Giant magneto-optical response in single-atom doped $(CdSe)_{13}$ nanocluster at room temperature

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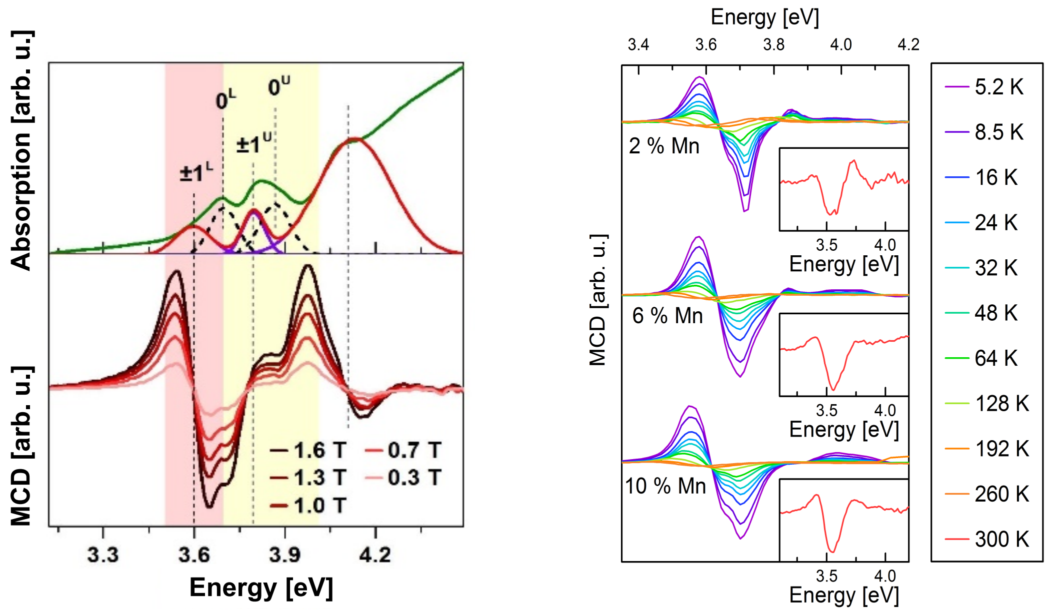
Magic sized nanoclusters containing a discrete numbers of atoms represent an exciting class of materials at the boundary between quantum dots and molecules. $(CdSe)_{13}$ consisting of only 26 atoms are the smallest stoichiometric clusters isolated as single sized family, yet exhibiting semiconductor characteristics such as a temperature dependent bandgap. Herein the individual replacement of atoms in the host lattice by magnetic dopants like Manganese (Mn) is expected to add additional functionality. Due to the small number of atoms within a magic size $(CdSe)_{13}$ cluster doping by just a single atom results in a significant doping concentration of 7.7 %.

Here we discuss the magneto-optical properties of Mn-doped $(CdSe)_{13}$ nanoclusters prepared by a colloidal chemistry approach. Successful doping is evidenced by giant Zeeman splittings with g-factors up to about 80 at cryogenic temperatures due to a pronounced *sp-d* exchange interaction between localized 3d electrons of the magnetic dopant and the charge carriers in the conduction and valence band states, respectively [1]. By comparing absorption and magnetic circular dichroism data we demonstrate a huge fine structure splitting of the exciton ground state enabling us to separate magneto-optically active and passive states. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry evidences the successful incorporation of either one or two Mn atoms into the $(CdSe)_{13}$ clusters while higher doping levels are not observed. Via a systematic variation of the average doping concentration the ratio between un-doped, mono-doped and bi-doped nanocluster can be adjusted. Among a series of clusters with different doping concentrations the giant Zeeman splitting is found to scale with the ratio of mono-doped clusters. This represents clear evidence that solely mono-doped clusters contribute to the magneto-optical response, while the spins of the Mn^{2+} dopants in bi-doped clusters predominantly align antiparallel and thus bi-doped clusters become magneto-optically inactive.

We were able to trace the giant magneto-optical response related to the *sp-d* exchange interaction all the way up to room temperature [2]. This demonstrates that the sp-d exchange interaction in single-atom doped ultrasmall magic size nanoclusters can create magneto-optical functionality even under ambient conditions.



Left: Absorption and magnetic field dependent MCD spectra of Mn-doped $(CdSe)_{13}$ clusters. **Right:** Temperature dependent MCD response for clusters with different average Mn concentration (right)

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2) F. Muckel, J. Yang, S. Lorenz, W. Baek, H. Chang, T. Hyeon, G. Bacher, R. Fainblat, ACS Nano **10**, 7135 (2016)