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Synthesis and optical properties of PbSe and CdSe colloidal quantum dots capped with oleic acid

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PbSe and CdSe nanocrystals capped with oleic acid have been synthesised starting from metal oleates and investigated by X-ray diffraction, transmission electron microscopy and optical spectroscopy.

Semiconductor nanocrystals are of interest because of their unique size-dependent properties, which cannot be obtained in bulk materials.[1–3] Semiconductor materials including CdSe, ZnSe and ZnO have been prepared as colloidal quantum dots in which an inorganic core was covered with a long-chain organic stabilizer.[4–6] The control of emission properties of quantum dots under particle size variation is important for practical applications, for example, in light-emitting diodes and solar cells.[7–9] CdSe quantum dots stabilised by trioctylphosphine oxide (TOPO) have been synthesised by a high-temperature organometallic method suggested by Murray *et al.*[4] This method necessitates the use of dimethylcadmium as an aggressive precursor. A success has been achieved in studies of the thermolysis of monomolecular complex precursors in TOPO.[10,11] Recently, Murray and co-authors prepared monodisperse PbSe quantum dots using oleic acid as a surfactant.[3] We report on the synthesis

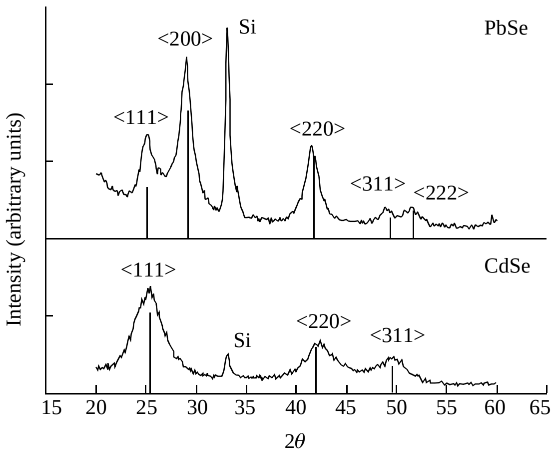

Figure 1 X-ray diffraction patterns of CdSe and PbSe samples. Hatches indicate corresponding bulk phase reflexes. The peak labelled Si is due to the silicon substrate.

of PbSe and CdSe quantum dots capped by oleic acid and on their investigation by X-ray diffraction, transmission electron microscopy (TEM) and optical spectroscopy.

The quantum dots were prepared from corresponding metal oleates in a non-polar high-boiling solvent. The synthetic procedure was based on the Murray method for PbSe.[3,12] For a typical synthesis, 0.5 mmol of a metal acetate [$Pb(MeCOO)_2 \cdot 3H_2O$ or $Cd(MeCOO)_2 \cdot H_2O$] and 2 mmol of oleic acid were dissolved in 5 ml of diphenyl ether. The reaction mixture was heated at 140 °C for 1 h in a continuos argon stream to remove water and acetic acid. Then temperature was stabilised at 120–130 °C in case of PbSe and 120–180 °C for CdSe, and 0.5 ml of a 1 M trioctylphosphine selenide solution in trioctylphosphine 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 quantum dots. Coagulated quantum dots were separated by centrifugation, twice washed with acetone and dissolved in a non-polar solvent (hexane or octane).

The phase composition was studied on a DRON-3M diffractometer using CuKα radiation. Samples were prepared by drying several drops of the quantum dot sol on a silicon <100> substrate. PbSe and CdSe phases (cubic modifications) were identified (Figure 1). The average crystallite size was estimated from diffraction reflections broadening using the Debay–Scherrer equation. Particle size increases with synthesis temperature and is within the range 3–5 nm for CdSe or 5–8 nm for PbSe. In case of CdSe sample grown at 120 °C, only an amorphous galo at 20° 2θ was observed without diffraction reflections. TEM investigations were carried out for quantum dot samples obtained by drying octane sol drops. Figure 2 presents the micrograph of the PbSe sample with close-packed nanocrystals with an average size of about 6 nm without agglomeration. The results of electron microdiffraction indicate a PbSe phase (Figure 2, inset). Clear ring pattern supports high crystallinity of the obtained nanoparticles.

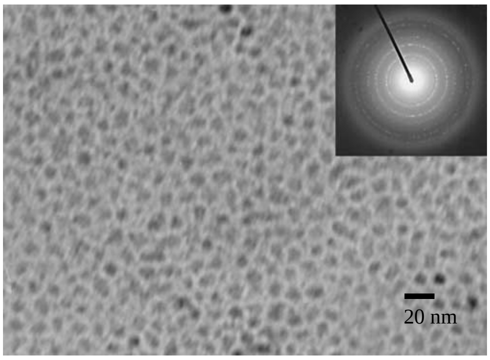

Figure 2 Transmission electron micrograph of a PbSe sample grown at 120 °C. Inset: electron diffraction ring pattern of the sample.

The optical absorption spectra were measured using a Perkin–Elmer Lambda-35 (UV-VIS) and SpectrumOne (near-IR) spectrometers. Spectra were obtained from hexane solutions of quantum dots. Photoluminescence measurements were recorded in the visible spectral range for CdSe samples by means of a spectrometer based on the quartz Littrov system with a photomultiplier tube (800–300 nm) as a detector and a pulse Kr^{++} laser (337.5 nm) for excitation.

The absorption spectra for CdSe samples grown at 120, 150 and 180 °C are given in Figure 3(*a*). The absorption band edge is shifted to lower energies as the particle size increased. In all cases, the spectra contained a peak of exciton absorption corresponding to the energies of 2.62, 2.44 and 2.21 eV in respect to the growth temperatures shown above. Such a structure of the spectrum indicates a strong effect of quantum confinement. The spectra of PbSe samples are given in Figure 3(*b*). Exciton peak position is shifted with particle size (an exciton absorption maximum occurs at 0.83 or 0.77 eV for the synthesis temperature of 120 or 130 °C, respectively).

CdSe samples are characterised by clear band-edge luminescence at room temperature [Figure 3(*a*)]. Luminescence peak position is shifted with particle size. The photoluminescence maxima for the samples grown at 120, 150 and 180 °C lie at 2.50, 2.36 and 2.11 eV, respectively, and are in accordance with exciton peak position with Stokes shift of about 100 meV. This value is larger than that found for TOPO-stabilised CdSe nanocrystals.[12] A wide photoluminescence peak at 1.97 eV was observed for the CdSe sample with a minimal particle size (growth temperature of 120 °C). It can be related to partial

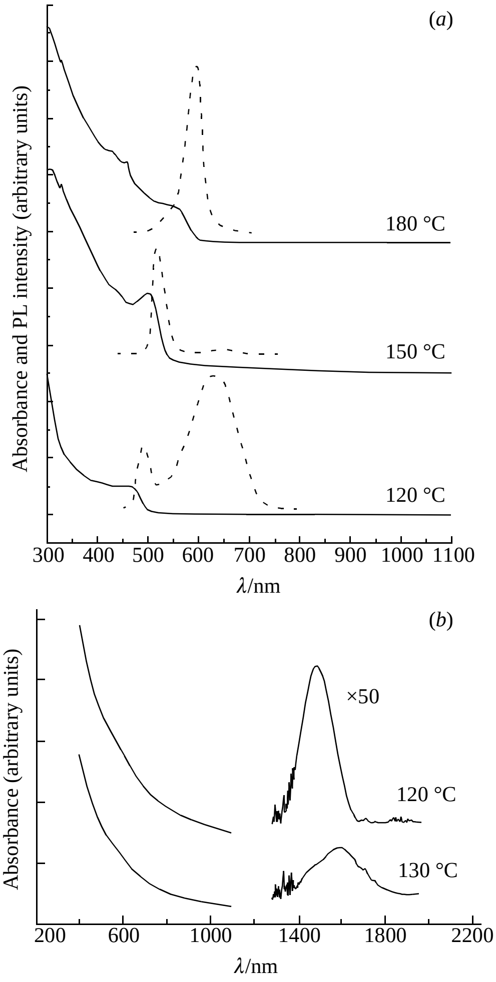

Figure 3 Optical absorption (solid lines) and photoluminescence (dot lines) spectra of (*a*) CdSe and (*b*) PbSe samples. Figures at the curves indicate growth temperatures. Spectra are shifted along absorbance axes to distinguish different samples.

oxidation of the sample under storage in air and correspond to the oxygen defect luminescence.

Thus, PbSe and CdSe quantum dots were synthesised using oleic acid as a stabilising agent. Optical measurements revealed the quantum-dimensional properties of the samples.

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