

Synthesis and magneto-optical studies of colloidal CdSe/ZnSe quantum dots doped with copper

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Colloidal semiconductor nanocrystals doped with transition metal ions are attracting a broad interest in fields as diverse as spintronics, phosphor technologies, bioimaging, and fundamental synthetic and physical inorganic chemistries.

Here we report on the synthesis of CdSe/ZnSe core/shell nanoparticles doped with copper ions. The synthesis used chemical co-precipitation from homogeneous solution. The CdSe:Cu core sizes (as measured by absorption edge position at room temperature after the first stage of the reaction) ranged from 2.7 – 3 nm. Then, during the second stage of the growth process relatively thick ZnSe shells were precipitated. The thickness of the shells ranged between 14 – 15 nm. The nominal amount of Cu introduced was 0, 2, 5 and 10 at.%. Samples were checked with x-ray diffraction which showed only the signal from the zinc blende shells. An attempt was made to observe the electron paramagnetic resonance and from those measurements it was deduced that Cu in as grown nanocrystals was at the first oxidation level, Cu⁺¹. We did not observe any changes of the charge state of Cu ions by illumination with blue light.

Photoluminescence spectra of the nanoparticles with various concentration of Cu doped was examined. Narrow band in the green region corresponding to the across-the-band-gap transition is observed. Increasing the concentration of Cu²⁺ led to luminescence quenching. The deposition of the shells led to a slight blue-shift of the luminescence peak energy (as compared to its position in the control batch of uncoated nanocrystals), probably due to the compressive strain introduced by the shells. Presence of ZnSe shells resulted also in a significant brightening of the PL. PLE studies allowed observation of additional, higher energy states.

Comparison of the polarization-resolved magneto-PL measured in field up to 8 T showed differences between doped and undoped nanoparticles. First, PL intensity in the presence of the field increased in the Cu-doped samples. Second, the degree of circular polarization, defined as a difference between intensity in two polarization $\sigma+$ and $\sigma-$, is opposite in the case when copper ions are present in the core of CdSe/ZnSe as compared to the undoped specimens. The polarization degree increases with doping concentration. In both cases it is due to the fact that the lower energy level of the Zeeman doublet is more populated. This difference in the sign of the polarization degree we tentatively relate to a contribution of sp-d interaction of carriers with the spins of copper ions at the second oxidation level, Cu⁺², the state which is induced by strong exciting UV light. The magnetic field dependence of the polarization degree at LHe temperature is consistent with this conjecture indicating that the sp-d interaction saturates at some value of the magnetic field. At higher temperatures, above 10 K, the polarization degree in the weak field region changes its sign becoming the same as in the undoped nanocrystals, indicating a smaller contribution of sp-d interaction, as expected. On the other hand, at fields higher than 4 T the polarization exhibits a peculiar behavior which points to a decreased spin relaxation rate in this field range in the copper doped nanocrystals.

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