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Modelling photooxidation of CdSe-ZnS nanocrystals

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We model the blueshift of the photoluminescence spectra of CdSe-ZnS nanocrystals under ultraviolet irradiation. The model is based on photo-assisted oxygen diffusion into the CdSe nanocrystal structure, which is believed to have a primary role in the observed blueshift of the photoluminescence peak wavelength by reducing the confinement core radius of the exciton wavefunction inside the CdSe nanocrystal core. We compare the predictions of this model with experimental data.

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1 Introduction In recent years colloidal nanocrystals have generated much interest for both fundamental research and technical applications. CdSe-ZnS nanocrystals possess strong size-dependent optical properties due to quantum confinement. In photoluminescence experiments it was found that the peak emission wavelength undergoes a blueshift over time when CdSe-ZnS nanocrystal samples are exposed to air, whereas this cannot be observed in a nitrogen rich environment [1]. Therefore, it is thought that the blueshift of the emission wavelength is primarily due to photo-induced oxidation, which reduces the confinement core radius of the exciton wave function within CdSe nanocrystals [1].

The time evolution of the blueshift of the photoluminescence spectra has been found to depend on the local environment. Effects other than oxidation can also influence the blueshift, such as extraction of the surface passivating molecules (typically organic ligands), generation of crystal defects in nanocrystals, and intermixing of the few atomic layer thick shell material with the core material of the nanocrystal [2]. Therefore, it is not surprising that the time evolution of the blueshift has been found qualitatively different from sample to sample by different groups. One of the most interesting results is that the photoluminescence wavelength decay has a linear dependence on the logarithm of time and therefore the blueshift can be described by

$$\lambda(t) = \lambda_0 - B \log(t) \quad (1)$$

where λ_0 is the initial wavelength and B is the decay parameter [3]. As shown below, a similar dependence is observed in the present study. Nevertheless, other dependencies of the time evolution of the blueshift have also been observed. For example, in Ref. [1] the blueshift can be qualitatively described by a function which decays as the square root of time, whereas in Ref. [2] this decay is shown to have a linear dependence on time. In addition, Ozasa et al. have found that the photooxidation blueshift is quicker for samples under 365nm irradiation than for samples radiated by a 435nm laser [2].

In this paper, we study the time evolution of the blueshift of the photoluminescence maximum by employing a macroscopic diffusion model to describe the penetration of oxygen into CdSe-ZnS nanocrystals under 325 nm irradiation and the subsequent reduction of the confinement radius of excitons. We compare this model with experimental data.

2 Theoretical model

2.1 Diffusion of oxygen The diffusion equation describes the time-dependence of the oxygen fraction at a position r within the nanocrystal. We assume that initially the nanocrystals do not contain oxygen. As the time advances,

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the oxygen fraction increases due to photo-assisted oxygen diffusion from the environment into the nanocrystals under irradiation. Mathematically, the problem is formulated as follows. At time $t = 0$, the oxygen fraction $n_0(r, t) = 0$ within the boundaries of the nanocrystal ($0 < r < L$), but it is assumed to be one elsewhere, e.g.

$$n_0(r, t = 0) = \begin{cases} 0, & \text{if } 0 < r < L \\ 1, & \text{elsewhere} \end{cases} \quad (2)$$

In order to determine the oxygen fraction at distance r at time t , we solve the one-dimensional (1d) diffusion equation of

$$\frac{\partial n_0(r, t)}{\partial t} = D \frac{\partial^2 n_0(r, t)}{\partial r^2}, \quad (3)$$

where D is the photo-induced diffusion coefficient of oxygen atoms. The solution of this diffusion equation within the nanocrystal boundaries is given by the Fourier series

$$n_0(r, t) = 1 + \sum_{k=1}^{M=\infty} \left(\frac{2}{k\pi} \right) [\cos(k\pi) - 1] \sin\left(\frac{k\pi r}{L}\right) \exp\left(-\frac{Dk^2\pi^2}{4R^2}t\right) \quad (4)$$

A few solutions of Eq. (4) are shown in Fig. 1.

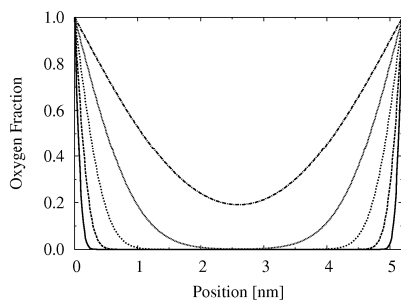


Figure 1 Time evolution of the oxygen fraction within the boundaries of the nanocrystal by solving Eq. (4). Diameter $L = 5.2$ nm, $M = 500$.

CdSe nanocrystals are spherical, three-dimensional (3d) objects and the above 1d diffusion model in principle can easily be extended to three dimensions analytically. However, this is not the scope of this paper and instead a 3d numerical solution will be provided in this paper. We note also that at initial times photo-assisted diffusion of oxygen should be qualitatively similar both in 1d and 3d case. This is because in general, at initial time t , the diffusion distance of oxygen atoms should be proportional to the square root of the diffusion constant multiplied by time, e.g. $d \propto \sqrt{Dt}$. Our numerical results justify this assumption, as shown in Sec. 4.

2.2 Emission wavelength vs radius The confinement core radius of the exciton wave function can be determined

using the time-dependent oxygen fraction given by Eq. (4). In our model we assume that the exciton wave function is confined to the volume where only a small amount of oxygen can be found. Mathematically, at time t the confinement core radius R_{cer} can be calculated from the implicit equation of

$$n_0(R_{cer}, t) = n_{crit}, \quad (5)$$

where n_{crit} is a constant (chosen to be equal to 0.8 in this paper).

The confinement core radius determines the photoluminescence emission wavelength of the nanocrystal. For CdSe nanocrystals it was found that with increasing nanocrystal radius the bandgap decreases, as shown in Fig. 2. Using the experimental data for CdSe nanocrystals in Fig. 2 from Ref. [4], we empirically found that for CdSe nanocrystals the size dependent energy gap can be described by the simple equation

$$E_g(R_{NC}) = 1.628 + 1/R_{NC} \quad (6)$$

where R_{NC} is the nanocrystal radius and E_g is measured in units of eV. Although the formula in Eq. (6) is only an intuitive empirical choice, it provides a reasonable description of the nanocrystal band gap energy against the nanocrystal radius in the relevant parameter range from 0.75 to 4 nm in radius and from 2 to 3.5 eV in energy, as shown in Fig. 2.

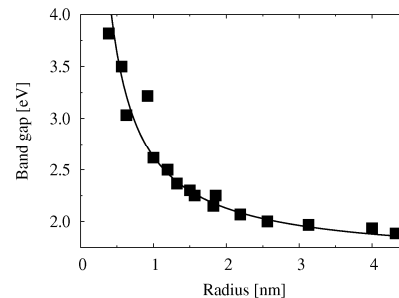


Figure 2 Experimental band gap energies (squares, from Ref. [4]) as a function of nanocrystal radius. The solid line represents the empirical “fitting” curve of Eq. (6).

2.3 Nanocrystal emission blueshift vs irradiance

For the photo-oxidation tests, commercial CdSe-ZnS core-shell nanocrystals (Evident Technologies) were mixed with the polymer poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO, American Dye Source ADS129BE) in a weight ratio of 1:10 and spin-cast on quartz substrates, using chloroform as the solvent, to form composite films approximately 50 nm thick. The initial nominal CdSe core diameter was 5.2 nm and the ZnS shell thickness was only a few atomic layers. Photoluminescence measurements were made on these films before and after irradiation with varying energy doses from a 325 nm laser using a beam power density below $100 \mu\text{W}/\text{mm}^2$ to prevent heating. At 325 nm the

nanocrystals absorb strongly whereas the absorption of the PFO is minimal. The nanocrystals phase-segregate to the top surface of the PFO film during film formation. They are thus exposed to both atmospheric oxygen and oxygen contamination within the PFO matrix. In the absence of 325 nm light irradiation the diffusion of oxygen is negligible over the time scales of the experiment.

3 Results We determine the theoretical nanocrystal emission wavelength at time t by combining Eq. (6) with the result for the confinement core radius in Eq. (5). Namely, at time t we determine the nanocrystal confinement core radius R_{ccr} using Eq. (5), which is then fed into our empirical description of the nanocrystal emission band gap energy against nanocrystal radius in Eq. (6). The dependence of the peak wavelength on time is then rescaled in terms of the laser energy dose applied to the sample during that time.

The calculated time-dependence of the blueshift of the nanocrystal emission wavelength in our model is presented in Fig. 3, as is the result for a numerical simulation incorporating three-dimensional diffusion. For short times (energy dose less than 100 mJ), our models describe qualitatively the general trends of the blueshift shown experimentally. However, for longer times (energy dose larger than 100 mJ) we observe a significant difference in the time evolution of the blueshift between our models and the experimental data.

We also found that the oxygen diffusion in the 3d model is quicker than in the corresponding 1d model. However, the qualitative trends for the two models are the same.

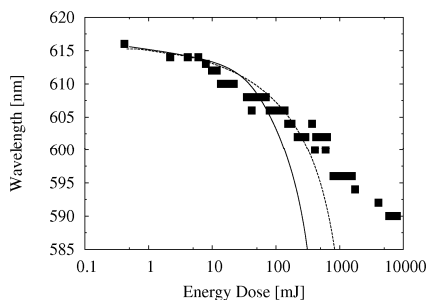


Figure 3 Blueshift of the peak wavelength against photo-irradiation energy dose. Solid and dotted lines are the results of our numerical 3d and analytical 1d diffusion models, respectively, when assuming $D = 6 \times 10^{-4} \text{ nm}^2/\text{s}$. Filled squares represent our experimental data.

4 Discussion The model presented in this paper describes the oxygen diffusion into CdSe when the nanocrystal samples are exposed to 325 nm light in the presence of oxygen. It is assumed that this leads to reduction of the confinement radius for excitons in CdSe-ZnS nanocrystals via oxidation of the periphery of the CdSe core and thus to a blueshift in their photoluminescence spectra.

The theoretical results presented in Fig. 3 are consistent with oxygen diffusion into CdSe nanocrystals in the initial stages. In particular, for irradiation doses below 100 mJ it is found that oxygen diffusion alone can both qualitatively and quantitatively describe the observed blueshift observed in experiments with a photo-induced oxygen diffusion constant of $D \sim 10^{-4} \text{ nm}^2/\text{s}$. For irradiation doses above 100 mJ the diffusion models predict a quicker blueshift in photoluminescence than observed experimentally. The discrepancies can arise for the following reasons:

(a) The model presented in this paper investigates a macroscopic problem where possible fluctuations at the atomic level are suppressed. Nevertheless, these atomic fluctuations can be very important, especially for systems at the nanoscale.

(b) In a full atomistic model we would expect to see a diminishing time dependent diffusion constant for oxygen when the system gets close to the saturation limit.

(c) For photooxidation to take place, oxygen has to diffuse through the ZnS shell covering the CdSe nanocrystals [1]. This effect is not currently included in our model, but may be related to the reduced slope in the experimental data of Fig. 3 below an irradiation dose of approximately 10 mJ.

(d) Finally, the blueshift of the photoluminescence spectra depends on the local environment and therefore other effects can also influence this blueshift, such as loss of the surface protecting molecules (typically organic ligands), generation of crystal defects, and intermixing of the few nanometre thick shell material with the core material of the nanocrystal. More sophisticated models would be required to study these effects of photooxidation.

5 Summary A diffusion based model has been developed to study the observed blueshift of the peak photoluminescence wavelength of CdSe-ZnS nanocrystals under exposure to 325 nm light in the presence of oxygen. The general trends are described within this simple model, which is based on solving the diffusion equation for oxygen. Further theoretical developments would be required to extend this model to describe the blueshift at longer times.

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References

- [1] W. G. J. H. M. van Sark, P. L. T. M. Frederix, A. A. Bol, H. C. Gerritsen, and A. Meijerink, *Chem. Phys. Chem.* **3**, 871 (2002).
- [2] K. Ozasa, S. Nemoto, M. Maeda, and M. Hara, *J. Appl. Phys.* **101**, 103503 (2007).
- [3] X. Wang, J. Zhang, A. Nazzal, and M. Xiao, *Appl. Phys. Lett.* **83**, 162 (2003).
- [4] S. Baskoutas, and A. F. Terzis, *J. Appl. Phys.* **99**, 013708 (2006).