

# Polarized Exciton at Room Temperature

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Localization of the charge in Q-semiconductor particles strongly change their absorption spectra at wavelengths near the absorption edge. This effect is attributed to the influence of excess electrons or positive holes on the optical transitions leading to the lowest excitonic state of Q-particles. The consequence of this "polarized exciton" is strong bleaching and a blue shift in the absorption spectra.

Extremely small colloidal semiconductor particles (Q-particles) have optical properties different to those of macrocrystalline materials. Optical spectra of Q-particles usually show different maxima in the absorption spectra. These effects are due to the restriction in space of the charge carriers produced by light absorption (size quantization effects).

These size effects are generally described by the well known quantum mechanics of a "particle in a box". The electron and the positive hole are confined to potential wells of small dimensions and this leads to a quantization of the energy levels.

The phenomena of quantization effects become significant when the size of colloidal semiconductor particles becomes comparable to the deBroglie wavelength.

The maxima in the absorption spectra are attributed to optical transitions to the lowest electronic state. This state may be regarded as a strongly compressed "exciton". In a macrocrystal, the exciton state is separated from the lower edge of the conduction band by only a few 0.01 eV and the orbitals have a diameter of about 5nm. The optical transition to the "exciton" state can only be resolved at liquid helium temperature.

In Q-materials, the energy difference between the "exciton" state and the lower edge of the semiconductor band is strongly increased i.e. much greater than the thermal energy,  $kT$ , at room temperature and optical transitions can, therefore, be resolved without cooling the sample.

Different maxima are attributed to the different transitions to the "exciton" state in particles of different size. In rather monodisperse samples the transitions of different electronic states may be considered.

A few years ago, it was discovered that Q-particles have optical and catalytic properties differing to those of the macrocrystalline materials. These differences are due to size quantization. Now there are reports of studies in which changes in the properties of the particles, occurring under illumination, are investigated. The charge carriers, produced by light absorption, may themselves change the optical properties of the particles, and these changes may result in non-linear optical effects.

Excess charge carriers can often be deposited onto the colloidal particles by free radicals produced in the bulk solution by irradiation. Strongly reducing radicals transfer an electron to the colloidal particle and strongly oxidizing radicals may inject positive holes. The advantage of this method of excess charge deposition lies in the fact that the effects of charge carriers of one sign can be investigated without being disturbed by recombination with carriers of the opposite sign. Both chemical reactions of the charge carriers and the influence of the carriers on the optical properties of colloidal semiconductor particles can be studied in this way.

The reaction of the hydrated electron with Q-particles has been studied using the method of pulse radiolysis and flash photolysis. A strong bleaching occurred at the wavelength where Q-particles already absorb



The same bleaching is observed when OH radicals attack the Q-particles. OH radicals pick-up electrons from "neutral" semiconductor Q-particles and produce particles which carry a positive hole.



In this case, we attribute the positive hole to be the S<sup>-</sup> radical.

Localization of electrons or positive holes at Q-semiconductor particles causes the bleaching in the absorption region of Q-materials and shift the absorption spectra to shorter wavelengths.

The bleaching is attributed to the influence of excess electric charge on excitonic state which is "polarized" in the field of excess electrons or holes. The consequence being a blue shift in the absorption spectrum. These effects can be understood as a "polarized exciton" at room temperature.

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