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Photoacoustic measurements of excitons in cdse nanorods

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Abstract. Photoacoustic (PA) spectra were obtained for CdSe nanorods (NRs) of different aspect ratios, prepared via the organometallic synthesis. The second derivative spectra were used to have an accurate determination of the different excitonic transitions. Using the lowest transition energy (band gap) $1S(e)-1S_{1/2}(h)$ and applying the effective mass model, the NRs diameters were determined. The obtained diameters were then compared to direct measurements of scanning tunneling microscopy (STM) and XRD. It is observed that the band gap depends on the diameter of the rods due to quantum confinement effect, since diameters are of the order of the bulk CdSe Bohr radius. The second derivative of the PA spectra for CdSe NRs also shows clearly a second excitonic transition $1P(e)-1P_{1/2}(h)$ in contrast to UV-Vis absorption spectra carried out for colloidal samples. The thermal parameters for samples were also measured and compared to the bulk values.

1. Introduction

Nano rods (NRs) of CdSe provide properties which are much different from that of spherical dots for example, with emission that is linearly polarized resulting in linearly polarized lasing [1]. Photoacoustic (PA) spectra were obtained for a group of eight CdSe NRs in the powder form with different aspect ratios. The spectra are then compared to UV-Vis absorption carried out for colloidal solutions. The effective mass approximation EMA (taking into account the valence band mixing effect and electron-hole Coulomb interaction) is applied to calculate the diameters of the NRs. The obtained dimensions are then compared to the direct measurements of STM and XRD analysis carried out for the samples. Also, the second derivative PA spectra shows a second excitonic transition corresponding to $1P(e)-1P_{1/2}(h)$ in CdSe NRs that is not observed in the case of UV-Vis. Careful analysis of the data for the thermal parameters (effusivity, diffusivity, and conductivity) obtained by the PA technique gives values that are less than bulk values in contrast to previously reported study [2].

2. Experiment

A conventional PA setup is used with a 750 W tungsten lamp and Princeton Applied Research Photoacoustic (PAR-PA) cell. The spectra were obtained at a modulation frequency of 16 Hz and the intensity was normalized using carbon black. The thermal parameters; thermal effusivity e , and thermal diffusivity α were obtained in the traditional way by taking the PA signal at different chopping frequencies using a thin layer of CdSe nanoparticles deposited on a glass plate.

3. Results and discussions

3.1. Absorption characterization

The PA absorption spectra were obtained for all the samples and the second derivative of the spectra are shown in Fig. 1. It is clear that the lowest excitonic transition, which represents the NRs band gap, is higher than that of the bulk (~700 nm) with a remarkable blue shift as the particle size decreases. This is due to quantum confinement effects. The size-dependent energy structure of CdSe quantum rods is calculated by A. Shabaev, and Al. L. Efros [3]. They have considered the NR as a crystalline that has an ellipsoidal shape. The motion of electrons and holes is analyzed within the EMA (the 6-band model) that has successfully described the optical spectra of CdSe nano crystals (NCs) [4]. The significant elongation of NRs ($l \gg a$), where l is the NR length and a is its radius, makes it possible, by using an adiabatic approximation, to separate the parallel motion from the perpendicular motion to the NR axis. This model calculation shows that the lowest transition is $1S(e)-1S_{1/2}(h)$ in case of NRs in contrast to $1S(e)-1S_{3/2}(h)$ in case of NCs. The particle widths are calculated using the dip of the second derivative of PA spectra and the EMA model with the inclusion of valence band mixing effect, and the electron-hole Coulomb interaction given by,

$$\left(E_g = E_g(\text{bulk}) + \frac{\hbar^2 \pi^2}{2m_e a^2} + \frac{\hbar^2 (5.76)^2}{2m_{hh} a^2} - \frac{1.77e^2}{\epsilon a} \right) \text{ where, } E_g(\text{bulk}) \text{ is the energy gap for bulk CdSe}$$

(1.75 eV), m_e is the electron effective mass (0.13 m_0), m_{hh} is the heavy hole mass, e is the electron charge, and ϵ is the dielectric constant. The obtained diameters are found to vary from 4.56 to 5.78 nm. The shape and size distribution of six NRs samples were determined from the images taken by OMICRON ultra high vacuum STM. The particles dimensions are found to vary from $l=19$, $w=4$ nm (Fig. 2-a) to $l=50$, $w=6.8$ nm. Fig. 2-b shows NRs of dimensions $l=40$, $w=5.6$ nm. It is to be observed that strong confinement is expected to hold for the radial direction, since the particles diameters are less than the CdSe Bohr radius (~ 5.7 nm), while weak confinement would hold for the axial direction. Hence, in our case the NRs band gap depends on the rod diameter and not on its length [5]. Furthermore, a PHILIPS X'Pert multipurpose diffraction diffractometer was used to collect the XRD patterns for the samples in powder form, the NRs width and length were determined by applying

Scherer's formula [6] ($D = \frac{0.9\lambda}{\beta \cos \theta}$ where λ is the wavelength of the X-ray used, and θ is the Bragg's

angle) on the (103), (002) reflection planes, respectively. Fig. 3 shows the diffraction pattern for one sample of $l=10$, $w=4.33$ nm on average. The widths of the NRs obtained from the PA spectra applying the EMA with the inclusion of valence band mixing are shown in Fig. 4-a, and without (Fig. 4-b). The directly measured values obtained from STM are shown in (Fig. 4-c). It is clear that NRs widths obtained using the second derivative spectra and applying the EMA model give accurate dimensions in agreement with that of STM and XRD results, when valence band mixing is taken into account. In the case of ignoring that effect the variations would be of the order of 30%. Furthermore, the second transition peak is found from this model to represent the $1P(e)-1P_{1/2}(h)$ transition. The change of this transition energy with the width of the NRs was beyond the accuracy of the experiment for that small range of diameters.

3.2. Thermal measurements

The amplitude of the PA signal " q ", In case of thermally thick and optically opaque samples, is given

by [7] $q = \frac{B}{e f}$ where $e = \sqrt{k\rho c}$ is the thermal effusivity of the sample, ρ is the density, c is the

specific heat, and f is the modulation frequency. The quantity B could be obtained from a reference sample Si ($e=1.57 \text{ W s}^{1/2} \text{ cm}^{-2} \text{ K}^{-1}$). The thermal effusivity for CdSe NRs is found to have a value of about $0.18 \text{ W s}^{1/2} \text{ cm}^{-2} \text{ K}^{-1}$ for all the samples used, which is much smaller than that of the bulk [8] ($0.34 \text{ W s}^{1/2} \text{ cm}^{-2} \text{ K}^{-1}$). Thermal diffusivity was determined using [9] $\alpha = f_c l^2$, where l is the thickness of the sample (0.015 cm) and f_c is the characteristic frequency (~14 Hz) at which the sample goes from thermally thick region to the thermally thin region. The obtained values for α for all the samples were

about $2.9 \times 10^{-3} \text{ cm}^2\text{s}^{-1}$ which is less than the diffusivity of the bulk ($14 \times 10^{-3} \text{ cm}^2\text{s}^{-1}$). From the above results, thermal conductivity $k (= e\sqrt{\alpha})$ for CdSe NRs is found to be $9.5 \times 10^{-3} \text{ Wcm}^{-1}\text{K}^{-1}$ which is about 25% of the corresponding bulk values. This is due to strong boundary scattering of energy carriers (phonons) resulting in a reduced heat diffusion in the sample. However, it is also observed that the PA technique is limited in resolving the changes in thermal parameters due to small variations in particle size, as well as, their dimension being small compared to the thermal wave.

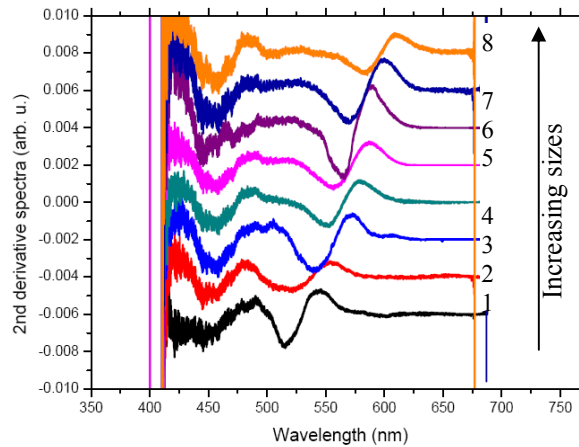


Figure 1. 2nd derivative spectra for CdSe NRs.

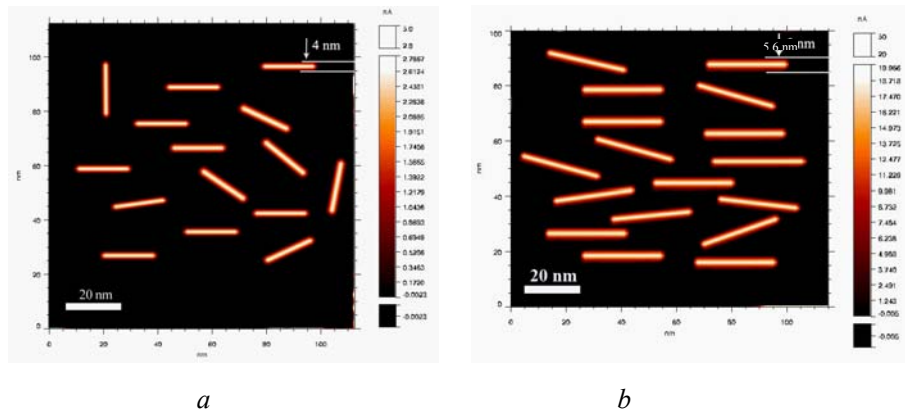


Figure 2. STM images for CdSe NRs of $l=19$, $w=4$ nm (a), and $l=40$, $w=5.6$ nm (b).

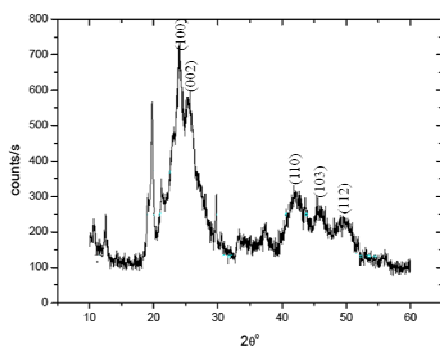


Figure 3. XRD for CdSe NRs of $l=10$, $w=4.33$ nm.

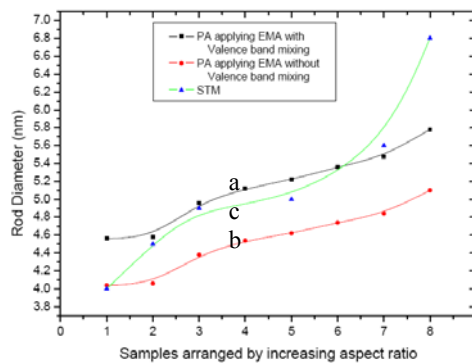


Figure 4. NRs widths obtained from PA spectra applying EMA with the inclusion of valence band mixing (a), and without (b). Width obtained from STM (c).

4. Conclusions

The dimensions of CdSe NRs obtained from the lowest energy transition peaks (E_g) of PA technique using the second derivative spectra and applying the EMA model (taking into account the valence band mixing effect), give a close values to the dimensions measured directly by STM and XRD. The transitions coupling the 1P electron state to the hole state $1P_{1/2}$ were clearly observed in PA spectra but not in UV-Vis spectra. The PA technique has also shown that the thermal parameters of CdSe NRs decrease significantly from the bulk values due to the large boundary scattering of phonons reducing the heat diffusion through the sample.

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