

Doctoral dissertation title:

“Influence of transition metal doping on optical processes in quasi-two-dimensional colloidal cadmium selenide nanoplatelets”

Abstract

This dissertation concerns the properties of defect emission and the changes in recombination dynamics brought about by doping colloidal CdSe nanoplatelets with Cu and Ag ions. These quasi-two-dimensional nanostructures combine an atomically defined thickness, until now reserved for epitaxially grown quantum wells, with the processability characteristic of colloidal nanoparticles. The optical dynamics of such structures at the single-nanocrystal level remains poorly understood, and colloidal synthesis additionally allows them to be reshaped after growth, for instance into nanorings, which epitaxial techniques cannot achieve. Doping such nanostructures with Cu or Ag ions amounts to more than simple substitution. A single ion introduces compressive and tensile strain that mixes the valence subbands, creates point defects, and alters the surface chemistry that governs the statistics of the optical processes. The resulting defect states capture carriers and open radiative and nonradiative recombination channels that compete with excitonic emission.

The aim of this work is to characterise and explain the effects that Cu and Ag ions produce in CdSe nanoplatelets. These include the ions' preference for forming point defects, the structural perturbations they cause, and the changes in exciton relaxation kinetics, all considered against the chemistry of CdSe and of both dopants. An open question is how well these ions fit the host, not only in ionic radius but also in oxidation state and preferred position in the lattice. The study combined precise synthesis, modification of the nanostructure geometry, *ab initio* calculations, and single-particle spectroscopy in order to link the observed photoluminescence bands to the configuration of defects and to their charge states predicted by the calculations.

The work applied synthesis procedures for CdSe nanoplatelets of varying thickness and controlled in-plane dimensions. Four-monolayer structures received particular attention, as they gave the most uniform samples and the highest degree of control over the synthesis parameters. Doping used Cu and Ag ions at low concentrations that limited their clustering. Following controlled-etching protocols reported in the literature, the work obtained nanorings whose diameter depends on the original nanoplatelet dimensions, in a manner inaccessible to epitaxial techniques. The change of shape affects the potential profile and the availability of surface states. The nanorings themselves, however, proved too prone to photodegradation for a reliable analysis of their emission dynamics. Controlling the in-plane dimensions tunes the position and width of the emission band.

The doped four-monolayer nanoplatelets were chosen for the kinetic study because their narrow green excitonic band and broad red-shifted defect band are spectrally well separated and differ clearly in decay time, as is already apparent in a measurement on the colloidal solution. Single-nanocrystal spectroscopy, which combines spectral selection with two-dimensional histograms of decay time and luminescence intensity, made it possible to separate the kinetics of the two emissions at the single-emitter level. This way of presenting the data supports the analysis of radiative recombination and also allows inferences about nonradiative recombination in these nanocrystals.

The emission of single nanoplatelets is intermittent. It switches randomly between defect levels and passes into a dark state in which the photoluminescence is quenched. The mechanism of this intermittency matches a model developed earlier for ternary quantum dots, in which radiative and trapping processes compete for the carriers, as indicated by a strong anticorrelation between intensity and decay times. By choosing the dopant and its concentration, one can influence the occurrence of the dark state in a controlled way and then measure the resulting changes in the kinetics.

Cu ions give longer and more complex relaxation dynamics, Ag ions shorter and simpler dynamics, partly because of their tendency to agglomerate at the edges. The differences in emission follow from the proportions among the active processes rather than from a single rigid trap state. This result is supported by *ab initio* calculations which, given the strong influence of the surface and of quantum confinement in the nanoplatelets, indicate a direction rather than a resolution. The formation energies and the relative ordering of the charge levels under selenium-rich and selenium-poor conditions suggest that the defect emission may originate from the interstitial dopants Ag_i and Cu_i , most likely in the form of defect complexes.

The isolated defect levels, which give long decay times and a clear spectral separation from the excitonic emission, make doped CdSe nanoplatelets candidates for stable room-temperature light sources. Linking the physicochemistry of the dopants to the kinetics of single nanocrystals has not been studied before for this class of systems. This work organises the picture of relaxation and defects in two-dimensional CdSe and shows how to choose the synthesis parameters for the desired optical properties.