

Infrared Fluorescence of Lead Selenide Colloidal Quantum Dots

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Abstract

The fluorescence of PbSe colloidal quantum dots are studied. At room temperature, we find that surface ligands have a dominant effect on the fluorescence and lifetime of PbSe nanocrystal, especially with the first exciton energy below 0.8eV. As temperature goes down from 300K to 14K, the lifetime increases dramatically, which fits the theoretical expectation. In the future study, I will try to improve the fluorescence by ligand exchange or shell synthesis, the low temperature behavior of PbSe will be interpreted quantitatively, and more low temperature measurement will be carried on to verify the interpretation.

Outline of the paper

Introduction

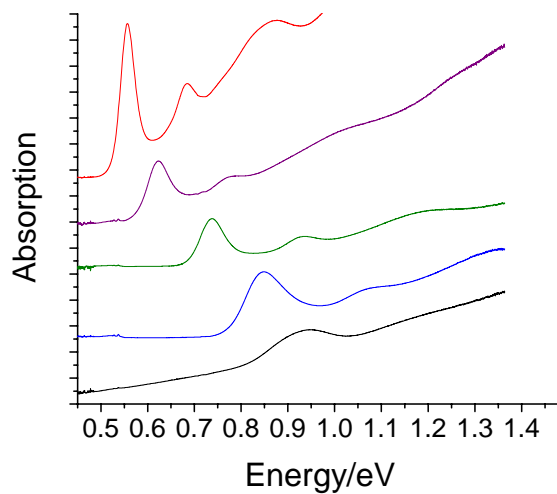
There has been progress made in our understanding of the electrical and optical properties of nanocrystal, since the first colloidal quantum dots have been prepared. Among various quantum dots, selenides semiconductors have applications as laser materials, optical sensors and so on.

Known to be narrow band gap semiconductor, PbSe colloidal quantum dots were found to exhibit a well-defined excitonic structure and have near-unity quantum yield with emission wavelength between 1.2 microns and 2 microns determined by the particle size. Thus PbSe has potential for application as monochromatic infrared light source.

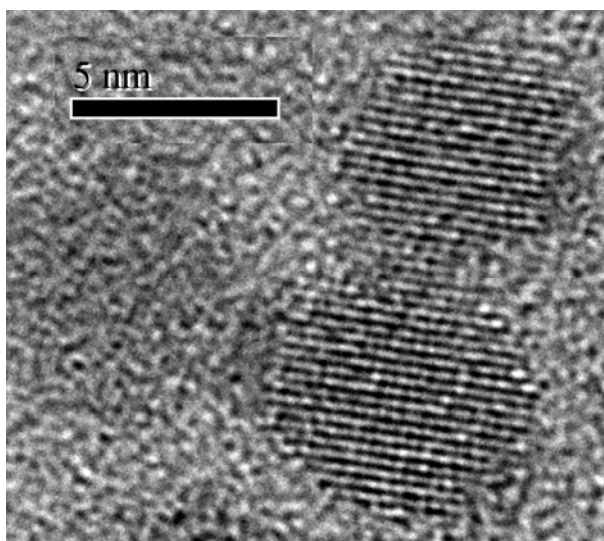
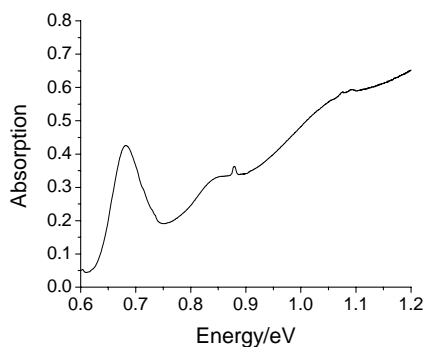
Materials and Synthesis

Two different methods have been adopted to prepare PbSe colloidal quantum dots, which are described in detail in Pietryga et al (JACS 2008, 130(14), 4879) and Talapin et al (Science 2005, 310, 86). The general idea is as follows: 0.54g lead acetate (1.66M) was dissolved in 1.8ml oleic acid and 10ml 1-octadecene (ODE). The solution was heated at 100°C in vacuum for around 2 hours to form and degas lead oleate. Then the temperature was increased into 180°C under atmosphere of argon. 4.5ml 1M TOP Se was injected into the solution as soon as the temperature reached 180°C. The reaction time varies from 5 seconds to 1 minute to obtain PbSe with desired sizes. The solution was cooled down by 5ml toluene and 5ml hexane.

The graph below is the absorption spectra of PbSe of different sizes in tetrachloroethylene (C₂Cl₄) solution:



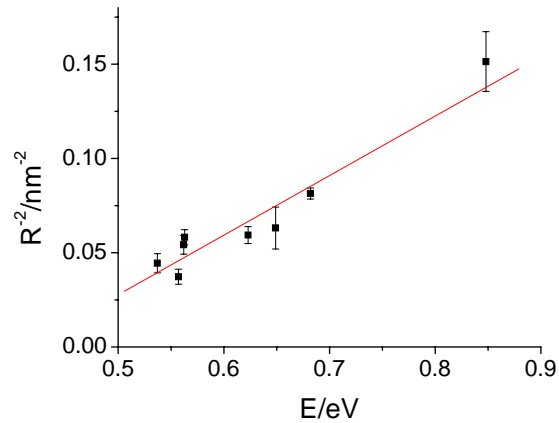
TEM picture of typical PbSe nanocrystals prepared by the method above (Left is the spectra of sample corresponding to):



Size dependence of energy gap

Based on infinite spherical potential barrier model, one can easily calculate the size dependence of the first exciton energy. More specifically, the energy gap is inversely proportional to the square of radius.

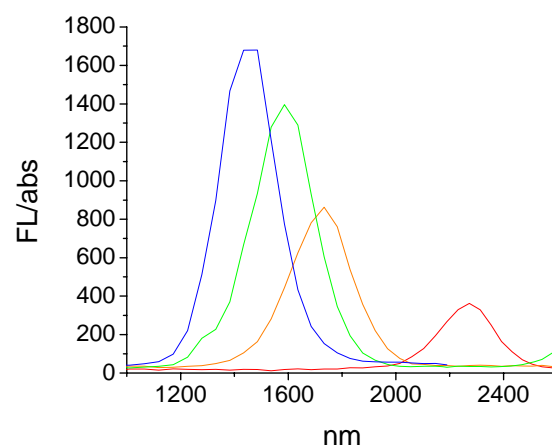
The graph shows the relationship between the first exciton energy and $1/R^2$:



Fluorescence and Energy relaxation at room temperature

When the electron-hole pair is generated in the nanocrystal due to absorption of a photon, it either recombines and emits a photon with longer wavelength, or transfer its energy in some nonradiative way. The former is usually referred as fluorescence and the later is called energy relaxation in most cases, which has been studied and discussed intensely in the past.

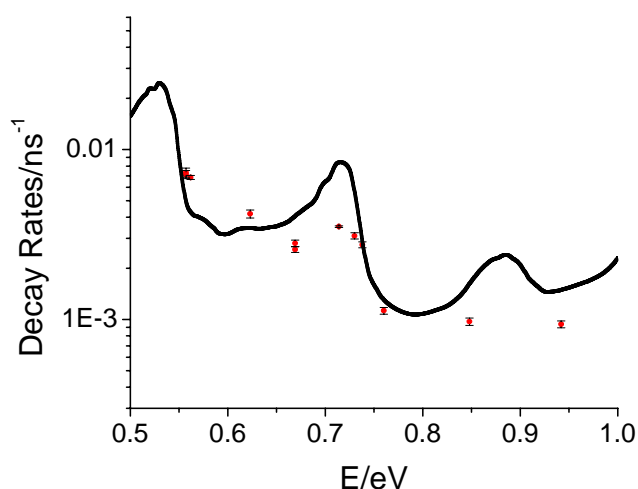
The graph below shows the fluorescence intensity of different-sized PbSe, which has been normalized by the concentration of PbSe quantum dots solution. The intensity increases significantly as the fluorescence energy goes from 0.5eV (red) to 0.9eV (blue). One possible explanation is at lower energy, the absorbance of ligands, which we believe is lead oleate, is generally higher. Therefore, the photon coming from the quantum dots have a higher probability to be absorbed by the ligand shell around the dots.



Such energy relaxation via vibrational mechanism is explained at Guyot-Sionnest et al (J Chem Phys 123, 074709, 2005). Here is the semi quantitative result using the ligand-vibrational model.

From quantum mechanics, radiative rates of a dipole in a medium can be written as $T_r^{-1} = 2e^2\omega^2\sqrt{\epsilon_1}f/3m_0c^3$, which is proportional to the energy square. From An et al (Nanoletter 7, 2129, 2007), the calculated lifetime for R=3nm ($E=0.88\text{eV}$, approximately) is around $1\mu\text{s}$. So for simplicity, the radiative rates is given by $T_r^{-1} = 1 \times 10^{-3}\text{ns}^{-1} * (E/0.88)^2$, where E in eV. Based on the vibrational mechanism, we estimate the nonradiative rates as $T_{nr}^{-1} = 0.183\text{ns}^{-1} * E^2 * A_{\text{ligand}}$, where E is the energy in eV, A_{ligand} is the absorbance of lead oleate. The additional assumption is that the number of ligands per unit area on the surface of nanocrystal is constant for all the samples.

The black line is the estimated total decay rates $T_r^{-1}+T_{nr}^{-1}$. The green dots are measured lifetime. All the measurements are done in tetrachloroethylene (C_2Cl_4) solvent.



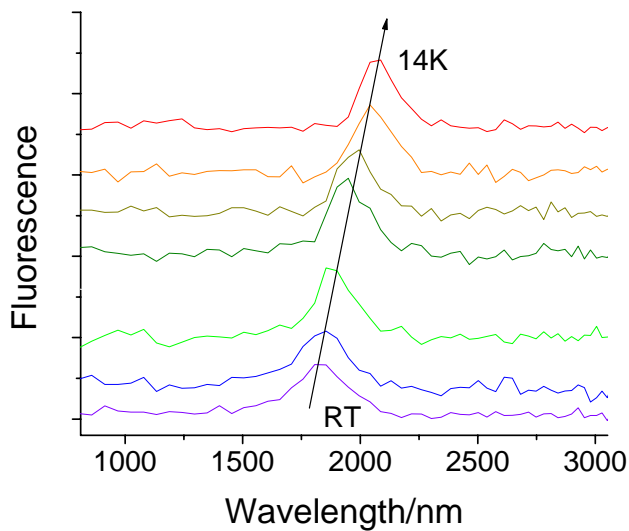
We can see that such estimation can not only give the proper order of magnitude, but also show the tendency, especially for the energy range below 0.8eV.

Low temperature measurement

A theoretical study indicates that radiative lifetime would increase by three orders of magnitude when the sample goes from room temperature to a few Kelvin. (Nanoletter 7, 2129, 2007) But in the experiment, such effect could be hardly observed, for the reason that nonradiative energy transfer can strongly suppress the total lifetime, as the radiative lifetime is too high.

The result below is the measurement of PbSe in heptamethylnonane solution with an energy gap at room temperature around 0.72eV. As the sample cools down from room temperature to 14K, its fluorescence shifts to the red around 100meV. Generally speaking, besides the radiative lifetime increases as temperature goes down, there are two effects on the total lifetime. One is near field absorption, corresponding to ligands vibration. The other is far field absorption, which rises from the absorption of the heptamethylnonane solvent. Because its absorbance in such energy region is higher than lead oleate, the heptamethylnonane is the dominant factor for the lifetime suppression in low temperature. But the quantitative interpretation is still needed to confirm the assumption above.

The graph shows the fluorescence shift from room temperature to low temperature. The fluorescence is dim, probably because the absorbance of heptamethylnonane is maximum in this energy region.



The temperature dependence of the lifetime and the corresponding decay rates are shown below. The lifetime increases by a factor of 5 as the temperature goes from 300K to 14K.

