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Synthesis and characterization of Ni^{2+}-doped CdSe and CdSe(S) quantum dots

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The Ni-doped CdSe and CdSe(S) nanocrystals were synthesized using oleic and pelargic acids as stabilising agents and investigated by transmission electron microscopy, optical spectroscopy and inductively coupled plasma atomic emission spectroscopy.

Doped semiconductor nanocrystals (NCs) have attracted considerable attention due to their unique properties, which cannot be obtained in bulk materials.[1] Covered with organic or inorganic stabilizer molecules, semiconductor NCs or quantum dots (QDs) can form sols in suitable solvents (colloidal QDs). During recent decades, the preparation and characterization of doped QDs have provided new advances in not only the theoretical understanding of the fundamental mechanisms that control doping but also the fabrication of novel materials.[2] Doping mechanisms and methods for the incorporation of impurities into NCs have been widely discussed.[3–6]

The optical properties of Group II–IV compounds are strongly influenced by doping with nickel.[7] The Ni impurity is important as a luminescence centre and charge compensation, as well as an electron trap, because it forms deep levels within the band gap of the host material;[8] this is of interest for the application of Ni$^{\mathrm{II}}$-doped compounds as phosphors and laser materials.

Here we report the synthesis of Ni-doped CdSe and CdSe(S) nanoparticles capped by oleic and pelargic acids and their characterization by transmission electron microscopy (TEM), optical spectroscopy and inductively coupled plasma atomic emission spectroscopy (ICP-AES).

The synthesis was based on a published procedure[9] for the preparation of pure CdSe QDs.[†] Table 1 summarizes the experimental conditions and the composition, shape and size of the synthesized nanoparticles. Synthesized samples were investigated by TEM, optical spectroscopy and ICP-AES.[‡]

Table 1 Experimental conditions, composition, form and size of the synthesized nanoparticles.

Sample	*T*/°C	Cd : Ni / Se : S (at%)	Nanoparticle shape and size
A	180	98.7 : 1.3 / 40.4 : 59.6	spherical, average diameter of 3.2 nm
B	220	92.3 : 7.7 / 4.8 : 95.2	cubic, average length of 5.7 nm
C	220	98.6 : 1.4 / 24.5 : 75.5	
D	180	99.4 : 0.6 / 100 : 0	tetrapodal, average length and diameter of tetrapod rays of 7.5 and 2.1 nm, respectively
E	220	98.7 : 1.3 / 100 : 0	rods, length distribution 10–20 nm, average diameter of 3.2 nm

A comparison of the compositions and shapes of the nanoparticles allowed us to define general differences in the two synthetic procedures. Using $[(C_5H_{11})_2NC(S)S]_2Ni$ as a Ni$^{\mathrm{II}}$ precursor results in a significant amount of sulfur impurity in nanoparticles. Furthermore, it leads to the preparation of QDs, which have a cubic form unusual for CdSe and CdS QDs [Figure 1(*b*)].

[†] Cadmium oleate used as a cadmium precursor in the synthesis of QDs was prepared by a published method.[9] $Cd(AcO)_2 \cdot 2H_2O$ (0.5 mmol) and oleic acid (2 mmol) were dissolved in diphenyl ether (5 ml). The mixture was heated at 140 °C for 1 h in a continuous argon stream to remove water and acetic acid; then, the mixture was cooled to room temperature. A 1 M trioctylphosphine selenide (TOPSe) solution in trioctylphosphine (TOP) was prepared by dissolving elementary Se in TOP.

For a typical synthesis, cadmium oleate (0.5 mmol) dissolved in a nonpolar high-boiling solvent (diphenyl ether) and $[(C_5H_{11})_2NC(S)S]_2Ni$ [100 mg (0.19 mmol) in the synthesis of samples A and B, 30 mg (0.06 mmol) in the synthesis of sample C] used as a Ni^{2+} precursor were combined and heated at 30–60 °C under Ar (to dissolve the nickel precursor). Then, the temperature was stabilized at 180 or 220 °C and 1 M TOPSe solution in TOP (0.5 ml) was injected into the reaction mixture with vigorous stirring. After the injection, the particle growth was carried out at the same temperature during 5 min; then, the reaction mixture was cooled to room temperature. An equal volume of acetone was added for the precipitation of nanocrystals. Coagulated nanocrystals were separated by centrifugation, dissolved in a non-polar solvent (hexane or octane), again precipitated by acetone, separated and dissolved in the solvent (this procedure was repeated twice to remove reagents and different reaction products).

In another series of experiments, $Cd(AcO)_2 \cdot 2H_2O$ (0.5 mmol), $Ni(AcO)_2 \cdot 2H_2O$ (0.2 mmol) and an organic acid (oleic or pelargic in the synthesis of samples D and E, respectively) (2.4 mmol) were dissolved in diphenyl ether (5 ml). The mixture was heated at 150 °C for 1 h in a continuous argon stream to remove water and acetic acid. Then, the temperature was stabilized at 180 or 220 °C and 1 M TOPSe solution in TOP (0.5 ml) was injected into the reaction mixture with vigorous stirring. After the injection, the particle growth was carried out at the same temperature during 5 min and the reaction mixture was cooled to room temperature. The procedure of receiving pure samples was made as previously.

[‡] TEM analysis was performed on a Leo Omega 912 electron microscope. Size measurements were obtained on a statistical subset of QDs by the manual calculation of QD images obtained by digitizing the micrograph negatives. The optical absorption spectra were measured with a Varian Carry 50 spectrophotometer (UV-VIS). The photoluminescence (PL) experiments were measured on an Ocean Optics USB 4000 spectrometer (excitation by a 30 mW laser at 405 nm). All measurements were taken at room temperature.

ICP-AES (Optima 4300DV) for elemental analysis was performed on the Ni-doped CdSe and CdSe(S) QDs samples. All samples were dissolved in conc. HNO_3 with adding a few drops of a 30% H_2O_2 aqueous solution. Then, the mixture was heated at 300 °C, dissolved in 4% HNO_3 distilled water solution with adding of H_2O_2 and the Cd, Ni, Se, and S concentrations were measured against known Cd, Ni, Se and S standards. The Cd emission was monitored at 226.502 and 214.440 nm, the Ni emission was monitored at 232.003 and 341.476 nm, the Se emission was monitored at 196.026 and 203.985 nm, and the S emission was monitored at 181.975 and 180.669 nm. The reported doping concentrations are the average values of three to five runs with an error of 1–2%.

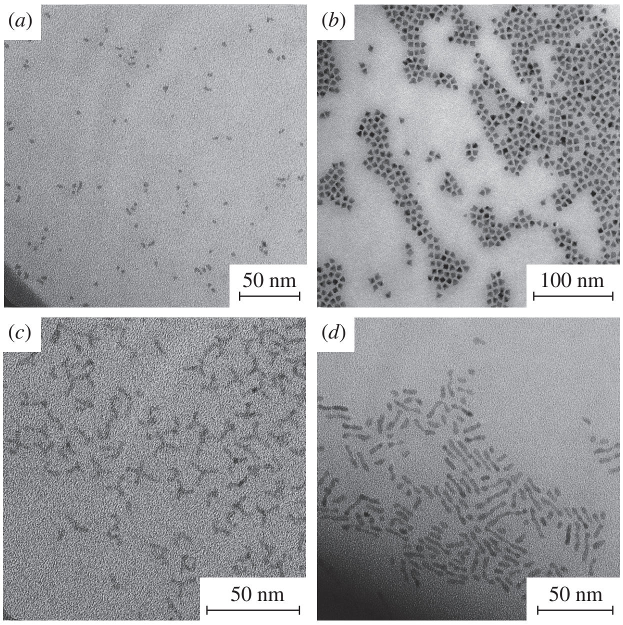

Figure 1 Transmission electron microscopy of samples (*a*) A, (*b*) B, (*c*) D and (*d*) E.

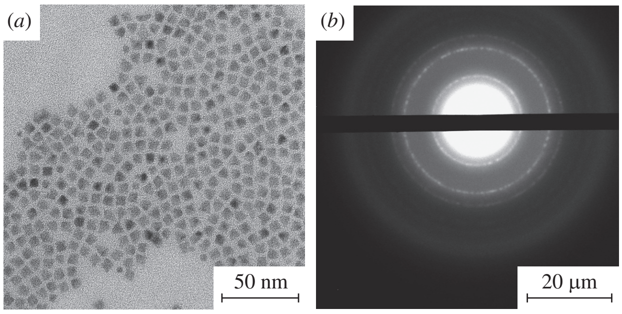

Figure 2 (*a*) Transmission electron micrograph of a Ni^{2+}-doped CdSe(S) sample and (*b*) electron diffraction ring pattern of the sample.

Using cadmium and nickel oleates or pelargonates provides the preparation of pure Cd(Ni)Se samples. Moreover, QDs synthesized from Cd and Ni oleates are spherical or tetrapodal; QDs received from Cd and Ni pelargonates have a rod-like form [Figure 1(*a*),(*c*),(*d*)].

Figure 2 presents (*a*) the micrograph of sample B with close packed nanocrystals with an average size of about 5.7 nm without agglomeration and (*b*) the electron diffraction ring pattern of the sample. The results of electron microdiffraction indicate a CdSe(S) phase (cubic modification with parameter $a = 5.90 \pm 0.02$ Å), clear ring pattern supports the high crystallinity of the obtained nanoparticles. Electron diffraction data collected from other samples confirm that CdSe and CdSe(S) materials were synthesized.

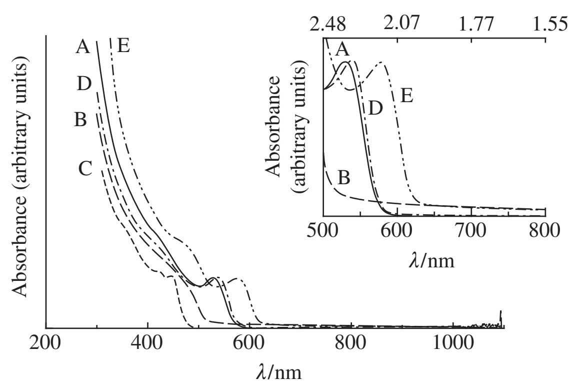

Figure 3 Optical absorption spectra of Ni^{2+}-doped CdSe and CdSe(S) samples.

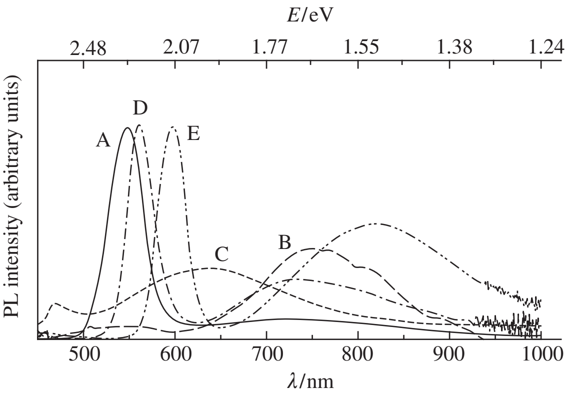

Figure 4 Photoluminescence spectra of Ni^{2+}-doped CdSe and CdSe(S) samples.

The absorption spectra of Ni-doped CdSe and CdSe(S) samples are given in Figure 3. The samples containing significant amounts of a Ni impurity have continuous absorption in the range of energies smaller than the energy of exciton transition, which is not observed in pure CdSe QDs. In all cases, the spectra contained a peak of exciton absorption corresponding to the energies of 2.35, 2.70, 2.78, 2.30 and 2.15 eV for samples A, B, C, D and E, respectively. Relatively wide absorbance bands can be related to size distribution. The absence of a pointed peak in the case of sample B is likely due to the formation of a solid solution of nickel in CdSe(S): the variety of nickel contents in the nanocrystals may lead to a peak widening based on the assumption that the substitution of Ni in CdSe and CdSe(S) changes the band gap values.

The respective PL spectra (Figure 4) also confirm the difference between pure and Ni-doped CdSe QDs. There are two peaks in the PL spectra: one is relatively narrow, and another in the range of smaller energies is wide. The first one is an exciton peak and a wide peak in the range of smaller energies corresponds to defect luminescence, it also could contain peaks connected with radiative electron transitions from excited states of Ni^{2+} ions to the CdSe or CdSe(S) valence band and electron transitions of Ni^{2+} ions. The difference in energy maxima for samples D and E (both are Ni^{2+}-doped CdSe nanoparticles) can be related to not only a Ni admixture but also a difference in the sizes of nanoparticles.

In summary, the Ni-doped CdSe and CdSe(S) nanocrystals were synthesized using oleic and pelargic acids as stabilizing agents. Optical measurements revealed that the optical properties of the samples are strongly influenced by doping with nickel.

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