

New materials for nonlinear optical applications: The nonlinear refractive index of colloidal PbSe quantum dots

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We present a detailed study of the nonlinear optical properties of colloidal PbSe quantum dot (Q-PbSe) suspensions and thin films. The nonlinear refractive index n_2 has been measured with the Z-scan technique as a function of wavelength (1.20 - 1.75 μm), optical intensity and nanocrystal volume fraction. The n_2 -spectra show negative resonances near the Q-PbSe optical transitions. We attributed the high n_2 to biexciton creation within the Q-PbSe. The n_2 of a close-packed thin Q-PbSe film is 6 orders of magnitude larger than values for bulk Si or GaAs at telecom wavelengths, suggesting that Q-PbSe might be a promising material for all optical signal processing.

Introduction

Silicon-on-Insulator photonic devices like ring resonators and Mach-Zehnder interferometers are excellent building blocks to create densely packed passive optical integrated circuits[1]. The application range of SOI photonic devices could be greatly enhanced however if SOI waveguides would have strong nonlinear optical properties. At telecom wavelengths, two-photon absorption in silicon only results in a small nonlinear refractive index ($n_2 = 0.45 \cdot 10^{-13} \text{cm}^2/\text{W}$) and a modest figure of merit (0.37)[2]. This limits the use of silicon in for instance all-optical signal processing. Using a strongly nonlinear material as a coating might be a potentially promising route to increase the n_2 . Colloidal lead selenide nanocrystals (Q-PbSe) are excellent candidates for this purpose. Since bulk PbSe has a small band gap (0.28 eV) at room temperature, the Q-PbSe band gap can be tuned over the entire telecom spectral range. The nanocrystals are produced by wet chemical synthesis, resulting in a suspension of particles, dispersed in an organic solvent. This has the advantage that the nanocrystals can subsequently be deposited on virtually any substrate by dropcasting, dipcoating, spincoating or Langmuir-Blodgett deposition, allowing for a facile coating of the silicon wires. In this paper, we will show that the Q-PbSe also have a very large nonlinear refractive index[3], which offers the potential of strongly enhancing the nonlinear optical properties SOI wires by applying a Q-PbSe coating.

Nonlinear Optical Properties

Q-PbSe nanocrystals were produced by an optimized version of the Murray-synthesis[4]. This synthesis yields Q-PbSe particle suspensions of uniform size and shape (size dispersion ca. 5%) with a mean Q-PbSe diameter that can be varied between 2 and 16 nm. The

Table 1: Size and volume fraction of the four samples used. λ_0 denotes the wavelength of the band gap transition.

sample	size (nm)	vol. fraction	λ_0 (nm)
A	5.9	$2.14 \cdot 10^{-5}$	1693
B	5.0	$2.01 \cdot 10^{-5}$	1555
C	3.6	$1.54 \cdot 10^{-5}$	1245
D	5.3	≈ 0.2	1588

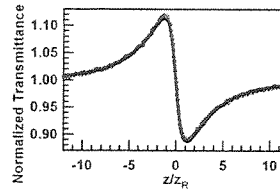


Figure 1: Experimental Z-scan trace and fit for sample A, measured at a wavelength of 1690 nm.

nanocrystal surface is passivated with oleic acid ligands, rendering the Q-PbSe suspendable in apolar organic solvents. The characteristics of the particles used for this study are summarized in table 1.

Samples A, B and C (with low volume fractions) were prepared by suspending a known amount of Q-PbSe in CCl_4 , the high volume fraction in sample D was achieved by drop-casting a known amount of Q-PbSe onto a glass substrate to produce a Q-PbSe thin film. The nonlinear refractive index was determined with the Z-scan technique[5], using a tunable femtosecond mode-locked laser operating at an 82 MHz repetition rate and at wavelengths in the range of 1200 – 1350 nm and 1540 – 1750 nm. Throughout the entire spectral range, a flat Z-scan curve was obtained for pure CCl_4 , implying that n_2 remains below the detection threshold of $10^{-13} \text{ cm}^2/\text{W}$. In contrast, strong nonlinear effects were immediately observed with sample A at a wavelength λ of 1690 nm (figure 1). The curve shows a peak-valley shape, indicative of a negative n_2 . A fit to the experimental trace yields a nonlinear refractive index $n_2 = -1.3 \cdot 10^{-11} \text{ cm}^2/\text{W}$.

Figure 2(a) shows the n_2 -spectra for samples A, B and C. These are obtained by measuring the Z-scan trace at different wavelengths, at a fixed optical intensity I_0 of 12 MW/cm². We observed a negative resonance for all three suspensions, strongly correlated with the absorbance peak of the band gap transition. For samples A and B, a similar resonance near the second absorbance peak is present. The width of the resonance is comparable to that of the absorbance peak, and it is slightly blue shifted. Instead of the typical dispersion-like spectrum predicted by theoretical calculations on colloidal quantum dots [6], we found a bell-shaped spectrum. Nevertheless, the results clearly show that n_2 has an electronic origin: the absorption of photons, and corresponding creation of electron-hole pairs (or excitons) is accompanied by a strong increase of the nonlinear refractive index. Similar results are obtained for sample D (figure 2(b)). The three Q-PbSe suspensions yield maximal n_2 values of -3 to -4 $10^{-11} \text{ cm}^2/\text{W}$, with a figure of merit $F = n_2 I_0 / (\lambda A)$ of 20-30 (A : absorbance). The maximal value of the Q-PbSe thin film equals -9 $10^{-9} \text{ cm}^2/\text{W}$, with

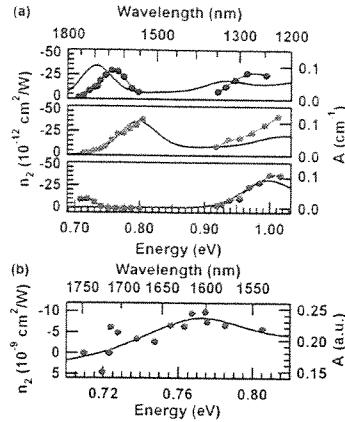


Figure 2: (a): n_2 -spectra for sample A, B and C (dots). All spectra show negative resonances, correlated with the peaks in the absorbance spectrum (black line). (b): n_2 -spectrum (dots) and absorbance spectrum (black line) for sample D.

$F \approx 1$.

The inset of figure 3 plots n_2 as a function of the Q-PbSe volume fraction (for sample A, $I_0 = 12 \text{ MW/cm}^2$, $\lambda = 1640 \text{ nm}$). As could be expected, the nonlinear refractive index increases with increasing Q-PbSe volume fraction. From the slope of the fitted line, an intrinsic value for the Q-PbSe nonlinear refractive index can be obtained. For sample A, we found $n_{2,\text{intr}} = -1.1 \cdot 10^{-6} \text{ cm}^2/\text{W}$. This value is more than 7 orders of magnitude larger than typical values for Si and GaAs at telecom wavelengths[2]. In the case of the Q-PbSe thin film, we found $n_{2,\text{intr}} = -4.8 \cdot 10^{-8} \text{ cm}^2/\text{W}$. Although 24 times smaller than the intrinsic value of a Q-PbSe suspension, a Q-PbSe thin film remains a far stronger nonlinear material than silicon at these wavelengths.

In order to further understand the origin of the nonlinear refractive index, we measured n_2 as a function of optical intensity (for sample A, $\lambda = 1640 \text{ nm}$). Figure 3 shows that the change in refractive index $\delta n(n_2, I_0)$ saturates at high I_0 . This confirms the electronic origin of n_2 . At energies close to the band gap, the energy spectrum of a quantum dot consists of discrete energy levels. Consequently, when measuring n_2 at the band gap using high optical intensities, the lowest unoccupied electronic energy level becomes fully populated and the change in refractive index will saturate. At wavelengths around the band gap transition, the Q-PbSe can be modeled as a two-level system and the change in refractive index can be written as: $\delta n = n_2 \cdot I_0 / (1 + I_0 / I_s)$, with I_s the saturation intensity. Fitting this equation to the experimental data yields $I_s = 39.6 \text{ MW/cm}^2$. This value can be compared to a theoretical calculation of the saturation intensity. We defined complete saturation when all Q-PbSe contain one exciton and calculated the steady state fraction of excited nanocrystals as a function of optical intensity. This gives a saturation intensity of only 3 MW/cm^2 . The experimental value is an order of magnitude larger than the theoretical estimate. The result suggests that the nonlinear refractive index further increases at optical intensities above 3 MW/cm^2 due to the creation of multiple excitons within the nanocrystals. This would be very advantageous, as the biexciton decay time, and therefore

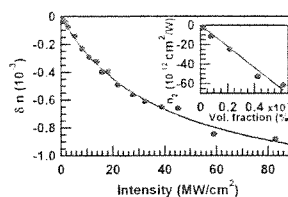


Figure 3: Intensity dependence of the change in refractive index δn (sample A). At high optical intensities, saturation is observed. Inset: Concentration dependence of n_2 (sample A). An intrinsic n_2 , for pure Q-PbSe, is obtained from the slope of the fitted line.

the decay time of the nonlinear effects, is of the order of tens of picoseconds[7].

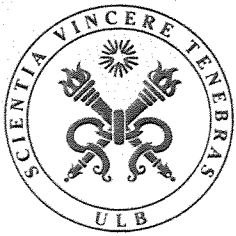
Conclusions

We have performed a detailed spectroscopic study of the nonlinear refractive index of diluted Q-PbSe suspensions and close-packed Q-Pbse thin films. We show that both in suspension and as a thin film, Q-PbSe possess very strong nonlinear optical properties. Although n_2 is reduced by a factor 24 in the case of Q-PbSe thin films, its value remains 6 orders of magnitude larger than silicon at telecom wavelengths. The n_2 -spectra show negative resonances, correlated with the Q-PbSe optical transitions. This demonstrates the electronic origin (excitons creation) of n_2 . The mechanism is further supported by the intensity dependence of n_2 . We observe a saturation of the change in refractive index, with an experimental saturation intensity that exceeds the theoretical one by an order of magnitude. This result suggests that the further increase of n_2 at high optical intensities is due to the creation of multiple excitons within the Q-PbSe.

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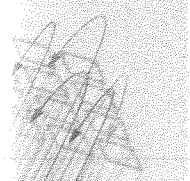
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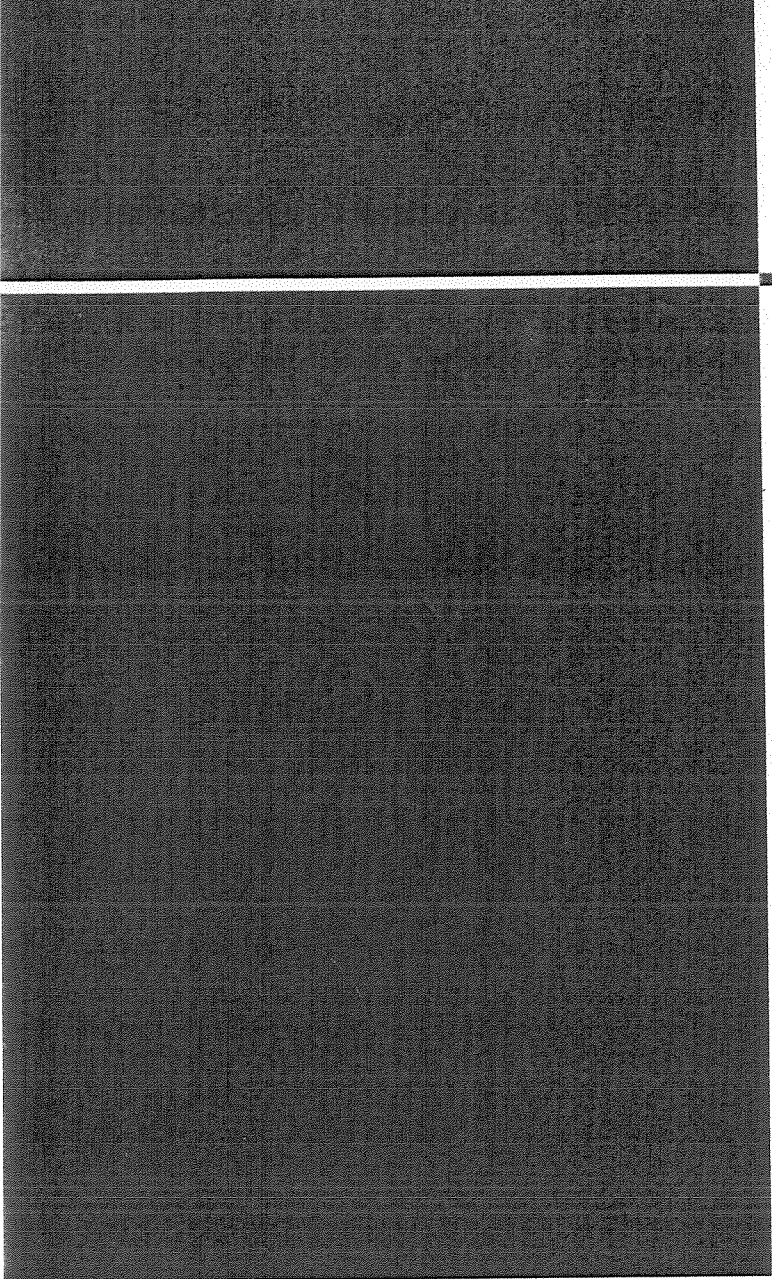
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