# Characterisation of photoluminescence of colloidal semiconductor nanocrystals

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## Application Note

### Introduction

Colloidal nanocrystals have been a subject of research for almost two decades. They combine good optical properties with easy, low-temperature synthesis and as such they are interesting for a variety of applications ranging from solid state lighting, display technology, medical imaging to energy harvesting. Due to their small sizes, usually with diameter less than 10nm, it is inherently difficult to perform structural characterization of the nanocrystals and indirect methods of characterization are very important. They provide a direct assessment of nanocrystals optical properties such as spectrum of emission or quantum yield. In order to gain insight into defect states present in the nanocrystals, it has been shown that time or temperature dependent photoluminescence (PL) can be used [1]. Such measurements accompanied by simulations have been used to determine the relative energy levels of the surface defects [2].

In order to assess new nanostructured semiconductor based photon emitters we have constructed an experimental setup which allows measurements of the integrated and time resolved photo- and electroluminescence in visible and near infrared wavelength spectral ranges (see Figure 1). The geometry of the setup was designed paying attention to the ability to accept a variety of sample forms (liquid, solid etc.) and to high flexibility for future developments.

### Experimental setup

A sample under investigation is positioned on a movable stage, which is configured to easily accommodate either solid state samples or liquid samples. A continuous wave or pulsed laser with a selectable wavelength is directed towards the sample using a suitable dichroic mirror which is chosen to reflect the laser light towards the sample but to transmit longer wavelengths PL. The laser beam is focused to a spot with an achromatic lens or infinity corrected objective lens with 20x magnification and NA of 0.42 if sample is to be imaged. Photoluminescence from the investigated sample is collected and collimated with the same lens and is then transmitted through the dichroic mirror into the detection part of the system. Depending on the range of wavelengths to be studied a flip mirror steers the light to one of the two Andor Shamrock SR-303i-B-SIL spectrographs. One of the spectrographs is equipped with an Andor Si CCD detector iDus DU401A-BV and with a Si single photon detector on the second output. The system was calibrated using a lamp with a known spectrum, which allows conversion of the counts recorded on the CCD into photons/nm/m$^2$. Such calibration is essential when comparing emitters emitting at different photon wavelengths or measuring the quantum yield. As it takes into account optics efficiency, it is also necessary for an acquisition of spectra over large wavelength range (for spectra stitching). The uncalibrated avalanche photodiode on the other hand can be synchronized with the pulsed laser and can thus measure the photoluminescence decay as a function of time which elapsed since last pulse of laser excitation. Similarly, the second Shamrock spectrograph is equipped with an Andor InGaAs photodiode array iDus DU490A-1.7 and an InGaAs avalanche photodiode.

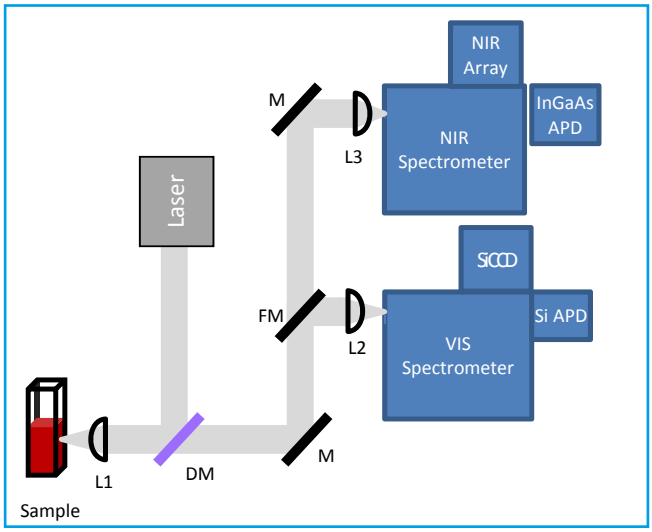


Figure 1: Schematic diagram of the experimental setup for measuring photoluminescence from nanoscale photon emitters. DM stands for a dichroic mirror, M – a mirror, FM is a flip mirror while L1 marks the laser focusing and PL collecting lens, L2 and L3 are lenses focusing collimated light onto the slits of the two spectrometers.

### Experimental results

As an example we used the above described setup to measure the PL from colloidal InP/ZnS nanocrystals, which are being considered as a nontoxic alternative to CdSe nanocrystals. The nanocrystals were synthesized using indium and phosphorus precursors, with zinc precursor added at the beginning of the reaction. Following the cores formation, precursors were added to form a ZnS shell around the cores.

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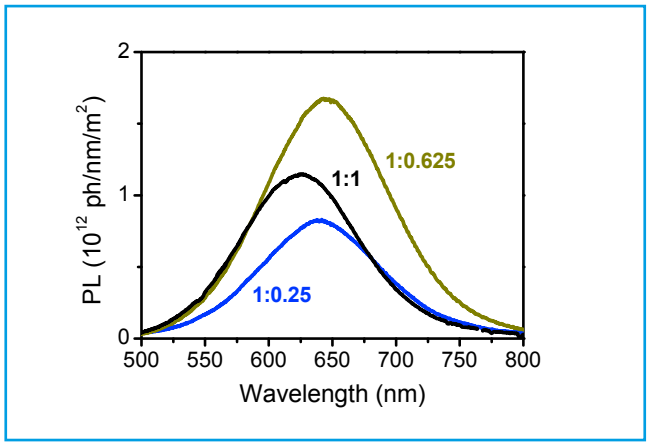


Figure 2: Photoluminescence spectra of three different nanocrystals batches, synthesizes with different ration of indium to zinc precursors during the growth of the core.

All nanocrystals have shells formed in the same way. Samples for the measurements shown here were prepared by performing the synthesis using the same parameters except the ratio of In:Zn. Each batch of nanocrystals was extracted from the reaction flask after shell formation and it was cleaned to remove the reactants. Such nanocrystals dissolved in chloroform were places in a silica cuvette with 5 mm light path. The concentration of each batch was adjusted to achieve an absorbance of 0.1 at the excitation wavelength of 405 nm. The absorbance of the solution could be monitored during PL measurements by the photodiode placed behind the cuvette.

Spectra from all such prepared samples were collected with the laser light focused at the same depth in the cuvette. Light collected with the lens is passed to the input port of the spectrometer dedicated to the analysis of light in the visible light range (lower light path in Figure 1). In order to remove the effect of dark counts and stray light a reference spectrum was collected with a cuvette with pure solvent as well. Spectra measured for the different nanocrystals are shown in Figure 2. Due to their broad emission, each spectrum was collected by acquiring two spectra centred at wavelengths of 610 nm and 700 nm. Such obtained spectra, after background removal and thorough optic system calibration, do not show discontinuity at the range of overlap as long as the nanocrystals are stable over time – such as those shown in Figure 2.

As the amount of Zn during the synthesis increases, the wavelength of emission shifts to shorter wavelengths. There is a clear optimum ratio of In:Zn for the maximum quantum yield around 1:0.625.

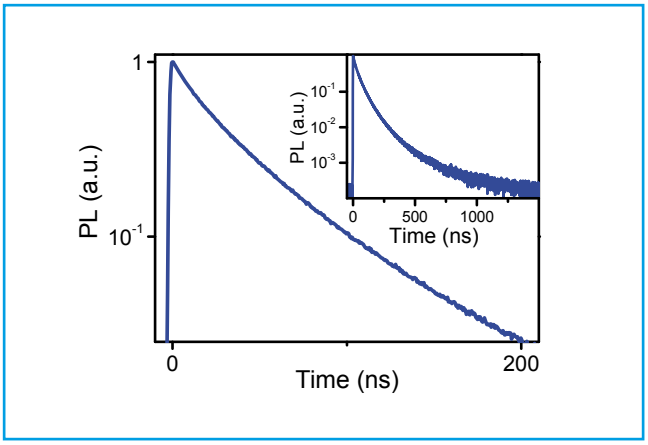


Figure 3: Time resolved photoluminescence from nanocrystals with In:Zn=1:0.625 over first 200ns and 1500ns, showing strongly non-exponential decay.

The results of time resolved PL measured for the highest efficiency nanocrystals are shown in Figure 3. The measurement was done by choosing the peak wavelength of PL emission as the central wavelength in the spectrometer and by steering the beam to a second exit. The slit on the second exit passed part of the spectrum with 5 nm bandwidth. A pulsed laser with a repetition rate of 500 kHz was used so the excited nanocrystals decayed fully between pulses. The observed multi-exponential decay rate is characteristic of multiple recombination channels present and therefore characteristic for nanocrystals with defects. Conclusions An effect of In:Zn ratio on PL quantum yield of InP nanocrystals has been studied. A simple setup incorporating a spectrometer, CCD camera and a fast detector allowed fast and reliable measurements of PL spectra and time resolved PL.

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**References**

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[2] M. Jones and G. D. Scholes, J. Mater. Chem. **20** (18), 3533-3538 (2010).

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