

FAST TRACK COMMUNICATION

Ligand removal from soluble CdTe nanocrystals evidenced by time-resolved photoluminescence spectroscopy

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Abstract

We present experimental studies on the effect of pyridine treatment on the optical properties of ligand-stabilized colloidal CdTe nanocrystals. We demonstrate, by quasi-stationary and time-resolved photoluminescence (PL) spectroscopy, a drastic reduction in the PL lifetime and a concomitant decrease in the PL yield by more than 90% when dissolving the nanocrystals in pyridine. The pyridine solvent efficiently removes the ligand shell and thus enables a rapid energy transfer from the quantum dot to optically dark surface states or into the solvent. The demonstrated removal of the ligand shell is a key step towards integrating such CdTe nanocrystals in hybrid organic/inorganic nanocomposites, where charges may be efficiently separated at the interface. Due to the small band gap of CdTe, such nanocomposites are likely to yield enhanced conversion efficiencies in photovoltaic devices.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The high level of control in the synthesis of soluble nanoparticles (NPs) in terms of their optical, electronic and geometric properties has opened up a wide field of application-oriented research [1, 2], e.g. in nanoelectronics [3], optoelectronics [4, 5], biosensing [6, 7] and photovoltaics [8]. In particular, such NPs may serve as counterparts for conjugated polymers in hybrid, organic/inorganic photovoltaic devices [9], combining interesting possibilities for a systematic study of charge transfer and transport processes in such heterojunctions with the advantage of processing the devices out of solution. Since common conjugated polymers show comparatively short excitation lifetimes in the nanosecond or sub-nanosecond range, an efficient charge separation after optical excitation is necessary to suppress recombination and to yield reasonable conversion efficiencies [10, 11]. The first

promising results on mixtures of conjugated polymers and NPs were obtained with CdSe nanocrystals [8, 9, 12]; however, the absorption of the material could be extended further to the near infrared (NIR) region by using CdTe NPs, which have a smaller band gap than CdSe NPs. Since synthesized NPs are usually stabilized by an organic ligand shell, inhibiting an efficient charge transfer in either direction, a crucial step towards realizing a functional device is the removal of these ligands from the NP surface [8, 9, 12, 13]. Previous optical studies have shown that the quantum yield of CdTe NPs can be enhanced by controlling the PH of the precursor solution [14], photoetching using UV irradiation [15] or by adding proteins [16]. In all these studies, however, the NP was surrounded by a ligand shell, which prevents the desired efficient charge transfer and transport processes.

In this paper, optical absorption spectroscopy and time-resolved photoluminescence (PL) measurements are used

to study the removal of the surface ligands from solution-processed CdTe NPs by a straightforward pyridine treatment. The experiments reveal a distinct decrease in the PL lifetime and a significant reduction in the luminescence yield after a single step of the pyridine procedure, thus evidencing efficient ligand removal upon dissolving the NPs in pyridine.

2. Sample preparation

The synthesis of monodisperse solutions of CdTe nanocrystals followed a new synthetic procedure including the generation of crystalline Cd⁰ NPs prior to the formation of CdTe-NP [17–19]. An amount of 12.8 g of Te (Fluka, purum p.a.) was dissolved in 211.2 g of tri-octylphosphine (TOP, Aldrich, 97%) at 200 °C under a nitrogen atmosphere. This mixture was filled with 1-octadecene (ODE, Merck, for synthesis) up to a total weight of 2 g. A total of 25.6 mg of CdO (Fluka, purum p.a., <99.0%) and 200 μ l of oleic acid (OA, Merck, herbal, purest) were heated to 300 °C in 10 ml of ODE to obtain a clear solution. Further heating to 310 °C led to the formation of a grey precipitate of Cd⁰ particles. The growth of the colloidal crystals was then initialized by injecting 2 g of the TeTOP solution into the flask and by reducing the temperature of the mixture gradually to 250 °C. The whole mixture was cooled down to room temperature after 5 min. This method leads to CdTe nanocrystals with diameters of a few nanometres and with OA molecules attached to their surface.

Residual synthesis products were removed by extraction, adding 1 ml each of n-hexane, chloroform and methanol per ml of the NP solution. The NPs were then precipitated from this mixture in an ultracentrifuge. By repeating this process several times, a clear, purified solution of CdTe NPs was obtained.

In order to remove the OA ligand molecules from the NP surface, we chose a pyridine treatment [9, 20] that exchanges the long organic chains by the much smaller pyridine molecules. During further processing and solvent evaporation these molecules eventually vanish from the NP surface, enabling the desired charge injection. We followed the procedure described in [21]: we added 1 ml of pyridine per 20 mg of purified and dried CdTe NP and dissolved the particles under permanent stirring for 1–2 h at 60–65 °C. The particles were isolated by further adding 6 ml of n-hexane and by centrifugation. Before the residual solvent could evaporate completely, another 1 ml of pyridine was added.

By repeating this process five times and dissolving the remaining NP in a small amount—usually 50–100 μ l—of pyridine for further analysis, we found that only less than 20% of the initial amount of NPs was still present in the solution. In the following, we study the effects of dissolving the NP in pyridine on the optical properties of the samples.

3. Experimental setup

We used continuous wave absorption, PL and time-resolved PL spectroscopy as tools to investigate the effect of pyridine treatment on the NPs. Absorption spectra were taken with a Cary 100 Scan spectrophotometer (Varian) using dilute

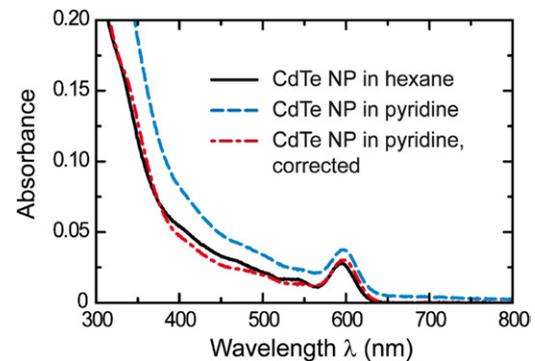


Figure 1. Absorption spectra of a CdTe nanoparticle sample in hexane (solid curve) and pyridine solution (dashed curve). The subtraction of a Rayleigh scattering background proportional to λ^{-4} from the latter results in the corrected spectrum of the pyridine-treated sample (dashed-dotted curve).

NP solutions with an absorbance near the lowest energy NP absorption resonance of less than 0.1. Transient PL data were taken using a time-correlated single photon counting (TCSPC) setup [22]. The samples were excited using ~ 20 ps laser pulses at a 4 MHz repetition rate, tunable between 300 and 335 nm. The laser pulses were generated by frequency doubling the output from a synchronously pumped DCM dye laser and were focused into the NP solution to a spot size of 100 μ m. Typical pulse energies were about 10–100 pJ. The resulting PL from the sample was collected in reflection in a confocal geometry, spectrally dispersed in a subtractive, 0.25 m double monochromator and detected by a micro-channel plate photomultiplier tube (PMT). In this geometry, the time resolution of the TCSPC setup, given by the full width at half maximum of the instrument response function, is 50 ps. The PL spectra of the samples were measured with the same setup by tuning the monochromator and integrating the signal over a fixed period of time.

4. Results

In order to investigate the effect of the pyridine treatment on the optical properties, we take a highly luminescent sample of NPs after synthesis and dry a part of it. Redissolving the dried particles in pyridine at 65 °C yields a slightly opaque suspension, having the same colour as the initial solution but showing significantly reduced fluorescence under UV-light illumination. The absorption and PL spectra as well as the transient PL of the as-prepared solution are measured and compared with the results for the untreated sample.

The absorption spectrum $A(\lambda)$ of the untreated sample (figure 1) shows a spectrally narrow lowest energy absorption peak at 595 ± 2 nm from which we infer an average band gap energy of $E_g = 2.09 \pm 0.01$ eV and, using the results of [23], an average particle diameter of $d = 3.7 \pm 0.1$ nm. The pyridine-treated sample shows essentially the same resonance structure in the absorption spectrum, yet an enhanced broadband absorption shoulder, in particular at high energies but also in the red part of the spectrum, at energies below the band gap. We assign this shoulder to an increase in

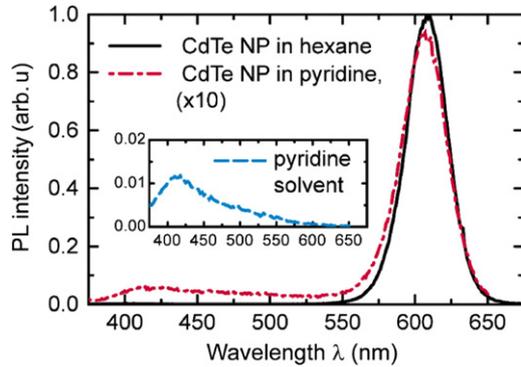


Figure 2. PL spectra of CdTe NPs before and after the pyridine treatment (solid and dashed–dotted lines, respectively). The spectrum of the pyridine-treated sample is multiplied by a factor of 10. The inset shows the PL of the pyridine solvent. All spectra were taken for an excitation wavelength of 315 nm.

Rayleigh scattering from the solution. In order to correct this, a fit $A_R(\lambda) = a \cdot \lambda^{-4}$ is performed in the low energy part of the spectrum ($\lambda > 650$ nm), where NP absorption is negligible. By subtracting $A_R(\lambda)$, with $a = 0.88 \times 10^9 \text{ nm}^4$, from the absorption spectrum of the pyridine-treated sample, we obtain the corrected spectrum (the dashed line in figure 1) which closely matches the absorption spectrum of the untreated sample. The main remaining difference between both spectra is a slight red shift by about 3 nm of the band gap absorption for the pyridine-treated NPs.

The most pronounced effect of the pyridine treatment can be observed in the quasi-stationary and time-resolved PL measurements. In figure 2, the PL spectra of the untreated NPs and the ones dissolved in pyridine are compared for an excitation wavelength of 315 nm. Both spectra exhibit a main emission band at around 610 nm, which stems from CdTe NP. In the hexane solution, the absolute PL quantum yield of CdTe NP is 0.87, as derived from a comparison of the NP PL spectra with that of the fluorescence standard cresyl violet in methanol solution [24]. For the pyridine-treated sample, we find essentially the same emission spectrum but with a considerably reduced intensity. Integrating the signals from 550 to 650 nm, we find the PL quenched by a factor of more than 10, reducing the absolute quantum yield to less than 0.09. The second broad PL band (see the inset in figure 2) with a maximum at 415 nm, which is observed for the NPs in pyridine, can be attributed to residual emission of the unpurified pyridine solvent. The absolute PL quantum yield of the pyridine-treated sample strongly depends on the exact details of the ligand-removal procedure. We have studied various samples and consistently found almost identical yields of the untreated sample as well as a pronounced PL quenching of the pyridine-treated samples with the absolute quantum yields varying between 0.003 and 0.09. In all the studied cases, the shape and strength of the NP absorption spectrum remained unchanged.

Figure 3 shows the normalized PL decay curve for the untreated sample together with a fit to a biexponential decay curve. The data were taken at an excitation wavelength of 315 nm and detected at 610 nm and were normalized to a maximum value of 1. The time constants and amplitudes for the biexponential decay obtained by the fit are $\tau_1 = 31.5$ ns,

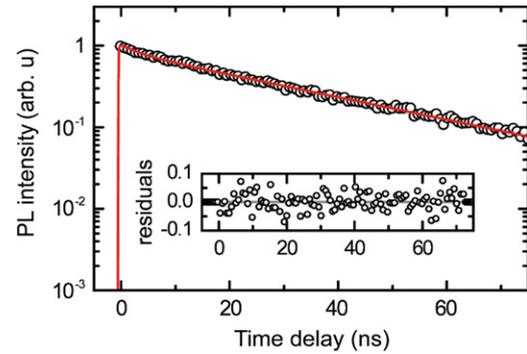


Figure 3. A normalized time-resolved PL decay curve of an untreated NP sample in hexane solution (open circles) at 610 nm taken with an excitation wavelength of 315 nm. The solid line shows a fit to a biexponential decay with parameters $\tau_1 = 31.5$ ns ($A_1 = 0.736$) and $\tau_2 = 3.1$ ns ($A_2 = 0.264$). The homogeneous distribution of the residuals (inset) supports the biexponential decay model.

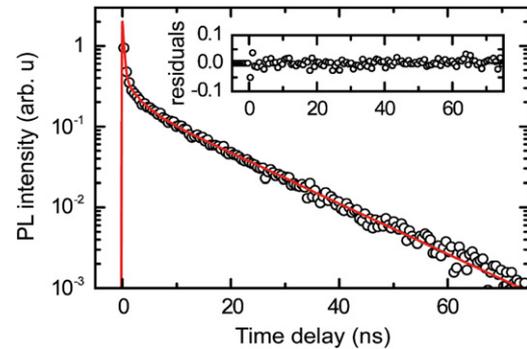


Figure 4. A normalized time-resolved PL decay curve of an NP sample redissolved in pyridine (open circles) at 610 nm taken with an excitation wavelength of 335 nm. The normalization has been carried out to yield the same excitation density as in figure 2. The solid line shows a fit to a tri-exponential decay with fit parameters given in the text, which is supported by the homogeneous distribution of the residuals shown in the inset.

$A_1 = 0.736$, $\tau_2 = 3.1$ ns and $A_2 = 0.264$, respectively, giving an average PL lifetime $\tau_{av} = \sum_i A_i \tau_i / \sum_i A_i$ of 24 ns. In the case of the pyridine-treated NPs, one finds a significantly faster PL decay (figure 3). Here the excitation wavelength was set to 335 nm to minimize the PL signal of the pyridine solvent. The data have been normalized to the same excitation density by using the absorption spectra in figure 1, where fluctuations of the excitation-pulse energy again lead to a relative uncertainty in the scaling of 50%. In the case of the pyridine-treated NPs, one finds a significantly faster PL decay (figure 4). A fit to a tri-exponential decay curve yields $\tau_1 = 13.9$ ns, $\tau_2 = 2.28$ ns and $\tau_3 = 0.25$ ns with amplitudes of $A_1 = 0.141$, $A_2 = 0.164$ and $A_3 = 1.743$, respectively, thus leading to an average PL lifetime of 1.36 ns. Including the uncertainty in the excitation-pulse energy, the time integral over the normalized PL $\sum_i A_i \tau_i$ is a factor of 8.6 ± 4.3 smaller than for the untreated sample, thus confirming the quenching of the PL by more than 90% as a result of the pyridine treatment. For the pyridine-treated sample, a large fraction—of about 15%—of the PL stems from the fast sub-nanosecond decay component.

5. Discussion

The most obvious and straightforward explanation for the fast decay of the PL in the pyridine-treated samples is the recomposition of the ligand shells of the NPs. Since the OA molecules surrounding the NPs electronically passivate the surface states of the NPs, they prevent excitons from being trapped into surface states. This significantly reduces nonradiative contributions to the exciton decay and enhances the PL quantum yield [25]. Pyridine is a much weaker stabilizing agent than OA such that surface passivation in the pyridine-treated sample is reduced [26], leading to a much larger surface trapping rate and thus to a decrease in PL intensity. In our experiments, we observe that a single step of the procedure quenches the PL and leads to a decay which is one order of magnitude faster than for an untreated sample. It is generally believed that this fast exciton decay is due to an efficient hole transfer from the NP into the surrounding trap state and/or solvent [9]. Our results are consistent with such an interpretation, yet they do not allow us to rule out all possible alternative explanations.

The ligand coating affects not only the PL dynamics but also the spatial confinement of the excitonic wave function in the CdTe nanoparticle. It effectively acts as a high potential energy barrier for excitons, thus reducing the spatial extent of the exciton wave function. The much weaker stabilizer pyridine allows the wave function to spread further from the CdTe material. This will result in a reduction of the exciton confinement energy and can therefore qualitatively explain the decrease in band gap energy observed by the small red shift in the absorption spectra.

An additional effect of the weaker stabilizer is that NPs dissolved in pyridine tend to form small aggregates. The probability of aggregation will increase in every step of the pyridine treatment. The observed opaqueness of the pyridine-treated sample and the enhanced Rayleigh scattering background point towards an aggregation of the removed ligands and a subsequent formation of macroscopic bundles in pyridine. This is supported by the observation of a colourless precipitate. This molecular network might enclose some of the NPs or their aggregates and thus lead to losses during the ligand exchange process and the sample purification.

6. Summary and outlook

In this paper, we have investigated the effect of pyridine treatment on the optical properties of CdTe nanocrystals passivated by organic ligand shells. Absorption and time-resolved PL spectroscopy measurements were carried out with the aim to give evidence for the removal of the ligand shell by the pyridine treatment. The PL experiments reveal a strong quenching of the PL after a single step of the pyridine procedure and a rapid decay of most of the optically generated excitons. We consider this as convincing evidence for the efficient ligand removal by the pyridine treatment. The

absorption spectra show a slight red shift of the NP absorption resonance, reflecting the change in exciton confinement upon ligand removal, and a decreased transmission due to enhanced Rayleigh scattering of the pyridine-treated solution.

The experimental results indicate that an efficient removal of organic ligands from CdTe NPs is highly possible. Finding a way to completely remove these molecules from the solution will be a substantial step towards creating samples of bare NPs, e.g. for applications in hybrid organic/inorganic photovoltaic systems where they can be added as electron acceptors to a corresponding polymer to achieve an efficient charge transfer as previously reported for CdSe NPs [8, 9].

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