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Unconventional photoluminescence upconversion from PbS quantum dots

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The authors report a type of photoluminescence upconversion that is directly attributable to the strong quantum confinement of charge carriers in PbS nanocrystals and does not involve the usual mechanism of thermally populated intermediate states. Absorption, emission, and excitation spectroscopy, combined with a simple spectral model, reveals that the upconversion process is consistent with single-photon absorption by an extremely broad single nanocrystal absorption line. This type of upconversion is a result of the time-energy uncertainty principle, indicating unusually rapid dephasing in this system, and stands in direct contrast to the mechanisms proposed for upconversion in other types of nanocrystal. © *2007 American Institute of Physics.*
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Photoluminescence upconversion (PLUC) in nanocrystal (NC) quantum dots is a property that has gained some attention in recent literature,[1–6] with many studies focusing on the physical nature of the phenomenon and using it as a means of studying the effect of interfacial and surface states. It is generally held that PLUC is a phonon assisted multistep process that involves intermediate states that are not fundamentally optically accessible. Moreover, many of the processes exhibit a linear absorption characteristic, suggesting that only a single photon is involved.[1–4] Evidence for the interaction with intermediate states has been supported by photoluminescence excitation (PLE) scans that show a dramatic departure from the NC absorption spectrum.[1,4] Thus in these cases it is clear that some intermediate process is involved and the PLE spectrum becomes a useful means for examining the nature of these processes.

One class of NC that has not received any attention with respect to PLUC is the lead chalcogenides. These are narrow band-gap semiconductors that have extremely large excitonic Bohr radii, so that strong quantum confinement is easily reached.[7] It has been predicted that NCs in the strong quantum confinement regime,[8] and the lead salts, in particular,[9] should exhibit enhanced coupling to acoustic phonons. This is supported by recent experimental evidence for large homogenous linewidths at room temperature in PbS NCs,[10,11] which have been directly attributed to enhanced acoustic phonon coupling.[12] These predictions and observations together suggest that small lead chalcogenide NCs may, in fact, provide strong PLUC via a direct intrinsic mechanism: that of a large energy uncertainty due to strong dephasing by acoustic phonons. Here we investigate PLUC in PbS NCs synthesised in the strong quantum confinement regime. We find efficient PLUC, but in contrast with other reports, our PLE spectra indicate that the PLUC is not only a linear single-photon process but that no intermediate states are involved. Thus the PLUC in PbS NCs is a phenomenon that naturally arises from an unusually large homogeneous linewidth. We discuss the origin and possible implications of this result with respect to the optical cooling of solids.[13,14]

Colloidal suspensions of oleic acid capped PbS NCs in the 2−3 nm size range were used in this study. The detail of the synthesis is described elsewhere.[15] Solutions were diluted in heptane to ensure absorbance in the Beer-Lambert limit (i.e., an absorbance of ~ 0.1 cm^{-1} at the exciton peak). Both the PLUC and PLE signals were obtained from a fluorimeter (Spex Fluoromax 3) using xenon lamp excitation with the fluorescence signal collected at 90° and detected with a photomultiplier tube (Hamamatsu R928), which provided the lower limit to the detection energy for the PLUC signals. A full description of the experimental procedure is also described elsewhere.[12]

Both the absorption and PL spectra for a typical PbS NC colloidal solution are shown in Fig. 1(a). The PL signal was obtained by exciting offresonance with an attenuated 532 nm laser and detected with a Si photodiode. The peak of the PL spectrum is Stokes shifted from the band-edge exciton peak in the absorption spectrum.[10] Figure 1(b) reveals the evolution of the PLUC signal by exciting at various points across the excitonic absorption peak (indicated by vertical arrows). As the excitation proceeds toward lower energies, the PLUC signal emerges as the uppermost limit of the spectra (indicated by an arrow). We note that the PLUC signal never exceeds the energy of the nonresonantly excited PL signal in Fig. 1(a) and that the PL portion of the signals in Fig. 1(b) smoothly transition into the PLUC signals. These data suggest that the PLUC signals have a similar origin to the PL signal and are correlated with absorption by the band-edge exciton. The high energy cutoff, where the PLUC signal merges with the noise floor, occurs at approximately 1.7 eV. For the lowest energy excitation at 1.37 eV, the PLUC signal represents an energy gain of 330 meV. This compares favorably with, or exceeds many of the anti-Stokes shifts, reported for other NC species.[1–6]

PLE is used to investigate the origin of the PLUC signal. This form of spectroscopy has been used to show that intermediate trap states are involved in PLUC in other NCs.[4] In Fig. 2 we show PLE signals from two different PbS NC samples spanning the range of average NC sizes (from 2 to 3 nm diameter) in the strong quantum confinement regime. The sharp spike in each spectrum is a directly scattered pump signal. The PLUC signal is that part of the spectrum on the low energy side of the spike (indicated by horizontal

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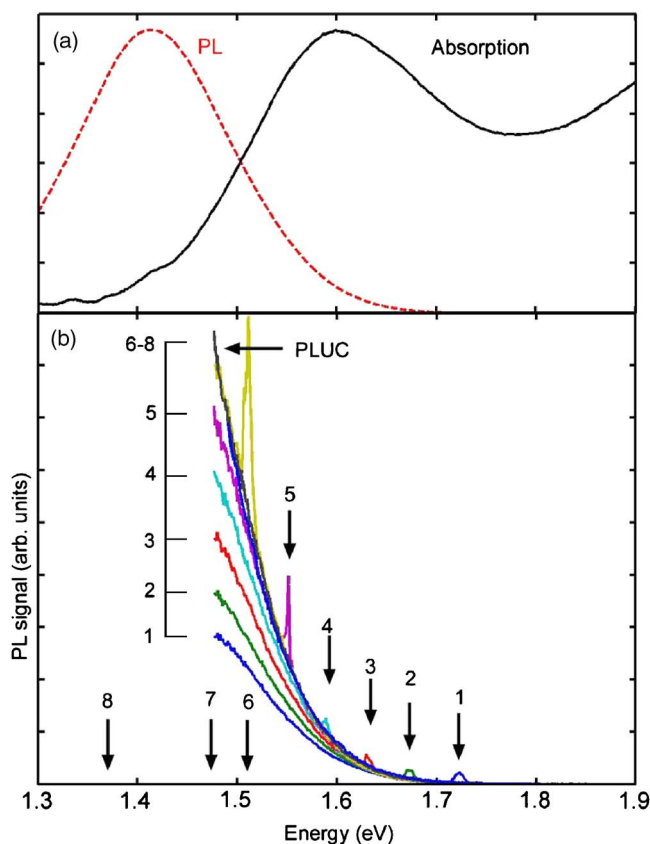
FIG. 1. (Color online) (a) Absorption (solid line) and PL spectra (dashed line) obtained from the colloidal suspension of PbS NCs under study. The PL spectrum was obtained with nonresonant excitation at 532 nm with detection using a Si photodiode. (b) A series of eight PL signals obtained at different pump energies (indicated by vertical arrows). The PL signals have been scaled so that the PLUC portions are aligned. Spectrum 1 is entirely PL signal, while spectra 7 and 8 are entirely PLUC (as indicated).

arrows). In all cases the PLE signals, including the PLUC contributions, only reveal the band-edge exciton. Specifically, there is no sign of an intermediate or trap state in the PLUC portion of the spectrum, in contrast to what has been reported elsewhere[1,4] (note: that any apparent structure at the
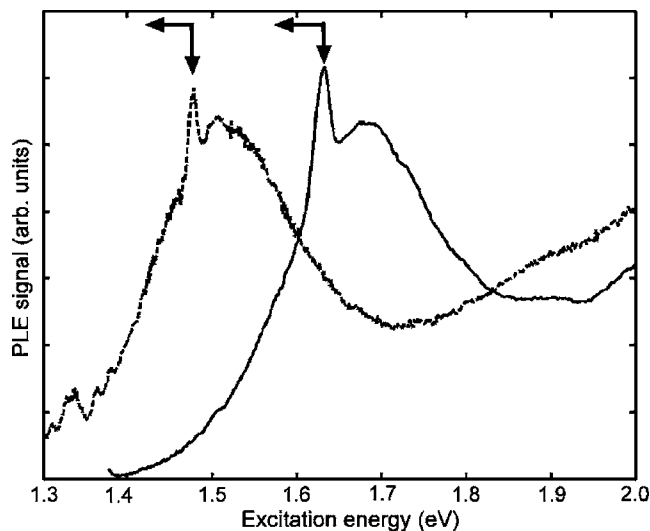

FIG. 2. PLE spectra from two different PbS NC solutions representing the extremes of the ensemble size range studied. The monitoring energy for each spectrum is indicated by a vertical arrow (and a sharp scattering peak), while the horizontal arrows indicate the PLUC portion of the spectra.

low energy tail is due to residual xenon lamp structure in a region where the reference Si diode response deviates from the calibration curve). Furthermore, the two spectra demonstrate that the PLUC signal is NC size dependent, which is evidence of excitonic origin.

We have developed a phenomenological model of ensemble absorption and emission that convolves an assumed single NC absorption/emission spectrum (based on a single exciton transition) with a Gaussian size distribution.[12] This model has given insight into single NC contributions to absorption, PL, and PLE data from ensemble measurements.[10,12] In Fig. 3(a) we show that this model provides an excellent fit to our data, including to the entire PLE spectrum with the PLUC component. This indicates that PLE spectra are solely attributable to band-edge exciton absorption, as no other PLUC mechanisms are included in the model.

In Fig. 3(b) the PL spectrum is decomposed into homogeneous and inhomogeneous linewidth components, as determined by the model. The PL linewidth is dominated by the homogeneous component. This unusually large homogeneous linewidth is the origin of the PLUC signal in PbS NCs. This is an excellent example of how strong quantum confinement can result in enhanced exciton coupling to acoustic phonons via the deformation potential.[8] While remarkable, this result was theoretically predicted by Kamisaka et al.[9] and has been corroborated by the observation of unusually large linewidths from single PbS NCs.[11] Furthermore, the temperature dependences of both the linewidth and peak shift are attributable to acoustic phonon interactions.[12] Thus the exciton line is composed of broad phonon sidebands corresponding to the absorption or emission of multiple acoustic phonons with each optical transition. This is the solid-state analog to pressure broadening in gases and presents no fundamental violation of energy conservation.

In Fig. 3(c) we use the model to calculate the PL spectrum (including the PLUC signal) that would result from excitation at 1.37 eV [the lowest energy used in Fig. 1(b)]. We find that the spectrum is redshifted compared to that shown in Fig. 3(a). The deviation of the modeled spectrum from the PLUC signal is due to the simplicity of the model.[12] A similar deviation of the modeled spectrum is also evident in the high energy periphery of the pure PL signal in Fig. 3(a). Nevertheless, if we accept the model's overall proficiency in describing the detected spectra, then according to the model the PLUC component comprises less than half of the total PL signal. So for this PbS NC sample, it would not be possible to use PLUC as a means for cooling.

The factor currently limiting the capacity of PLUC to cool the PbS NCs is the large Stokes shift of the PL emission from the absorbing transition, which has been attributed to the trapping of one of the charge carriers.[10] Recently, Lifshitz et al. have shown that improving the surface passivation of PbSe NCs can remove a similar Stokes shift.[16] As the spectral properties of PbSe NCs and PbS NCs are closely related,[17] it is therefore likely that improved surface passivation of lead PbS NCs in the strong quantum confinement regime could also remove the Stokes shift of the emission, which would then allow PLUC to be used for cooling.

In summary, we have found that large 330 meV energy gains are possible at room temperature from PLUC in strongly quantum confined PbS NCs. Furthermore, we show that the PLUC results from an intrinsic conversion mechanism that is a direct result of a large homogeneous linewidth
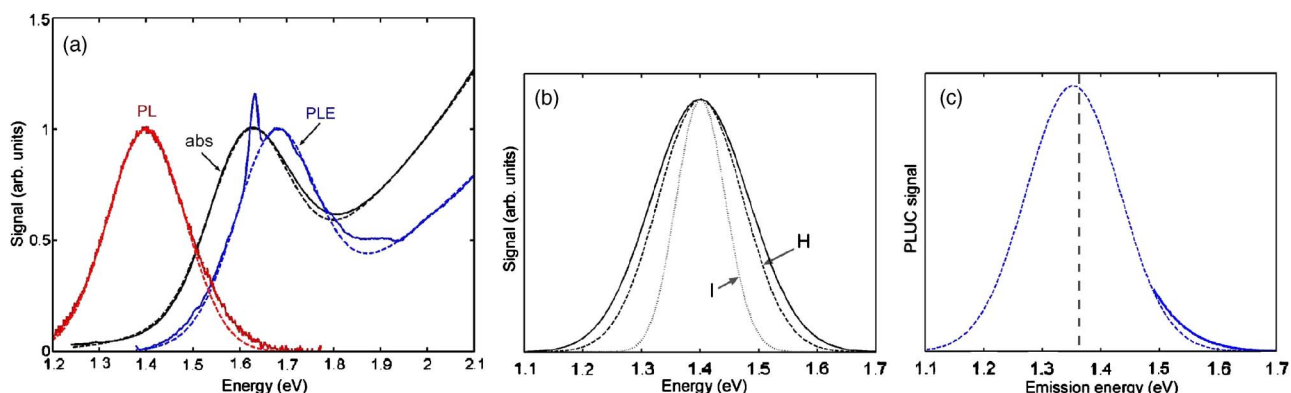
FIG. 3. (Color online) (a) PL, PLE, and absorption spectra obtained from a PbS NC solution. A model has been used to generate the dashed curves that fit each spectrum. (b) The contributions to the PL line shape from the homogeneous component (H) and inhomogeneous (I) size distribution component as determined by the model used to fit the spectra. (c) The predicted PL spectrum obtained by pumping at 1.37 eV (dashed) and the PLUC fragment obtained in the experiment.

at room temperature. This represents an unconventional form of PLUC interaction that does not rely on anti-Stokes emission from thermally populated intermediate states, but is rather a natural consequence of enhanced phonon coupling in strongly quantum confined NCs. In the cases studied, we find that the conventional PL signal still dominates the PLUC signal, preventing PLUC from being used to cool the sample. This is due to the large Stokes shift of the emission. However, improved surface passivation should be able to remove this Stokes shift altogether.

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