Exciton fine structure of a single highly anisotropic CsPbBr$_3$ nanocrystal

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Abstract. We measured the photoluminescence (PL) of single CsPbBr$_3$ nanocrystals (NCs) that have a highly anisotropic shape and orthorhombic crystal phase. As the thickness of these NCs is much more smaller than the other two dimensions, they are also called nanoplatelets (NPLs). We obtain PL spectra characterized by doublets separated in energy by about 2 meV in average and showing orthogonal and linearly polarized polar lines. We identified these doublets as the two bright-exciton states of the exciton fine structure contained in the plane of the NPLs. By a comparison between theory and experiments, we were able to obtain fundamental parameters as tetragonal and orthorhombic crystal field. We measured and analysed the time-resolved PL evolution as a function of temperature of small ensemble of NPLs. We thus succeed at framing the experimental value of the bright-dark exciton splitting (5-7 meV) that is slightly smaller than the theoretical value.

In last years, lead-halide perovskites appear as a new generation of promising semiconductor materials for photovoltaic and optoelectronics applications [1,2]. The obtention by chemical methods of perovskite nanomaterials as nanowires, nanoplatelets and nanocrystals (NCs) and so the control of shape and size introduces essential parameters to control and enhance their optical and emission properties opening also new domains of application like quantum optics and quantum information.

Here, we center our study on NCs band-edge emission whose origin is related to confined excitons (confined electron-hole pairs interacting via coulomb interaction). In order to carry out an in-depth analysis of the exciton emission in terms of fine structure of the confined exciton, we report on the photoluminescence of a single Br-based NC (µ-PL) with highly anisotropic shape (12 nm x 12 nm x 1.8 nm) at very low temperature (10K). This analysis is not accessible in ensemble and room temperature studies due to broadening effects. These highly anisotropic NCs obtained by chemical methods are the analogous to the quantum wells fabricated by MBE techniques and they are called nanoplatelets (NPLs)[3].

Figure 1 a) PL of a single CsPbBr$_3$ NPL at 10K.
In μ-PL experiments, single CsPbBr$_3$ NPLs responses are clearly identified under the form of sharp spectroscopic lines forming doublets. A typical spectrum is presented in Figure 1a. The polarization analysis of this doublet structure (polar plot in Figure 1b) indicates the crossed polarized nature of each component. We have also calculated the exciton fine structure in 2D halide perovskite materials. It consists on four states with one dark state (D) at lower energy and three bright states (B), fully splitted in energy in NCs with orthorhombic crystal phase. In NPLs, two groups of B-excitonic states are distinguished due to the electronic confinement: those with dipole in the plane of the NPL and the one with dipole perpendicular to the plane. The latter one is less coupled with the light due to dielectric screening [4].

Time-resolved PL as a function of temperature has also been performed. We discuss and compare our μ-PL data for CsPbBr$_3$ NPLs with the theoretical results. We identified the doublet as the in plane B-excitonic states and from the measured splitting of the doublet we deduced fundamental parameters as the tetragonal and orthorhombic crystal fields. From an analysis of the time resolved experiments by using a model taken into account the thermal mixing via a one phonon process between D and B-excitonic states we were able to obtain a domain of values of the B-D exciton splitting that is close but slightly smaller than the theoretically predicted one.

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References