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Air-induced fluorescence bursts from single semiconductor nanocrystals

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We observe a dramatic enhancement of the fluorescence intensity from single core/shell CdSe/ZnS nanocrystals upon sudden exposure to air from an evacuated surrounding. Both the number of particles contributing to emission increases as well as the average emission intensity from a single particle, leading to an overall fluorescence rise by a factor of 60. A common power-law distribution of both on- and off times of single nanocrystals is observed independent of shell thickness and environment. We propose that electron transfer to oxygen, which is facilitated by the presence of water, leads to a neutralization of charged, nonemissive nanocrystals. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1769585]

Semiconductor nanocrystals (NCs), or colloidal quantum dots, are an interesting class of materials, which combine both the benefits of solution-based processability with conventional bulk inorganic semiconductor physics.[1] NCs are potentially useful because of their optical properties, such as high fluorescence quantum yields and ready tunability of the emission wavelength from the UV to the near infrared, as well as large absorption cross sections upon excitation into the continuum. In addition, NCs exhibit a range of intriguing photophysical properties. In particular, there have been a number of recent reports that the fluorescence intensity of NCs can actually be enhanced in the presence of air,[2–4] in marked contrast to, for example, organic semiconductors, which generally photo-oxidize and bleach irreversibly in air. Surprisingly, no corresponding fluorescence increase has previously been observed from single particles upon exposure to air.[5,6] In the contrary, flushing single particles with different atmospheres was actually found to lead to a slight reduction of the overall fluorescence intensity.[5] This discrepancy in literature to date between ensemble and single NC measurements suggests that the air-induced fluorescence rise is a property of the ensemble (due to, e.g., a change in aggregation properties) and not of the individual particles. We demonstrate here that a direct comparison of the same *single* NCs in air and in a vacuum yields a significant enhancement both in terms of the single particle fluorescence intensity and in terms of the number of optically active particles. Particles which appear dark under a vacuum and thereby limit the overall quantum yield of the ensemble[7–10] can be switched on upon exposure to air. We find a strong dependency of the fluorescence increase on the thickness of the wide band gap semiconductor shell covering the NC emitting core, which most likely explains the discrepancy in literature.

We studied the photoluminescence (PL) intensity of single CdSe/ZnS core/shell NCs (core diameter 4.4 nm) stabilized by hexadecylamine/trioctyl phosphine/trioctyl phosphine oxide (TOPO) ligands.[11] The NCs were dispersed in a polystyrene matrix (~20 nm thick) in order to facilitate processing and substrate wetting, and deposited on top of a silicon wafer covered by 300 nm of silicon dioxide. We investigated four samples of NCs with nominal shell thicknesses from 1.2 to 4.2 monolayers. The nominal ZnS shell thicknesses were calculated from the added average mass of ZnS per particle, estimated from the amount of Zn and S precursors used in the synthesis. Fluorescence was recorded using a homebuilt widefield imaging microscope with a long distance objective lens [numerical aperture: 0.55]. The samples were mounted in a Cryovac microscope cryostat and could be evacuated down to a pressure of 10^{-7} mbar and subsequently purged with a gas in under 3 s. Figure 1(a) shows room-temperature fluorescence images from CdSe NCs coated by 1.2 monolayers of ZnS, excited using the 457.9 nm line of an argon-ion laser with an average excitation density of 25 W cm^{-2} and a spot size of ~80 μm. Under vacuum, only three fluorescent spots are clearly resolved and a number of further shadows indicate the presence of more weakly emitting species. The right-hand side panel

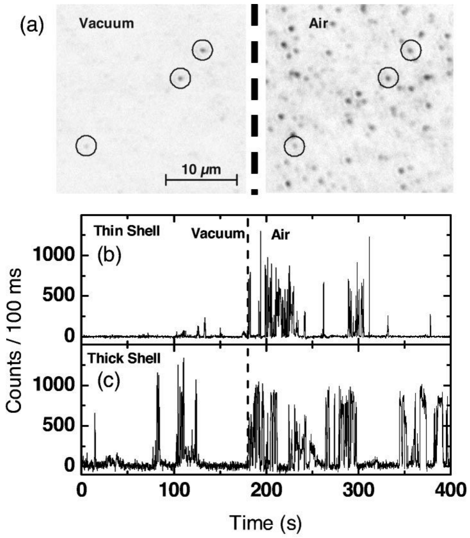

FIG. 1. (a) Fluorescence microscope images of the same single CdSe/ZnS NCs (marked by circles) in vacuum and in air. (b) and (c) Fluorescence intensity trace of a single particle with a nominal ZnS shell thickness of 1.2 and 4.2 monolayers, respectively.

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shows the fluorescence image of the same sample position under sudden exposure to air. The same three NCs are marked in both images for comparison. We find that both the intensity of the individual NCs increases (by a factor of 8.5) as well as the absolute number of visible NCs (by a factor of 7), leading to an overall fluorescence intensity increase (by a factor of 60) upon purging. The effect was found to be reversible. Repeated venting and evacuating yielded the same result, except that the overall number of emitting particles gradually decreased due to irreversible photobleaching. PL time traces were recorded in 100 ms integration windows every 138 ms. Figure 1(b) shows the effect of purging on the fluorescence intensity time trace of a single NC with a shell thickness of 1.2 monolayers. In a vacuum, only a small number of weak fuorescence bursts are observed. After purging the chamber, a blinking feature characteristic of single NCs[7] is recorded with increased overall intensity. Figure 1(c) shows the same experiment for a NC with a thick (4.2 monolayer) ZnS shell. Prior to purging the particle is much brighter than the NC in Fig. 1(b). Close inspection of the data, which contains almost 3000 data points reveals switching between discrete levels as in previous reports.[7,9,10] Directly after purging the fluorescence turns on following a prolonged off period of almost 1 min. The average intensity during a fluorescence burst under air is comparable to the thinner shell in panel (b), but the total time the particle spends in the on state is increased.

The fluorescence intermittency of single NCs such as in Fig. 1 may be characterized by determining the probability distribution of a single particle spending a particular time in the on- and the off-state. A universal scaling behavior of these probability distributions independent of temperature and shell thickness has previously been reported,[10] and attributed to a tunnelling mechanism, which gives rise to ionization and neutralisation of the particle. This in turn affects the tendency for nonradiative Auger recombination to compete with spontaneous emission, as Auger recombination is much more likely for charged particles.[12,13] We characterized a number of fluorescence intensity time traces in terms of the probability of observing a certain on or off time following the previously described procedure.[10] These times, which are extracted from the blinking traces, are binned and plotted in a histogram showing the probability of a certain on or off time occurring. Figure 2 shows a comparison of fluorescence intermittency histograms measured in vacuum (triangles) and in air (open circles) for CdSe NCs with a thin (1.2 monolayers) and a thick (4.2 monolayers) ZnS shell. All histograms follow a power-law distribution. The exponent for all on times is -1.55, which is in good agreement with previously reported results.[10] For the off times the exponent is -1.25 with one significant deviation observed for the thin shell particles in vacuum, for which the exponent changes to -1.05. We, therefore, conclude that the particles with thin shells spend a significantly longer time in dark states under vacuum than particles with a thicker shell do or than either type of particles do in air. We note that previous studies of single particle intermittency dynamics in dependence of the atmospheric conditions have not revealed such a strong dependence of the off time power-law distribution on atmosphere.[5,6] This is most probably due to the fact that a direct comparison between vacuum and air has not been made previously, but only a comparison of different gas environments.[5]

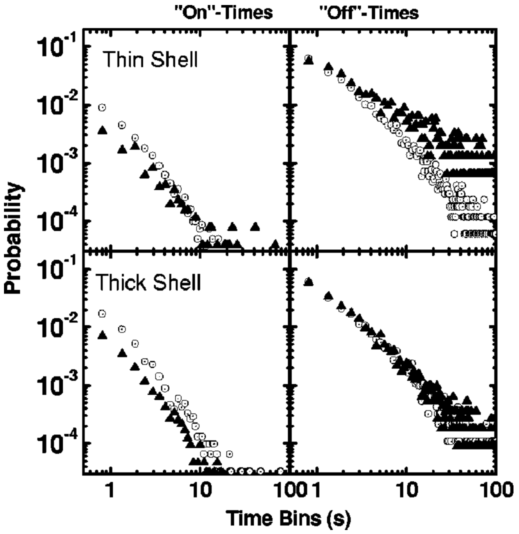

FIG. 2. Histograms of on and off times of fluorescence intensity traces of single NCs in air (⊙) and in vacuum (▲) displaying a common power-law scaling behavior. Note that the off time histogramm of the thin shell NCs in a vacuum differs significantly from the other distributions.

Our observations are consistent with the picture that a dark state exists in the particle, which has a very long lifetime in vacuum and depends sensitively on the immediate environment (i.e., a gas or a ZnS shell) of the CdSe core. The lifetime of the dark state is significantly shortened in the presence of air. The fact that the on times remain almost unaffected by the presence of air suggests that the atmospheric environment does not influence the probability of the particle switching to the dark state. The *reduced* probability of the particle staying in the dark state under air on the other hand shows that this state can be depopulated by a reaction with the air atmosphere. The fact that the effect is reversible upon repeated evacuation and venting suggests the formation of a charge transfer state rather than actual chemical modification of the NC, such as a major ligand rearrangement or dangling bond saturation through covalent bonding. It is, however, conceivable that part of the ligands evaporate from particles close to the surface of the thin polymer film, resulting the creation of dangling surface bonds which can be saturated by the air atmosphere. It should be noted, though, that complete removal of surface ligands is likely to result in an entirely nonemissive state under atmospheric conditions, as recently demonstrated in electron microscopy measurements.[14] Modification of the NC surface through partial ligand removal could explain the increased sensitivity of the NC blinking statistics to the local atmosphere when compared to previous investigations.[5,6]

In order to identify the mechanism for the enhancement, we purged the evacuated sample chamber with a number of different gases. Helium showed no noticeable effect on the fluorescence. The low quantum yield of NCs with no shell or a thin shell is explained by a high charging rate of this type of colloidal quantum dot due to trapping of one of the excited charge carriers at surface defects such as dangling bonds.[15] As hydrogen is often used to saturate such dangling bonds on bulk semiconductors such as silicon, we purged the cryostat with a mixture of hydrogen (10% by volume) and nitrogen. As in the case of purging with helium, no effect was observed, so we conclude that hydrogen based reactions play no role. Upon purging of the thin shell NC sample with

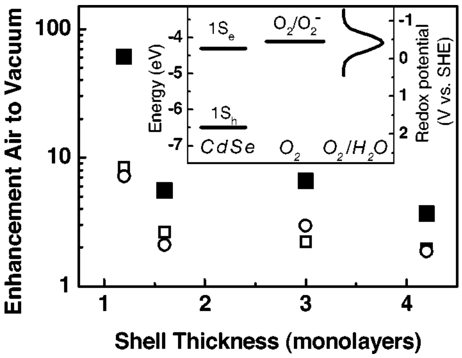

FIG. 3. Plot of the average enhancement factor upon purging with air in dependence of the shell thickness. (○): number of emitting NCs; (□): average enhancement per emitting particle; (■): overall enhancement factor. The inset shows an energy level diagram of CdSe NCs (Ref. 19) in contact with an aqueous solution containing dissolved oxygen. Redox potentials are given with respect to the standard hydrogen electrode.

dry oxygen (99.98% purity) the fluorescence intensity increased by a factor of 9, which arose due to an average intensity enhancement per particle of 2 and an increase in the number of emitting particles by a factor of 4.5. As we still observe a significant effect upon purging with dry oxygen—in contrast to previous reports on bulk films[2] but in agreement with recent investigations on solutions[4]—we conclude that oxygen alone plays a significant role in the fluorescence enhancement effect. However, the enhancement is over six times as strong upon purging with air. The major difference to the above named gases and an air atmosphere is moisture. We therefore conclude that water molecules in the atmosphere play an important role in the passivation of the NCs. A number of scenarios for photochemical fluorescence enhancement in ensembles of NCs have been put forward previously.[2,16] As we observe a quasi-instantaneous effect in the solid state at extremely low particle concentrations dispersed in a matrix, we think that it is unlikely that ligand reactions take place at the surface of the NC. Instead, we propose that a direct oxidation (i.e., electron transfer) occurs from the NC core to oxygen, which leads to a neutralization of the charged, nonemissive particle. This depends on the relative redox potentials of the O_2/O_2^- redox couple and the CdSe lowest occupied molecular orbital. The relative energy levels of the CdSe–O_2 system are shown schematically in the inset of Fig. 3. Electrochemical data[17] suggest that there is a slight barrier for electron transfer from CdSe to O_2 and thus for the formation of O_2^-. However, the presence of a strongly polar medium such as water leads to a broadening of the O_2 LUMOs,[18] thereby facilitating electron transfer. This could explain the dependence of the fluorescence burst on oxygen and water and provide a reason for the full reversibility we observe.

To check our model, we carried out a systematic investigation of the influence of the ZnS shell thickness on the PL burst. Different samples with increasing shell thicknesses from 1.2 monolayers to 4.2 monolayers were purged with air. The fluorescence enhancement effect was found to be reduced dramatically by increasing the shell layer thickness. Figure 3 shows a plot of the relative increase in the number of emitting NCs (circles), the average intensity increase per NC (squares) and the overall enhancement (number × intensity, solid squares), plotted on a logarithmic scale. The largest difference is observed upon going from a nominal shell thickness of 1.2 monolayers to 1.9 monolayers, and a further small decrease is observed upon going to a thickness of 4.2 monolayers. The strong decrease of the air-induced fluorescence enhancement with increasing shell thickness is in agreement with our proposal that a reaction between the CdSe core and the environment takes place, which is increasingly inhibited by the ZnS shell. It is interesting to note that efficient charge transfer apparently still occurs through a nominally completely covered core. The dramatic drop in the enhancement upon increasing the shell thickness to 1.9 monolayers suggests that the core may not be fully covered by 1.2 monolayers and that the ZnS growth on the CdSe core is therefore not entirely uniform.

We have demonstrated a dramatic increase in the fluorescence from single NCs by a factor of up to 60 upon sudden purging with air. Evacuation apparently fundamentally affects the NC photophysics, which may be due to partial ligand removal and the creation of unsaturated dangling bonds on the NC surface. This effect need not necessarily be parasitic in nature. The fact that our fluorescence intermittency histogram is identical for particles of different shell thickness in air, but not in vacuum, suggests that *extrinsic* effects such as charging dominate the photophysics of NCs *in vacuum*. Reducing the probability of a prolonged charged period by either minimising the probability of charging by growing a shell or by enabling rapid decharging by electron transfer to oxygen leads to the common power-law behavior of the off-time distribution.

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