Anisotropic local field factors determine the absorption coefficient of colloidal quantum rods.

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The absorption coefficient is an interesting quantity for the quantitative study of the optical properties of colloidal semiconductor nanocrystals. Related to the molar extinction coefficient and the absorption cross section through the size and the shape of the particles, it is a convenient quantity to determine the concentration of nanocrystal suspensions and it gives access to the oscillator strength of the bandgap transition, For spherical PbSe, PbS and CdSe semiconductor nanocrystals or quantum dot, it was shown that the absorption coefficient at short wavelengths, i.e., with energies well above the bandgap transition, largely coincides with a theoretical value calculated using bulk optical constants[1-5]. A key element in this comparison is the local field factor, which relates the externally applied electric field to the electric field present within the quantum dots. In this presentation, we extend this work to colloidal quantum rods (QR), where we use CdSe QRs to demonstrate that shape anisotropy and the resulting anisotropic local field factor lead to an anisotropic absorption coefficient.

As a first step, we analyse the absorption of a suspension of colloidal CdSe QRs, 5 nm wide and 18 nm long (as shown in figure1), under the application of an electric field. It has already been shown in the literature that electric fields induce an alignment of suspended QRs with their long axis along the direction of the field, an effect that was attributed to the presence of a permanent dipole moment[6]. Here, we show that upon application of an electric field, the absorbance of a QR suspension at short wavelength drops, with larger fields resulting in larger absorbance changes. To understand this absorbance drop and its dependence on the electric field strength, we model a QR as an ellipsoid with a permanent dipole moment. Introducing anisotropic local field factors that describe the different screening of the electric field parallel and perpendicular to the long axis of the rod, we find a close correspondence between experiment and theory presuming the QRs have a permanent dipole moment of about 200 Debye, a typical value reported in literature[6] (In figure2b. *shift in absorbance/absorbance Vs electric field is plotted)*.

Importantly, the anisotropy of the local field factors not only shows up upon rod alignment. Since there are two directions perpendicular, yet only one parallel to the long axis of the rods, the absorption coefficient of a randomly oriented ensemble of quantum rods will be different from that of a similar ensemble of quantum dots. Therefore, we use inductively coupled mass spectrometry in combination with transmission electron microscopy and UV-Vis absorption spectroscopy to determine the intrinsic absorption coefficient of CdSe QRs (Intrinsic absorption spectrum is given in figure2a.). We find that the experimental value at short wavelength is about 30% larger than the value expected for CdSe quantum dots. Again, we demonstrate that this difference can be understood by considering the anisotropy of the local field factors.

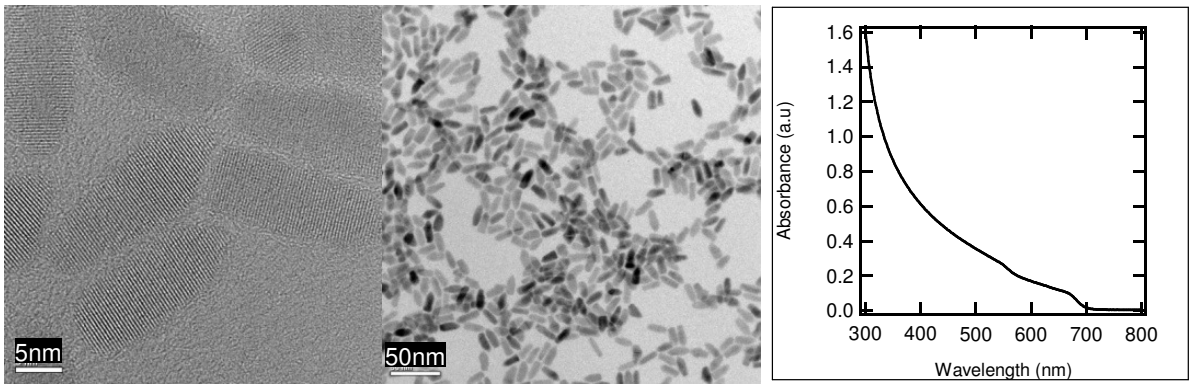

Figure1. TEM images of CdSe rods, Absorption spectrum of CdSe rods.

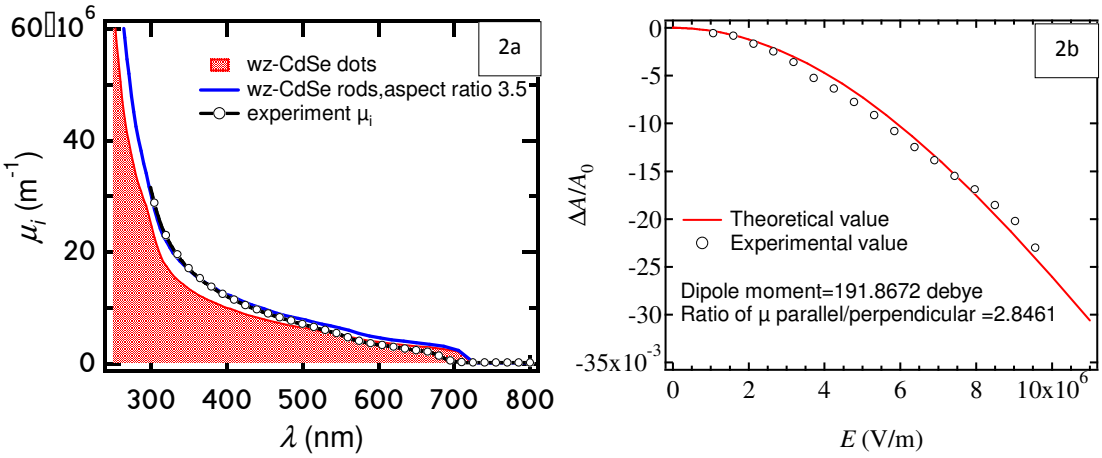

Figure2a. Intrinsic absorption spectrum**, Figure2b.**shift in absorbance/absorbance Vs electric field

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