light scattering by clusters of ZnO particles. A complete redispersion of precipitated colloidal particles can be difficult owing to the formation of clusters. For ethanol as a solvent, experiments were performed on a suspension directly after preparation (no light scattering) and on a suspension after redispersion of the particles (light scattering). During the first period of UV irradiation (directly after saturating the suspension with nitrogen), the intensity of the visible emission decreased at similar rates for both ethanolic suspensions. This rate was also similar to that of the suspension in 2-propanol. However, the constant value that was reached eventually was higher for the suspension that showed light scattering. After the suspensions were kept in the dark for a couple of minutes, both the transparent and the non-transparent suspensions behaved identically, and again similar to the suspension in 2-propanol. For the other solvents (propylene carbonate and DMF), the results of these measurements are presented in Figure 7. In the case of propylene carbonate as a solvent, the intensity of the visible emission quenches only very slowly. For DMF, a similar quenching behavior is observed as for ethanol and 2-propanol. With respect to the amount of time it takes for the visible emission intensity to recover completely, differences were observed for the various solvents. It was already mentioned that for a suspension in 2-propanol (and ethanol), the visible emission intensity recovers within about 5 min. For DMF as a solvent, keeping the suspension in the dark for half an hour only leads to a recovery of 50%, and for propylene carbonate the recovery time is even longer.

4. Discussion

When a semiconductor is photoexcited, electrons (e) are promoted from the valence band (VB) to the conduction band (CB), leaving a hole (h) in the valence band:

$$ZnO \xrightarrow{h\nu(UV)} ZnO\ (e_{CB}, h_{VB}) \tag{1}$$
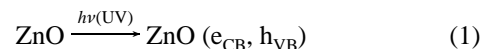
Previously, the relaxation processes of a photoexcited nanocrystalline ZnO particle have been described in detail.[5] Schematically, they can be summarized as follows:

$$ZnO\ (e_{CB}, h_{VB}) \rightarrow ZnO + h\nu\ (UV) \tag{2}$$

$$ZnO\ (e_{CB}, h_{VB}) \rightarrow ZnO\ (e_{CB}, h_S) \tag{3a}$$

$$ZnO\ (e_{CB}, h_S) \rightarrow ZnO + h\nu\ (vis) \tag{3b}$$

$$ZnO\ (e_{CB}, h_{VB}) \rightarrow ZnO\ (e_S, h_S) \tag{4a}$$

$$ZnO\ (e_S, h_S) \rightarrow ZnO + heat \tag{4b}$$

In these formulas, S denotes the surface of the particle. After photoexcitation (eq 1), three competing processes can take place, viz., eqs 2, 3 and 4. The processes 2 and 3 are radiative processes
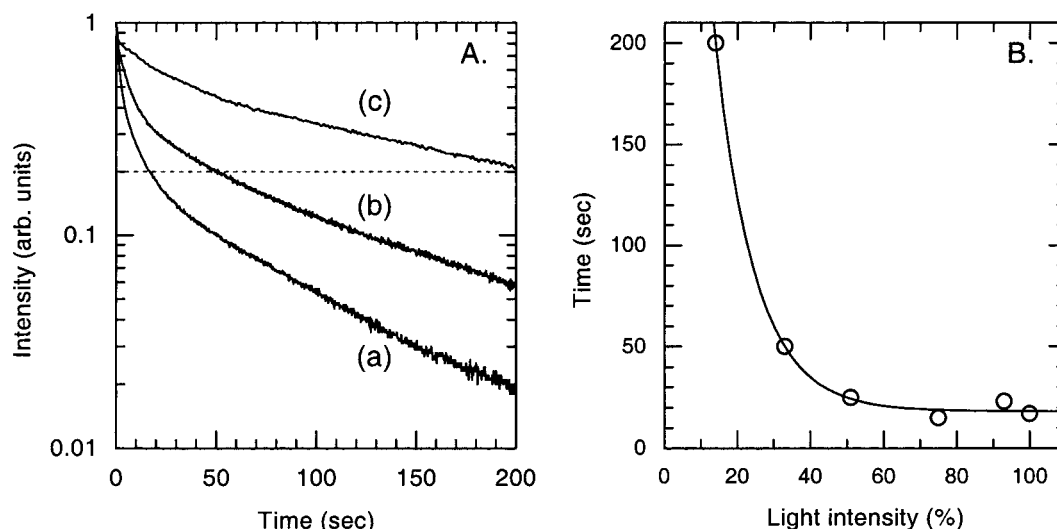
Figure 4. (A) Intensity of the trap emission at 2.2 eV as a function of time while illuminating with UV radiation (4.3 eV). The measurement is performed at room temperature on a suspension of nanocrystalline ZnO particles in 2-propanol that has first been saturated with nitrogen and illuminated with UV radiation for 45 min. Filters with varying transmission at 4.3 eV were placed in the UV beam: (a) no filter, (b) 33%, and (c) 14% transmission. (B) Time at which the trap emission intensity has decreased to 20% of its initial value (see dashed line in (A)) versus the light intensity at 4.3 eV. The solid line is a guide to the eye.
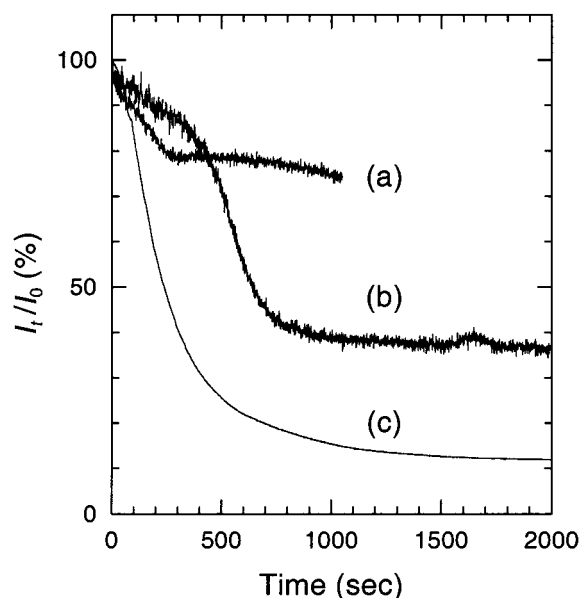

Figure 5. Intensity of the visible emission of a suspension of nanocrystalline ZnO particles in propylene carbonate (a) and DMF (b) during UV irradiation (4.3 eV). The suspensions were first saturated with nitrogen. On the vertical axis the intensity at time t (I_t) is given as a percentage of the intensity at $t = 0$ (I_0). For comparison, the results of the measurement in 2-propanol are shown as curve c. The fact that curves (a) and (b) have a lower signal-to-noise ratio than curve c is due to a difference in concentration with respect to the 2-propanol suspension.

Figure 6. Absorption spectra of a suspension of nanocrystalline ZnO in DMF (a) and ethanol (b).

resulting in UV and visible emission, respectively. It has to be remarked that formula 3b is a simplified description of the visible emission process. More details concerning this process have been presented in a previous paper.[5] Process 4 is the predominant relaxation process of a photoexcited ZnO nanoparticle, viz., nonradiative decay via surface states. It is assumed that for a nanocrystalline semiconductor particle nonradiative recombination in the bulk is negligible compared to nonradiative recombination at the surface of the particle.

The presence of chemisorbed species on the particle surface can influence the relaxation processes. One of such species are
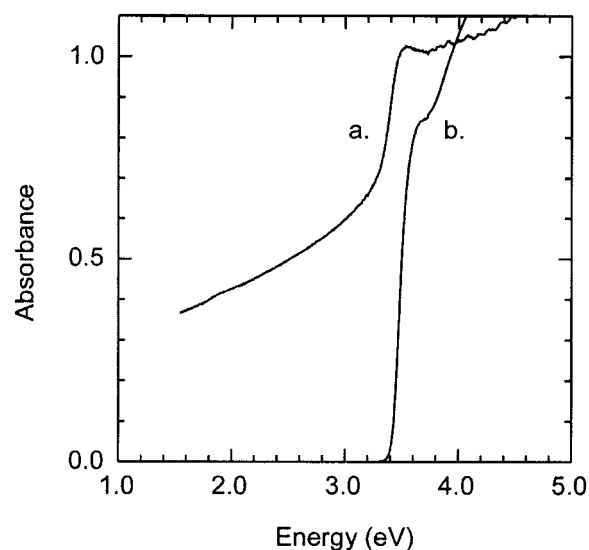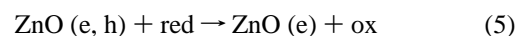
solvent molecules. After photoexcitation of a ZnO particle, the photogenerated hole can be used to oxidize (red → ox) an adsorbed solvent molecule:

$$ZnO\ (e, h) + red \rightarrow ZnO\ (e) + ox \qquad (5)$$

Another important species that can be chemisorbed quite strongly to the surface of a ZnO particle is oxygen. Upon saturating a suspension with an inert gas, only the free oxygen molecules are removed, which explains why the emission properties have not changed after saturating with nitrogen. UV excitation of a suspension of ZnO particles can lead to a photoinduced desorption of chemisorbed oxygen molecules via the formation of hydrogen peroxide:[6]

$$ZnO\ (e, h) + {}^1\!/_2 O_2 + H^+ \rightarrow ZnO\ (h) + {}^1\!/_2 H_2 O_2 \qquad (6)$$
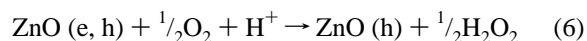
When there are no other oxygen molecules present in solution to replace the desorbed ones, it is possible to make the surface of the ZnO particles free of adsorbed oxygen by UV irradiation.
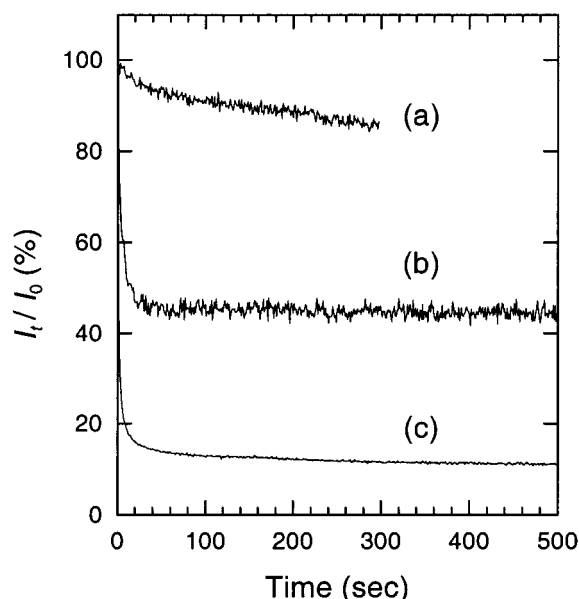
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Figure 7. Intensity of the visible emission of a suspension of nanocrystalline ZnO particles in propylene carbonate (a) and DMF (b) during UV irradiation (4.3 eV). The suspensions were first saturated with nitrogen and illuminated with UV radiation until the intensity had reached a constant value. Before the measurement was performed, the suspension was kept in the dark for several minutes. On the vertical axis the intensity at time t (I_t) is given as a percentage of the intensity at $t = 0$ (I_0). For comparison, the results of the measurement in 2-propanol are shown as curve c. The fact that curves a and b have a lower signal-to-noise ratio than curve c is due to a difference in concentration with respect to the 2-propanol suspension.

When the processes 5 and 6 both take place, the photoexcited ZnO particle has relaxed to its ground state nonradiatively.

In the absence of free oxygen molecules in the suspension, the photodesorption process 6 is accompanied by a decrease of the intensity of the visible emission, as shown in Figure 2 between $t = 0$ and $t = 2000$ s. A detailed explanation for this quenching will be given later. The fact that the rate of quenching is slow is due to the experimental conditions. The UV radiation beam only illuminates a small part of the suspension inside the quartz cuvette, and the semiconductor particles can diffuse in and out of this area. At any given time, less than 5% of the total number of ZnO particles will be illuminated by the UV beam.

As was mentioned in the Introduction, different explanations have been suggested for the quenching of the visible emission of ZnO under UV irradiation. Subsequent experiments have indicated that a photoinduced dissolution of the material is not responsible for the observed behavior.[16] Also, a shuttle mechanism based on adsorbed oxygen[6] was not in agreement with results obtained by further experiments.[20] The results presented in this paper provide further evidence that the shuttle mechanism is not responsible for the visible emission. The mechanism requires the presence of adsorbed oxygen to observe trap emission for nanocrystalline ZnO particles. This would mean that the recovery of the trap emission intensity while the ZnO suspension is in the dark is due to a resorption of oxygen molecules that are still present in solution. Suppose that such a resorption can take place, UV irradiation should quench the recovered trap emission at a similar rate as before. It can be seen in Figure 2 that this is not the case. After the initial slow desorption of chemisorbed oxygen (accompanied by a slow quenching of the visible emission), the decrease of the visible emission intensity is fast following the recovery of the signal.

To explain these results, we propose a mechanism based on charging of the ZnO particles to account for the quenching of the trap emission upon UV irradiation.

When a ZnO particle is photoexcited in the absence of adsorbed electron scavengers (such as oxygen), it can be negatively charged because the photogenerated holes can still be efficiently scavenged by adsorbed solvent molecules (see process 5). For a thin film consisting of ZnO particles, it has been observed that charging with electrons leads to a decrease of the trap emission intensity while at the same time the intensity of the exciton emission increases.[23] This was explained by a filling of electron traps resulting in an increase of the number of free electrons. It was assumed that the recombination of free electrons with free holes (exciton emission) was the most probable radiative process. Charging effects have not only been observed for nanoparticulate ZnO electrodes but also for suspensions of nanocrystalline ZnO particles,[10,16] as was already mentioned in the Introduction. The observed quenching of the trap emission can be explained by the presence of excess electrons on the ZnO particles. The recovery of the trap emission intensity while the suspension is kept in the dark is due to decharging of the ZnO particles. Even in the absence of electron scavengers such as oxygen, a slow decharging of the particles will take place. From the time scale of the recovery (full recovery after 300 s), information can be obtained on the lifetime of the charged particles. The present explanation for the quenching of the visible emission explains the observations shown in Figure 2. In the freshly prepared colloidal suspension the oxygen that is adsorbed on the surface of the ZnO particles acts as an electron scavenger. The quenching of the visible emission is slow because all the oxygen has to be removed before the particle can be charged. After the recovery of the signal in the dark, the quenching is much faster. Photoexcitation of electron–hole pairs and the subsequent scavenging of the holes by 2-propanol (or ethanol) immediately results in the formation of charged particles, as no efficient electron scavengers are present.

As was mentioned before, the quenching of the visible emission upon UV irradiation is accompanied by a shift of this emission band of 30 meV to higher energies. The intensity of the exciton emission band increases and shifts by some 30 meV to lower energies. This suggests that predominantly the emission characteristics of the bigger particles in the suspension are affected by UV irradiation. For nanocrystalline ZnO particles that show quantum size effects, it is known that the emission bands are broadened owing to a distribution in particle sizes. The low-energy side of the emission band originates mainly from the bigger particles and the high-energy side from the smaller particles in the distribution. Charging of particles results in an increase of the UV emission and a quenching of the visible emission, as discussed above. The shift of the UV and visible emission to lower and higher energies, respectively, can be explained if the larger particles are charged more easily upon UV irradiation. The low-energy side of the visible emission band originates mainly from the bigger particles and the high-energy side from the smaller particles. When the visible emission from the bigger particles quenches, the maximum of the visible emission band shifts to higher energies owing to a larger contribution from the smaller particles. The opposite applies for the exciton emission band. The exciton emission originating form the bigger particles increases upon UV irradiation, resulting in a shift of this emission band to lower energies. Apparently, the bigger ZnO particles can be charged with electrons more easily than the smaller ones. It has been shown before that the

redox potential of quantum-sized ZnO increases with particle size.[24] The potential at which electron injection into ZnO occurs increases with decreasing particle size. This behavior is expected when electrons are transferred into the quantized electronic levels of ZnO because the conduction band edge shifts to higher energies as the size of the particle decreases.

To describe in more detail the way in which the presence of excess electrons in a ZnO particle results in a decrease of the trap emission intensity, it is necessary to know what kind of transition is responsible for this emission. We have been able to assign the trap emission of ZnO to a transition of a photogenerated electron from a shallow level close to the conduction band to a deeply trapped hole in the bulk of the particle.[9] Furthermore, it is assumed that the trapped hole is a $V_O^{\bullet\bullet}$ center.[5] The $V_O^{\bullet\bullet}$ trapped hole center is created by trapping of a hole by a $V_O^{\bullet}$ center, probably via surface states.[5] $V_O^{\bullet}$ centers (oxygen vacancies containing one electron) are the most abundant paramagnetic defects in ZnO.[25] The $V_O^{\bullet}$ center is located about 2 eV below the conduction band edge.[26] Each of these centers can trap an additional electron to form $V_O^{\times}$ centers (oxygen vacancies with two electrons). Charging of the ZnO particles with electrons will raise the electron quasi-Fermi-level, which means that the oxygen vacancies will exist as $V_O^{\times}$ for most of the time during which the particle is charged. Effectively, this means a removal of the $V_O^{\bullet}$ centers by charging of the particles, which explains the quenching of the visible emission. At the same time, owing to the higher concentration of conduction band electrons, the recombination rate of excitons increases, thus explaining the increase of the exciton emission intensity. Apparently, Auger effects do not play an important role, for if they did the exciton emission intensity would decrease when a charged semiconductor particle is photoexcited. When an electron−hole pair is created in a charged semiconductor particle, the energy released by the recombination of the electron−hole pair can be absorbed by the excess electron resulting in an increase of its kinetic energy. This electron can be emitted from the semiconductor particle, or it can dissipate its energy by emitting phonons. Auger effects have been observed in semiconductor particles; they are involved in the photodarkening of CdS particles[27] and the fluorescence intermittency of CdSe particles.[28]

The possibility to charge a semiconductor particle with electrons is influenced by the nature of surface adsorbates. Of course, an electron scavenger (such as oxygen) should not be present, which is why the suspensions were saturated with nitrogen. Next, the photogenerated holes should be removed from the particle by a suitable hole scavenger. From the results as presented in Figure 7, it is clear that 2-propanol (and ethanol) and DMF are equally capable of scavenging photogenerated holes from a ZnO particle. For these solvents, the visible emission intensity quenches at a similar rate under UV irradiation. From Figure 7 it can also be seen that propylene carbonate is much less able to scavenge holes as the emission intensity hardly decreases at all upon UV irradiation. This is in agreement with results from experiments on ZnO electrodes in propylene carbonate under comparable conditions.[29] In these experiments no significant oxidation of propylene carbonate was observed.

The observation that in DMF the visible emission of the ZnO particles only quenches to about 40%—instead of 10% in 2-propanol—could be due to cluster formation of ZnO particles. This would mean that clusters of particles are difficult to charge. Possibly the particles inside such a cluster are hardly charged because they are "shielded" by the outer particles from the cluster.

5. Conclusions

Experimental evidence is presented for a model explaining the quenching of the visible emission from oxygen-free suspensions of nanocrystalline ZnO particles in alcohols such as 2-propanol and ethanol under UV irradiation. The quenching is due to charging of the ZnO particles. In the absence of an electron scavenger such as oxygen, the removal of photogenerated holes from the particles by solvent molecules results in the formation of negatively charged ZnO particles. In these particles, the $V_O^{\bullet}$ centers that are involved in the visible emission process, are converted into $V_O^{\times}$ centers resulting in a quenching of the visible emission.

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