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Thiol-stabilized CdSe and CdTe Nanocrystals in the Size Quantization Regime: Synthesis, Optical and Structural Properties

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SUMMARY: We report on the recently developed method for the synthesis, optical, and structural properties of CdSe and CdTe nanocrystals. They were formed in aqueous solutions at moderate temperatures by a wet chemical route in the presence of thiol molecules as effective stabilizing agents. The size-selective precipitation technique was applied for the post-preparative nanoparticle fractionation into a series of CdSe and CdTe nanocrystals with extremely narrow size distributions exhibiting mean cluster sizes in the range of 2 to 4 nm. The nature of stabilizing agent (mercaptoalcohols and mercaptoacids) had an important influence on the particle size and determines largely the photoluminescence properties. The nanocrystals were characterized by means of UV-vis absorption and photoluminescence spectroscopy, X-ray diffraction, and high resolution transmission electron microscopy (HRTEM).

Nanometer-sized semiconductor particles belong to a state of matter in the transition regime between molecules and bulk materials. Because of the quantum confinement effect, nanoparticles show unique physical and chemical properties when their size is smaller than the dimension of the exciton. Control of the nanoparticle size, the size distribution and the nanoparticle surface allow us to understand and utilize their special properties: size-dependent bandgap shift, photoluminescence and electroluminescence behavior, nonlinear optical properties, structural and phase transitions [1-3]. Therefore, the small particle research includes three main topics: synthesis of nanoparticles with narrow size distribution and controlled surface properties, their precise structural and optical characterization followed by the utilization of their unique properties in nanotechnology. In this communication we report on the wet chemical synthesis of a series of CdSe and CdTe nanocrystals with extremely small sizes stabilized with thioalcohols or thioacids.

Aqueous colloidal solutions of CdSe and CdTe nanoparticles have been synthesized through the addition of freshly prepared oxygen-free NaHSe or NaHTe solutions to N_2-saturated $Cd(ClO_4)_2 \cdot 6H_2O$ solutions at pH 11.2 in the presence of different thiols (RS) as stabilizing agents

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following the method described in Ref. [4]. The molar ratio of Cd^{2+}:Se^{2-}(Te^{2-}):RS^- was chosen as 1:0.5:2.4. The particle size was controlled by the duration of the heat treatment and through post-preparative size-selective precipitation. The nature of stabilizing agent (2-mercaptoethanol, 1-thioglycerol and thioglycolic acid) also had an important influence on the cluster size. Red shift of the absorption egde accompanied by the growth of the cluster occured about 6 times faster for thioglycolic acid-stabilized nanoparticles in comparison with thioglycerol-stabilized ones.

The size-selective precipitation technique [4] was applied for the post-preparative nanoparticle fractionation into a series of CdSe and CdTe nanocrystals with extremely narrow size distributions exhibiting mean cluster sizes in the range of 2 to 4 nm. This technique allows the gram scale preparation of redispersible cluster powders which can be handled like ordinary chemical substances. The nanocrystals were characterized by means of UV-vis absorption and photoluminescence spectroscopy, X-ray diffraction and high resolution transmission electron microscopy (HRTEM).

All nanocrystals synthesized were in the size quantization regime and showed a well-developed maximum near the absorption onset which was ascribed to the first excitonic transition. In some cases transitions at higher energy were also observed. The size dependent shift of the bandgap energies was described reasonably by a finite depth potential well model in the framework of the effective mass approximation [5]. Two types of nanocrystal photoluminescence were observed for different cluster samples: an emission near the absorption onset tunable with particle size ("excitonic" photoluminescence) and a broad emission strongly red-shifted from the absorption onset which is practically independent of the particle size ("trapped" photoluminescence from surface trap states).

Crystal structure and particle sizes for CdSe and CdTe samples were derived from powder X-ray diffractograms and HRTEM images. Both CdSe and CdTe nanocrystals exhibited cubic (zincblende phase) crystalline structure. The broadness of the diffraction peaks increased gradually with a decrease of particle size. A reflection maximum appeared also in the small-angle region of X-ray diffraction patterns of CdSe and CdTe samples due to a periodicity of the cluster arrangement which is a confirmation of the narrow size distribution of the particles. The existence of the lattice planes in the HRTEM image further confirmed the crystallinity of CdSe and CdTe nanoparticles. A predominance of edged crystallites was seen from the HRTEM micrographs.

Some characteristics of CdSe and CdTe nanoparticles capped with different thiols are summarized in Table 1.

Table 1. Comparison of size, position of the first excitonic transition, crystal structure and photoluminescence behaviour of CdSe and CdTe nanocrystals capped with different stabilizers

CdSe nanocrystals			
Stabilizer	2-mercaptoethanol	1-thioglycerol	thiglycolic acid
Crystal structrure	cubic CdSe		
Photoluminescence	trapped		
Position of the first Excitonic transition, nm	360-450	360-450	450-530
Size, nm	2.0-2.5	2.0-2.5	2.4-3.6
CdTe nanocrystals			
Stabilizer	2-mercaptoethanol	1-thioglycerol	thiglycolic acid
Crystal structrure	cubic CdTe		
Photoluminescence	excitonic + trapped		
Position of the first Excitonic transition, nm	460	470-620	470-620
Size, nm	2.5	2.5-4.0	2.5-4.0

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