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Photoluminescence enhancement in thin films of PbSe nanocrystals

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Remarkable photoluminescence enhancement (PLE) in submonolayer films of PbSe nanocrystals (NCs) upon continuous illumination was observed. The intensity increase from films on InP substrates was highest in vacuum, while for films on Si/SiO₂ substrates the PLE was stronger in air. The magnitude of the PLE was found to depend on the excitation intensity, being higher for a weaker irradiation power. The possible mechanisms behind the phenomenon of the PLE are discussed and it is suggested to originate mainly from charge trapping outside the NCs core.

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Semiconductor nanocrystals (NCs) have gained significant attention due to their unique size-dependent optical properties.^{1,2} One of the most intriguing phenomena observed with NCs is the enhancement of their photoluminescence (PL) over time during continuous illumination.^{3–14} This effect was reported so far mostly for CdSe and CdSe/ZnS NCs and has induced extensive discussion in literature. Recently it was observed also for PbS NCs embedded in thin polymer films¹⁴ and for PbS NCs in glasses.⁷ Different mechanisms were proposed to explain the PL enhancement but its nature still remains controversial due to the strong dependence of the NCs emissive properties on their surface quality,^{3–5} as well as on the excitation intensity,^{5–8} film morphology,^{4,8,9} substrate-NCs interactions,^{4,10} and environmental conditions.^{11–15}

The PL enhancement (PLE) has not been reported previously for PbSe NCs. This type of NCs became very attractive over the last few years as (near) infrared emitters because of the well controlled liquid-synthesis procedures developed recently^{15,16} and the very large Bohr radius (46 nm) allowing for fine tuning and control of their optical properties.^{17–19} In this letter we report on a remarkable PL enhancement observed in submonolayer films of PbSe NCs upon continuous irradiation. The process was found to be complex and the influence of different parameters is investigated. The possible mechanisms responsible for the observed PL behavior are discussed. The phenomenon of PLE, besides being intriguing from a fundamental point of view, we believe, can be of large relevance for technological applications.

PbSe NCs were synthesized according to the procedure described in Ref. 15, which yielded monodisperse (size-distribution ~7%–8%, estimated from transmission electron microscope images and the width of the first absorption peak) nanoparticles with a PL quantum yield of about 40%–60% in solution. The PbSe NCs used in this work have a diameter of about 4.7 nm with the first exciton peak located at 1.48 μm for particles dissolved in chloroform. Solutions of the NCs were kept in oxygen- and water-free atmosphere

in a glovebox. Submonolayer films [with a particle surface coverage of about 80%, as judged from atomic force microscopy images, see Fig. 1(a)] of these PbSe NCs were prepared by spin-coating solutions of the particles in chlorobenzene on a substrate. The films were prepared in a glovebox and prior to measurements samples were exposed to air only for about 2–3 min while loading them into the vacuum chamber. The chamber was filled either with air or evacuated to a desired low pressure. The PL measurements were performed on the PbSe NCs films using a Nd:YAG (yttrium aluminum garnet) laser operating at 532 nm (second harmonic) as an excitation source and a liquid-nitrogen-cooled InGaAs detector to collect the PL signal. Time sequences of the PL spectra under continuous illumination of the films were recorded.

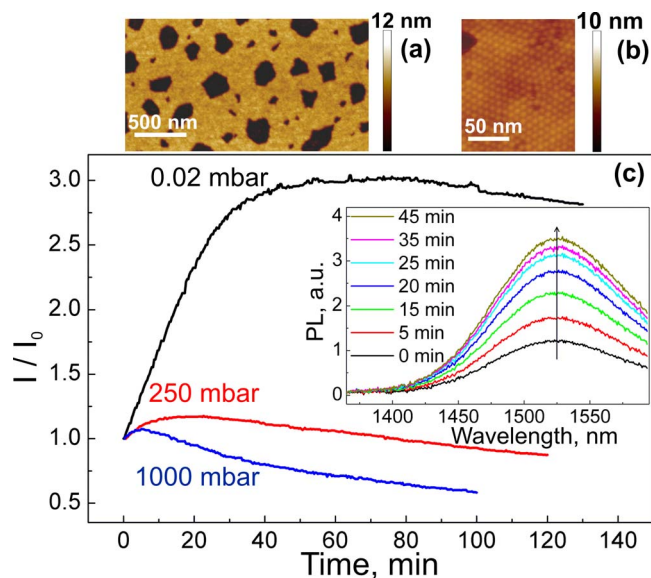


FIG. 1. (Color online) [(a) and (b)] Atomic force microscopy images (height) of (a) a submonolayer film (surface coverage ~80%) of PbSe NCs on an InP substrate, (b) single, ordered NCs in the film. (c) Normalized PL peak intensity vs illumination time for films of PbSe NCs on InP substrates measured in vacuum (0.02 mbar), air (1000 mbar), and at intermediate pressure (250 mbar). Inset—PL spectra of the sample in vacuum for several illumination periods.

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The intensity and wavelength of the PL peak were followed over time for each sample. Multiple samples were measured under nominally identical conditions to verify that the results are reproducible. All measurements were carried out at room temperature.

The first set of experiments was performed with PbSe NCs deposited on InP substrates. By changing the pressure inside the vacuum chamber, the influence of the surrounding atmosphere (more specifically oxygen and water, as the effect of nitrogen was found to be insignificant¹⁵) on the PL of the NCs films was verified. Figure 1(c) shows the time evolution of the PL peak intensity I normalized to the peak intensity at zero time (I_0) for three films measured in air (1000 mbars), in vacuum (0.02 mbar), and at intermediate pressure (250 mbars). In the inset the PL spectra of the sample under vacuum are plotted for several illumination periods.

When the sample is kept in air an initial increase of the peak intensity is observed for the first 6–7 min, then the intensity starts to drop. However, for the sample kept under vacuum, a very strong enhancement in the PL is observed in the course of about 40 min—the intensity reaches a value as high as three times that of the initial intensity (at the beginning of the irradiation). After that it starts slowly to decay. The sample placed at intermediate pressure showed intermediate enhancements of the PL intensity, as seen from Fig. 1. If the mechanism of PLE is strongly related to oxygen (and/or water) it would not be observed at low pressure (where the presence of oxygen and water is less). In fact, our results show the opposite—the PL increase is highest in vacuum. The PL enhancement in vacuum can be understood in terms of two of the proposed mechanisms for PL increase in NCs films—photoinduced surface transformation^{3,5,12,14} and photoelectrification.^{4,20,21} In the first case, upon illumination of the NCs, optimization of surface-ligand passivation occurs, which neutralizes the existing surface defects. In the case of photoelectrification, the PLE is believed to be caused by photoionization of a certain fraction of the NCs in the film due to trapping of carriers into traps outside the NC core²² (in the organic ligands⁴ or in the substrate¹⁰). This would leave the photoionized NCs in a nonemissive (dark) state²² but the electrostatic potential that they create will increase the barrier for ionization of the surrounding neutral (emissive) NCs (electrostatic blockade effect).^{4,20} Hence, the total emission efficiency of the NCs ensemble would increase due to prolongation of the average “on” period of the neutral NCs in the film.²¹ We believe that both of the above discussed mechanisms can be related to the PLE phenomenon we observe in vacuum. Addition of oxygen (and/or water), however, has a significant effect on the strength of the enhancement and on the time scale at which it happens—going from vacuum to ambient pressure the process of enhancement becomes shortened and weaker. This suggests that by introducing oxygen/water molecules additional paths for nonradiative decay are opened,¹⁵ which counteract and suppress the PL enhancement.

We have performed preliminary measurements on the reversibility of the phenomenon of PLE in which the sample chamber was repeatedly evacuated and flushed with air during continuous illumination of the sample. The results show that the enhanced PL intensity in vacuum drops back to almost its initial value after flushing with air and increases again during subsequent evacuation. More detailed experi-

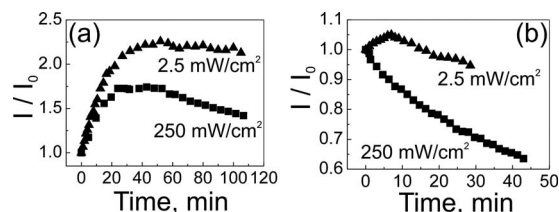


FIG. 2. Time evolution curves of the normalized PL peak intensity for films of PbSe NCs on InP substrates irradiated with a weak (2.5 mW/cm^2) and a strong (250 mW/cm^2) excitation intensity in vacuum (a) and in air (b).

ments on this process are subject of a forthcoming publication.

After reaching a maximum value the PL intensity starts to decrease, even for the sample in vacuum. For the sample in air this decay can be related to irreversible photo-oxidation of the NCs surface, which reduces the core size.¹⁵ A corresponding blueshift ($\sim 8 \text{ nm}$) of the emission peak position is observed. The samples at low and intermediate pressure showed none or a slight redshift, which rules out the possibility for photo-oxidation in these cases. The PL decay then might be due to additional nonradiative recombination channels induced during prolonged irradiation²³ or to the creation of unsaturated dangling bonds at the surface by partially removing ligands during evacuation.²⁴

Next, we followed the time evolution of the PL from submonolayer samples illuminated with a weak (2.5 mW/cm^2) and a strong (250 mW/cm^2) laser intensity in air and in vacuum. For the samples in vacuum [Fig. 2(a)], the PL for both excitation intensities increased in the beginning and then started to decrease, but the enhancement was stronger and persisted over a longer period for the sample under weak excitation. The PL decay was also slower for this sample. If the PLE is caused mainly by the photoinduced surface recovery, then one expects the initial PLE rate $[(dI/dt)/I]$ to increase proportionally to the excitation intensity.⁵ However, we found rather similar values for the increase rate of the samples at low and high excitation powers, which suggests that either the phototransformation of the surface is not the main mechanism behind the PLE phenomenon or there is a process that counteracts the process of PLE at higher excitation intensities. According to the photoelectrification model, Auger ionization of the NCs¹ is such a process, which at higher powers starts to compete with thermally driven ionization. Hence, it increases the number of dark (ionized) NCs over the NCs with suppressed ionization rate, thus impeding the PL enhancement.^{6,8}

For the films measured in air, no PLE was observed at high illumination power—the intensity started to decrease from the beginning of irradiation, as seen from Fig. 2(b). In the case of the weaker excitation intensity, a small initial increase followed quickly by PL decay was observed. Together with that a blueshift in the peak position was observed in both cases, much stronger for the sample illuminated with higher intensity. These results suggest that the simultaneous effect of the PL quenching due to irreversible photo-oxidation of NCs surface in air (as judged from the blueshift) and the darkening effect of the Auger ionization at high illumination power is strong enough to fully eliminate any PL enhancement in this case. Thus, the phenomenon of PLE is found to be very sensitive to the excitation intensity, being

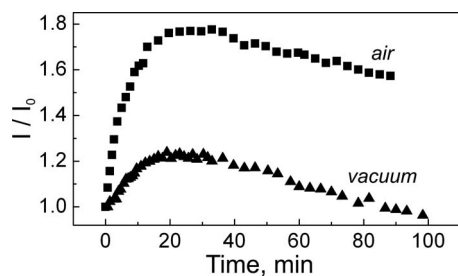


FIG. 3. Change in the normalized PL peak intensity over time for films of PbSe NCs on Si/SiO₂ substrates in vacuum and in air.

observable or not in air depending on how strongly the film is irradiated.

At the end, we briefly show that the mechanism of PL enhancement is related to substrate-NCs interactions. We measured the PL kinetics in vacuum and in air for PbSe NCs films deposited on *silicon* substrates with a 50 nm thick SiO₂ layer on top and compared it to that for films on InP substrates. The normalized PL intensities for Si/SiO₂ substrates are plotted versus illumination time in Fig. 3, which shows that, in contrast to the samples on InP substrates (Fig. 1), the sample on Si/SiO₂ substrate in air has much higher PL increase than the sample in vacuum. In other words, the air atmosphere in the case of Si/SiO₂ substrate facilitates the PLE rather than suppressing it, as was the case for InP substrates. This remarkable change in the behavior of the PL proves that the substrate (and the existing charge trap centers there) has a significant effect on the PL kinetics. SiO₂ layers were found to contain more trap sites in air than in vacuum,²⁵ thus in air there is a higher probability for the charges to be trapped after leaving the NC core. This would lead to an increased probability of photoionization suppression of the remaining neutral NCs in the film,¹⁰ and as a result a stronger PLE, as we observed. Apparently, the favorable effect of an increased trap density on the SiO₂ layer in air is strong enough to overcome the quenching influence (due to photooxidation of the NCs surface, as seen from the slight blueshift of about 3.5 nm in the peak position) of the oxygen/water molecules on the NCs' PL.

In conclusion, we have demonstrated enhancement in PL from thin (submonolayer) films of PbSe NCs under continuous illumination. The process of enhancement is found to be complex in nature and depending strongly on the environmental conditions (i.e., presence of oxygen and/or water), excitation intensity, and on the substrate. Our results so far suggest that the main possible mechanism that can explain the PLE phenomenon is the photoionization of NCs in the film by ejecting charges outside the core (in the organic ligands and/or in the substrate) followed by the suppression

of the ionization probability of the neighboring neutral NCs. It is possible, though, that under certain conditions other processes (such as the photoinduced surface transformation/passivation) can also contribute to the PLE. This is subject of ongoing work.

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