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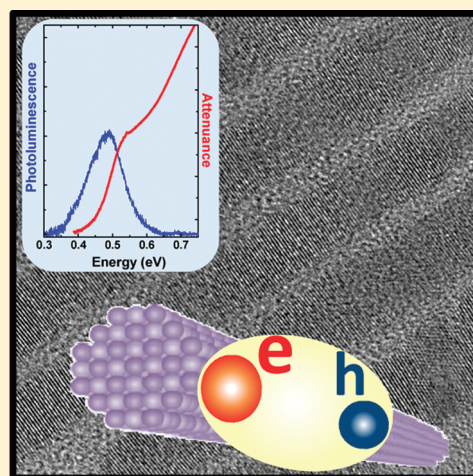
Size and Temperature Dependence of Band-Edge Excitons in PbSe Nanowires

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S Supporting Information

ABSTRACT: We report the attenuation and temperature-dependent photoluminescence spectra of PbSe nanowires with diameters between 5.6 and 26.4 nm (12–23% relative standard deviation) and lengths greater than 1 μm . The nanowire first exciton energy varies between 0.3 and 0.6 eV as the diameter decreases from 26.4 to 5.6 nm, respectively. Compared to spherical PbSe nanocrystals, PbSe nanowires show less quantum confinement and larger Stokes shifts. The band gap temperature coefficient (dE_g/dT) decreases as the nanowire diameter decreases, consistent with previous results for PbSe spherical nanocrystals.

SECTION: Nanoparticles and Nanostructures



One-dimensional semiconductor nanowires (NWs) have garnered significant interest because they possess exceptional physical properties which make them attractive for devices such as photovoltaics,^{1,2} photodetectors,³ and thermoelectrics.⁴ Their anisotropic shape allows NWs to simultaneously demonstrate quantum confinement and efficient electron transport.^{3,5} In NW films, electrons are able to travel directly through the NWs, whereas in spherical nanocrystal (NC) films, the electrons and holes must “hop” or tunnel from particle to particle.^{6–8} This direct transport leads to higher conductivity in films of NWs as compared to that in NCs.^{9,10} Additionally, it has been demonstrated that NWs can have polarization-sensitive light emission and absorption along the NW axis,^{3,11} significantly higher absorption cross sections as compared to those of NCs,^{12–14} and possibly efficient multiple exciton generation (MEG).¹⁵ Utilizing these exceptional physical properties in an optoelectronic NW device, however, will require an understanding of the NW optical properties.¹⁶

While the size dependence of the band gap of NCs has been extensively studied in a variety of semiconductor materials,^{17,18} the band gap size dependence in NWs and nanorods (NRs) has only begun to be explored.^{15,16,19–26} For example, NW and NR band gaps were shown to increase as the diameter decreases,^{15,16,19–26} and the band gap of InP NCs was found to be larger than that of NWs with the same diameter.¹⁹ Recently, Bartnik et al.¹⁵ have developed a four-band effective mass model of

the energy level diameter dependence in PbS and PbSe NWs and NRs. They have shown that the model describes quantitatively the experimentally determined size dependence of the energy levels in PbSe nanorods.^{15,26} However, the energy level size dependence of PbSe NWs has not yet been studied experimentally. In this Letter, we grow PbSe NWs of controlled diameters and examine their attenuation and temperature-dependent photoluminescence spectra. We demonstrate quantum confinement in the PbSe NWs and compare their optical spectra to PbSe NCs.

PbSe NCs with average diameters between 3.7 and 8.2 nm were synthesized from PbO and Se powder using a standard solution synthesis.²⁷ These NCs have relative diameter standard deviations (σ_{rel}^d) ranging from 10 to 15%. PbSe NWs were synthesized using two different published procedures, hereafter denoted Method 1²⁸ and Method 2.²⁹ PbSe NWs were synthesized with average diameters between 5.6 and 7.4 nm using Method 1 and between 8.1 and 26.4 nm using Method 2. For both methods, the NW lengths are on the order of micrometers, and the σ_{rel}^d (between NWs) are between 12 and 23%. Although NWs with different surface roughnesses can be achieved using these reactions, we only studied smooth NWs (relative diameter standard deviations along one NW = 8–11%), as shown in

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Figure 1b. The NC and NW dimensions were obtained from transmission electron microscope (TEM) images, and a minimum of 150 measurements were included in the average and $\sigma_{\text{rel}}^{\text{d}}$ (see Supporting Information for more details). TEM images of PbSe NCs with an average diameter of 5.8 nm and PbSe NWs with an average diameter of 6.5 nm are shown in Figure 1a and b, respectively. The PbSe NCs and NWs have the rock salt structure, and the NWs grow along the $\langle 100 \rangle$ direction,^{27–29} the latter of which affects the band gap and effective mass of PbSe NWs.¹⁵

Figure 1c and d shows the photoluminescence (PL) and attenuation^{30,31} spectra of the PbSe NCs and NWs shown in Figure 1a and b, respectively. The spectra obtained are similar to previously reported spectra of PbS NWs³² and PbSe NRs.^{15,26,33} Comparison of the attenuation and PL spectra of PbSe NCs and NWs with similar diameters demonstrates the difference between zero- and one-dimensional excitons in PbSe. The full width at half-maximum (fwhm) of the NC PL spectra is smaller than that of the NW PL spectra because the NCs have smaller diameter distributions than the NWs ($\sigma_{\text{rel}}^{\text{d}}$ = 10–15% vs 12–23%). In particular, the PL fwhm and $\sigma_{\text{rel}}^{\text{d}}$ of the NCs in Figures 1c are 0.06 eV and 13%, respectively, whereas the PL fwhm and $\sigma_{\text{rel}}^{\text{d}}$ of the NWs in Figure 1d are 0.12 eV and 20%, respectively. Furthermore, the energy relative standard deviation for both the PL peak and the first exciton attenuation peak are consistent with the $\sigma_{\text{rel}}^{\text{d}}$ values of the NCs and NWs (see Supporting Information). This indicates that the PL and attenuation spectra line widths are due to inhomogeneous broadening given by the diameter size distributions.

There are two well-defined features at 0.668 and 0.843 eV in the PbSe NC attenuation spectra, Figure 1c, which are assigned to the $1S_{\text{h}} \rightarrow 1S_{\text{e}}$ and $1S_{\text{h}} \rightarrow 1P_{\text{e}}/1P_{\text{h}} \rightarrow 1S_{\text{e}}$ transitions, respectively.^{34–36} In the PbSe NW attenuation spectra shown in Figure 1d, there is only one broad feature at 0.526 eV, which is identified as the $1\Sigma_{1/2}^{\text{h}} \rightarrow 1\Sigma_{1/2}^{\text{e}}$ transition, following the notation by Bartnik et al.¹⁵ The less pronounced feature for the $1\Sigma_{1/2}^{\text{h}} \rightarrow 1\Sigma_{1/2}^{\text{e}}$ transition is most likely due to closer-spaced energy transitions as a result of decreased confinement.¹⁵ To more accurately resolve the $1\Sigma_{1/2}^{\text{h}} \rightarrow 1\Sigma_{1/2}^{\text{e}}$ transition, a background subtraction was performed on the NW attenuation spectra using a commercial software package (OPUS from Bruker Optics). The background-subtracted spectrum of the attenuation spectrum is shown in Figure 1d with a black line.

By controlling the NW diameter, the PbSe NW band gap can be tuned to more than twice the bulk band gap (0.28 eV at room temperature).³⁷ Figure 2 shows the PL and background-subtracted attenuation spectra for PbSe NWs with average diameters between 5.6 and 26.4 nm. As the NW diameter decreases from 26.4 to 5.6 nm, the lowest-energy exciton of the NWs is tuned from ~ 0.3 to ~ 0.6 eV. Both PL and attenuation spectra for all samples show a single peak with a fwhm consistent with the measured size distribution. The structure observed in the PL for the thickest NWs is an artifact due to absorption of the emitted light by H_2O , CO_2 , and the ligands surrounding the NWs.

Method 1 was used to synthesize the three thinnest NWs shown in Figure 2, and Method 2 was used for the three thickest. The attenuation spectra of the thickest three NWs did not show well-defined transitions even after background subtraction. This could be because the larger NWs have lower absorption coefficients, which result in the attenuation features not being distinguishable above the scattering. However, it has been shown that larger PbSe NCs have higher absorption coefficients, making this explanation unlikely.^{38,39} The featureless spectra could also be attributed to the

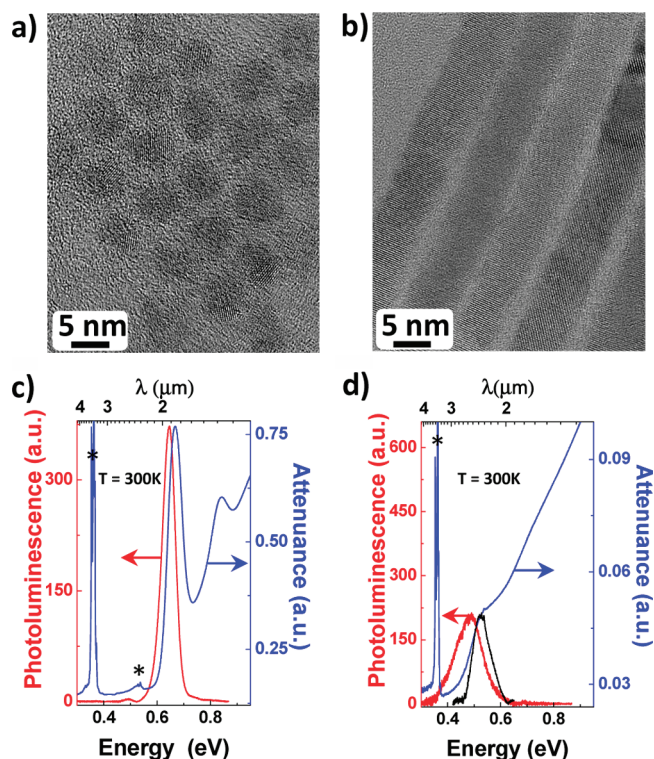


Figure 1. TEM images of (a) 5.8 nm (14%) diameter PbSe NCs and (b) 6.5 nm (20%) diameter NWs. The percentage in parentheses is the relative diameter standard deviation, which, for the NWs, is between NWs. The room-temperature PL and attenuation spectra of (c) the NCs in (a) and (d) the NWs in (b). The * symbols mark the peaks from ligands surrounding the NCs and NWs.

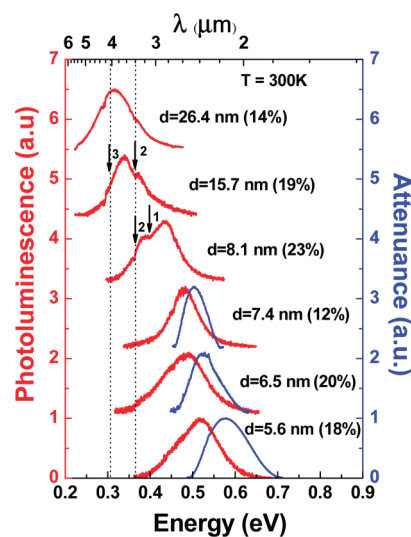


Figure 2. Room-temperature PL and attenuation spectra of NWs with different diameters. The arrows indicate the location of absorbance features from the O—H stretches from H_2O and the ligands (arrow 1), the C—H stretches of the ligands (arrow 2), and the asymmetric stretch of CO_2 (arrow 3).

thicker NWs having closely spaced energy transitions that are more susceptible to thermal broadening, resulting in a smoothing of the peaks.¹⁵ Low-temperature attenuation spectra of the larger NWs may help determine if this is indeed the case.

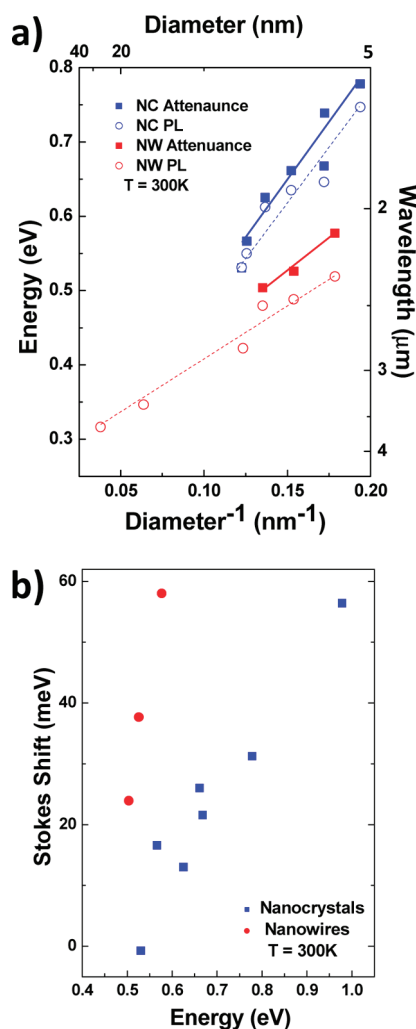


Figure 3. (a) The energy of the first exciton absorbance for NCs (blue ■) and NWs (red ■) and the PL peak for NCs (blue ○) and NWs (red ○) as a function of diameter⁻¹. The solid and dashed lines are only guides for the eyes. (b) The Stokes shift as a function of first exciton absorbance energy for NCs (blue ■) and NWs (red ●).

The NCs first exciton energy, found from the attenuance and PL spectra, varied with diameter (d) as $d^{-0.80}$ and $d^{-0.66}$, respectively. In comparison, the first exciton energy of the NWs found from the attenuance and PL spectra varied with diameter as $d^{-0.49}$ and $d^{-0.33}$, respectively. For clarity, the first exciton energies are plotted versus d^{-1} in Figure 3a, even though the energy–size dependence is not d^{-1} . In the strong confinement regime, the energy dependence is expected to be d^{-2} ; however, this is not the case for PbSe due to the nonparabolicity of the conduction and valence bands.³⁶ For a particular diameter, the first exciton energy of the NCs is consistently larger than that of the NWs, which indicates that the PbSe NCs experience more confinement than the PbSe NWs. Figure 3b shows how the Stokes shift (the energy difference between the first exciton absorbance peak and the emission peak) for both the NCs and the NWs depends on the energy of the first exciton absorbance peak. The Stokes shift increases with confinement, which has been seen previously for NCs^{40,41} and is due to the energy splitting of the ground exciton states increasing with decreasing diameter.⁴² Additionally, Figure 3b shows that the Stokes shifts are larger for PbSe NWs as compared to those for NCs with

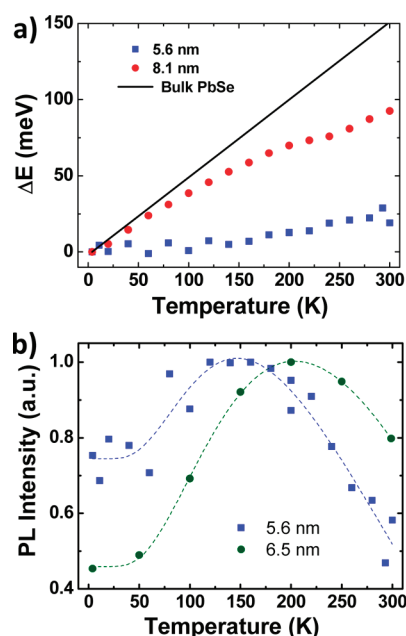


Figure 4. (a) The change in PL peak energy relative to its value at 4 K as a function of temperature for (blue ■) 5.6 nm (18%) diameter NWs, (red ●) 8.1 nm (23%) diameter NWs, and (—) the bulk. At 4 K, the PL energies of 5.6 nm NWs, 8.1 nm NWs, and the bulk are 489, 330, and 145 meV, respectively. (b) Temperature dependence of the spectrally integrated PL for (blue ■) 5.6 nm (18%) diameter NWs and (green ●) 6.5 nm (20%) diameter NWs. The dashed lines are only guides for the eyes.

similar confinement energy. This is consistent with previous research, which has shown that NRs exhibit larger Stokes shifts than NCs.^{11,26,33,43} It is likely that the NWs and NRs have larger Stokes shifts because diameter fluctuations along the axis result in charge/exciton localization in thicker parts of the NWs,⁴⁴ that is, the absorption contributions come from all sections of the NW while the emission contributions come from thicker sections of the NW.⁴⁴ Using the average diameter standard deviation along one NW, we calculated the energy fluctuations across the NW (see Supporting Information). This energy fluctuation is on the order of 30 meV for all NW diameters, which is consistent with the Stokes shift difference between the NCs and NWs, confirming that charge/exciton localization is probably responsible for the higher Stokes shifts in NWs as compared to those in NCs. Other mechanisms, such as fine structure,^{33,42} might also contribute, to a lesser amount, to the difference in Stokes shifts between NWs and NCs.

Figure 4a shows how the change in energy of the PbSe PL peak (relative to its value at 4 K) varies with temperature for the bulk and two NW ensembles with different diameters. The band gap temperature coefficient (dE_g/dT) decreases as the NW diameter decreases, which is consistent with previous results found for PbSe NCs.^{45,46} Olkhovets et al.⁴⁵ have shown that for PbSe NCs, dE_g/dT is mainly determined by thermal expansion of the lattice as well as interband electron–phonon coupling. As the size of the NC decreases, dE_g/dT weakens because the energy levels become controlled by quantum confinement rather than the lattice constant. Also, the increased energy gaps of the smaller NCs lower the interband electron–phonon coupling contribution to dE_g/dT . It is likely that these same mechanisms are responsible for the decreased dE_g/dT seen in Figure 4a.

The normalized spectrally integrated PL as a function of temperature for two NW ensembles with different diameters is shown in Figure 4b. The intensity increases as the temperature is increased from 4 K but then decreases, reaching its maximum at 150 and 200 K for the 5.6 and 6.5 nm diameter NWs, respectively. This differs from what has been seen previously in PbSe NCs, which have been shown to have an integrated PL intensity maximum near 10 K.⁴⁷ Further investigation is required to determine why NWs and NCs have different PL intensity temperature dependences and if the temperature of the maximum PL intensity is a function of nanowire diameter.

In summary, the attenuation and photoluminescence of PbSe NWs made from a solution synthesis were examined and compared to that of PbSe NCs, demonstrating that quantum confinement is relaxed in PbSe NWs as compared to that in PbSe NCs. By changing the NW diameter, the first exciton energy varies between 0.3 and 0.6 eV, and the NW Stokes shift is found to be larger than the NC Stokes shift. Finally, dE_g/dT was found to decrease as the PbSe NW diameter decreased, and an unexpected temperature dependence of the PL peak intensity was observed.

EXPERIMENTAL METHODS

Materials. Lead oxide (99.9+%), oleic acid (90%), 1-octadecene (90%), selenium powder (99.5+%), trioctylphosphine (90%), and diphenyl ether (99%) were purchased from Sigma-Aldrich. Tetradecylphosphonic acid (TDPA, 98%) was purchased from Alfa Aesar. Heptane (96.7%) and hexane (99.9%) were purchased from Fisher Scientific. Ethanol (200 proof) was purchased from The Warner Graham Company. All chemicals were used as received.

PbSe NC Synthesis. The synthesis of PbSe NCs and NWs was performed under inert conditions using standard Schlenk techniques. PbSe NCs were synthesized using a previously published method.²⁷ In order to create the two largest NC diameters (8.0 and 8.2 nm), a second dropwise injection of a mixture of room-temperature lead oleate and TOPSe in 1-octadecene was utilized.⁴⁸

PbSe NW Synthesis. Method 1: The three thinnest NWs were made using the method developed by Cho et al.,²⁸ except that PbO was used as a lead source instead of $Pb(CH_3COO)_2 \cdot 3H_2O$. Method 2: The three thickest NWs were made using a published procedure.²⁹ More NW synthesis details are given in the Supporting Information.

TEM Characterization. TEM samples were made by making dilute NC or NW chloroform solutions and drop casting a small volume (<500 μ L) onto lacey carbon TEM grids. TEM images were obtained on a JEOL 2200F3 transmission electron microscope operating at 200 kV. The CCD camera on which the images were recorded was calibrated with a gold lattice magnification standard.

Optical Characterization. Attenuance spectra of PbSe NCs and NWs films, prepared by drop casting onto glass slides, were obtained at room temperature using a Bruker VERTEX 80v Fourier-transformed infrared (FTIR) spectrometer equipped with a CaF₂ beamsplitter and a DLaTGS detector. A portion of the glass slide which was not coated with the PbSe film was used as a reference. The samples were evacuated to 1.6 Torr in the Bruker VERTEX 80v sample chamber in order to minimize oxidation of the PbSe surface and to suppress H₂O and CO₂ absorption features in the attenuance spectra. The PL spectra of

films of PbSe NCs and NWs drop cast onto silicon wafers were obtained with a BOMEM DA8 FTIR spectrometer utilizing an InSb detector and a KBr beamsplitter. A quartz beamsplitter was used for PbSe NCs with first exciton energies above 0.76 eV. The PL samples were mounted in an Oxford Instrument cryostat equipped with a KRSS window and pumped to 10^{-5} mTorr. The samples were mounted in the cryostat in order to keep them under vacuum, which, as mentioned above, minimized oxidation of the PbSe surface and the absorption features in the PL spectra from H₂O and CO₂. Using liquid helium to cool the cryostat, PL spectra were taken at temperatures between 4 K and room temperature. The samples were excited with an 808 nm laser diode chopped at 21 kHz. The 21 kHz modulated PL was deconvoluted with a Stanford Research SRS830 lock-in amplifier. The deconvoluted signal was sent to the BOMEM DA8 FTIR connected to a computer to record and perform a mathematical Fourier transform to obtain the PL spectra.

ASSOCIATED CONTENT

S Supporting Information. More detailed information regarding the NW synthesis procedure, the diameter measurements, the relationship between the energy and diameter distributions, and the calculation of the energy fluctuation along one NW. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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