THIOL-CAPPED CdSe AND CdTe NANOCLUSTERS: SYNTHESIS BY A WET CHEMICAL ROUTE, STRUCTURAL AND OPTICAL PROPERTIES

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ABSTRACT

CdSe and CdTe nanoclusters were formed in aqueous solutions at moderate temperatures by a wet chemical route in the presence of thiols as effective stabilizing agents. The nature of the stabilizing agent (thioalcohols or thioacids) had an important influence on the particle size and largely determined the photoluminescence properties. The nanoclusters were characterized by means of UV-vis absorption and photoluminescence spectroscopy, powder X-ray diffraction, high resolution transmission electron microscopy, and extended X-ray absorption fine structure measurements. CdSe and CdTe nanoclusters were crystalline, in the cubic zincblende phase, with mean sizes in the range of 2 to 5 nm depending on the preparative conditions and the post-preparative size-selective fractionation, and showed pronounced electronic transitions in the absorption spectra. Thioglycerol–stabilized CdTe nanoclusters possessed sharp band–egde photoluminescence being tunable with particle size.

INTRODUCTION

The properties of semiconductor nanoclusters whose size is smaller than the dimension of the respective bulk exciton are largely determined by their size and surface chemistry. Semiconductor nanoparticles showing a number of unique structural and optical features [1-4] have become the object of investigation in one of the most rapidly growing branches of chemistry and physics in the last decade. Generally the small particle research includes three main topics: the 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 and the structural and optical properties of a series of CdSe and CdTe nanoclusters with extremely small sizes stabilized with thioalcohols or thioacids.

EXPERIMENT

Aqueous colloidal solutions of CdSe and CdTe nanoclusters have been synthesized through the addition of freshly prepared oxygen-free NaHSe or NaHTe solutions to N_2-saturated $Cd(ClO_4)_2\ 6H_2O$ solutions at pH 11.2 in the presence of different thiols (RS) as stabilizing agents following the method of Ref [5]. 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, through post-preparative size-selective fractionation, and by the nature of the stabilizing agent (2-mercaptoethanol, 1-thioglycerol or thioglycolic acid).

The size-selective precipitation technique [6] was applied for the post-preparative nanoparticle fractionation into a series of CdSe and CdTe nanocrystals with narrow size distributions. This technique allows the gram scale preparation of redispersible cluster powders which can be handled like ordinary chemical substances.

RESULTS

The crystal structure and particle sizes for CdSe and CdTe samples were obtained from powder X-ray diffractograms and HRTEM images. Figure 1 shows typical XRD patterns of CdSe and CdTe nanoparticles with different sizes. For both CdSe and CdTe nanoparticles a predominant cubic (zincblende phase) crystalline structure could be derived from the diffractograms. The broadness of the diffraction peaks increased gradually with a decrease of particle size. A reflection maximum appeared also in the small-angle region due to a periodicity of the cluster arrangement which is a confirmation of the narrow size distribution of the particles. The mean particle sizes obtained from the diffractograms using the Bragg (small angle region) and Scherrer (wide angle region) equations laid between 2 and 5 nm.

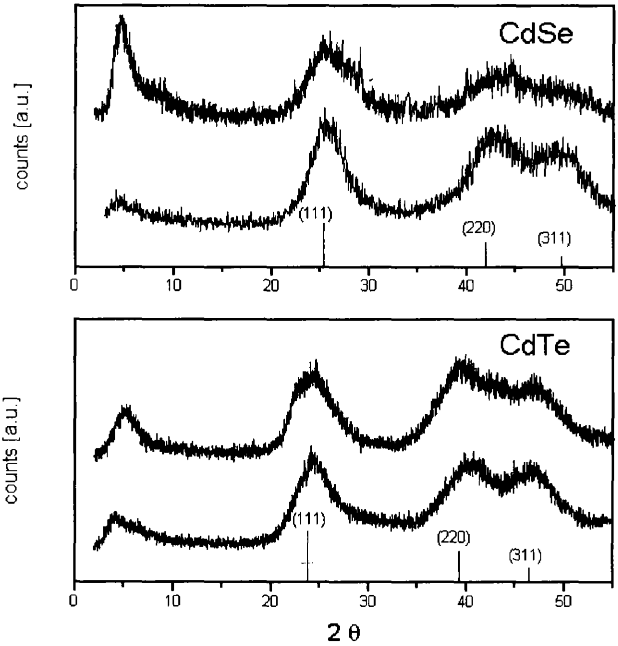

Figure 1. X-ray diffractograms of CdSe and CdTe nanoclusters with different sizes. In each panel: top spectrum – smaller, bottom – larger nanoparticles. The line spectra give the bulk CdSe and CdTe zincblende reflections with their relative intensities.

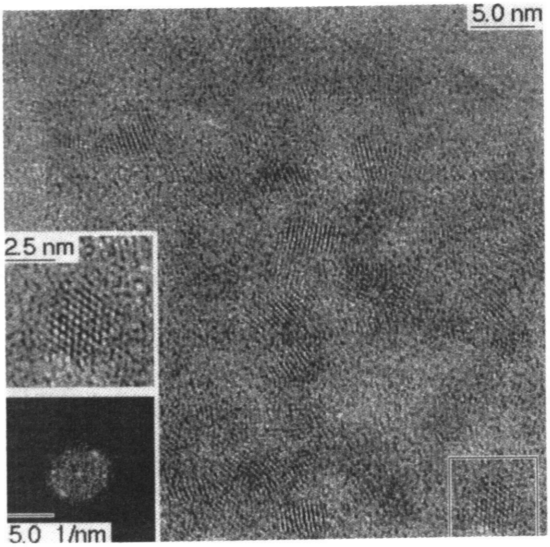

Figure 2. HRTEM image of CdSe nanoclusters. Inserts show a single CdSe particle with a corresponding FFT.

Figure 2 shows a HRTEM image of the nanoparticles (here: CdSe) with a corresponding Fast Fourier Transformation (FFT). The existence of the lattice planes in HRTEM images further confirmed the crystallinity of CdSe and CdTe nanoparticles. The average sizes estimated from HRTEM micrographs is generally larger than those obtained from XRD patterns. The reason could be an overestimation of the relative content of larger particles which are better seen in TEM.

As has been shown recently on a series of CdS colloids and colloidal crystals, EXAFS provides a valuable tool to determine structural and dynamical properties of nanoclusters [7]. Therefore, temperature-dependent EXAFS measurements were performed on 2-mercaptoethanol-stabilized CdTe nanocrystals in order to study properties of the CdTe core and the Cd-SR shell separately. Figure 3 shows the Fourier transforms of the EXAFS spectra of thiolcapped CdTe nanoclusters taken at the Cd K-edge and at the Te K–edge at 8K. The observed splitting of the first coordination shell into two contributions clearly indicates that the coordination of the Cd atom consists of Te atoms (from the cluster core) and S atoms (from the ligand shell). Attempts to fit this splitted peak by replacing sulfur by oxygen or by using an additional oxygen coordination resulted in poor fits with non-reliable fit parameters. In contrast, the respective Fourier transform taken at the Te K-egde shows only one coordination of tellurium which is identified as a Cd shell.

Based on the coordination numbers and the Cd/Te-ratio determined by EXAFS, the formula $[Cd_{54}Te_{32}(SCH_2CH_2OH)_{52}]^{8-}$ was suggested for these extremely small (2.5 nm in diameter) CdTe nanoclusters [8]. The underlying structure is a tetrahedral CdTe core (zincblende) partially coated by a Cd-SR surface layer.

The interatomic distance of the Cd-Te bonds was slightly contracted in CdTe nanoparticles with respect to the bulk material whereas a significant expansion of Cd-S bonds is observed. An isotropic model of elastic strain distribution in a spherical core-shell system of a zincblende CdTe core, heteroepitaxially overgrown by a CdS monolayer described the experimental results reasonably well [8].

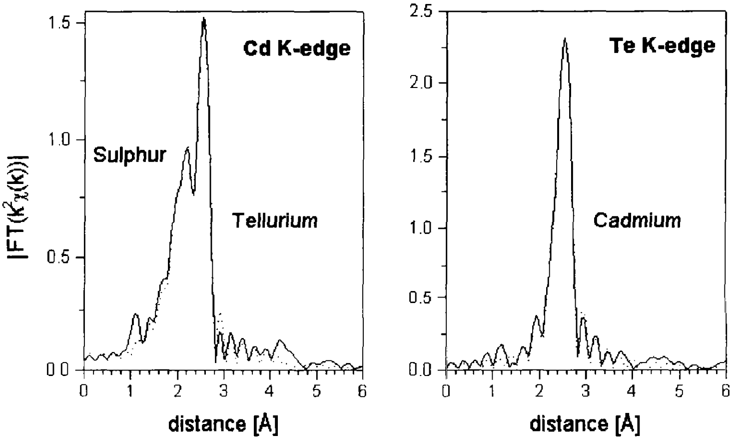

Figure 3. Fourier transforms (measured curves - solid, fits - dashed lines) of the EXAFS spectra of 2-mercaptoethanol-stabilized CdTe nanoclusters at 8 K at the Cd K-edge and at the Te K-edge.

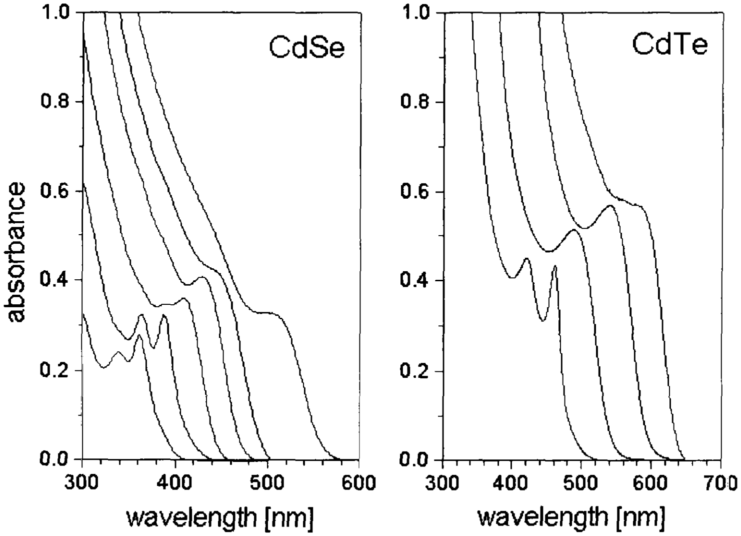

Figure 4. Absorption spectra of CdSe and CdTe nanoclusters with different sizes.

All nanoparticles 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 (Figure 4). In the case of the smallest CdSe and CdTe nanoclusters transitions at higher energy were also observed. The size dependent shift of the bandgap energies was described reasonably well by a finite depth potential well model in the framework of the effective mass approximation [9].

Both CdSe and CdTe nanoparticles possessed photoluminescence. All CdSe nanoparticles showed only a relatively weak broad emission strongly red-shifted from the absorption onset which is practically independent of the particle size ("trapped" photoluminescence). The smallest (2–mercaptoethanol stabilized) CdTe nanoparticles also showed the trapped photoluminescence only, which coincides with the proposed EXAFS–based model of a CdTe tetrahedral core partially coated by a Cd-SR layer with some uncoordinated Te atoms on the surface providing hole trap states [8].

In contrast, CdTe nanoparticles capped with 1–thioglycerol or thioglycolic acid possessed, besides a weak trapped emisson, a sharp emission near the absorption onset ("excitonic" photoluminescence) which was tunable through the visible spectral range from green to red (Figure 5) with particle size. The quantum yield of this excitonic emission at room temperature was approximately 3–5 %. It was found for CdTe nanoparticles stabilized with thioglycolic acid that the photoluminescence efficiency strongly depends on the pH value of the colloidal solution [10]. The maximum quantum yield at room temperature increased up to 18 % when the pH value of the CdTe solution was brought to 4.5. The optical spectroscopy studies implied that the pH-dependent behavior of the CdTe nanocrystals' photoluminescence was caused by structural changes on the surface. In the acidic range a shell of cadmium-thiol complexes was formed around the CdTe core causing the drastic enhancement of the photoluminescence quantum yield.

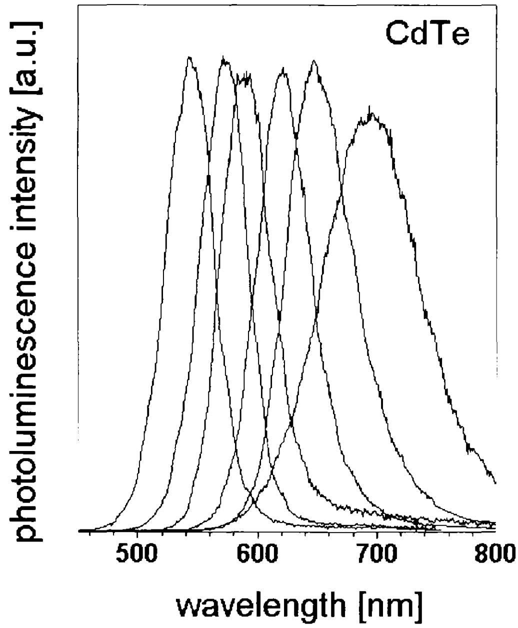

Figure 5. Luminescence spectra of 1–thioglycerol–capped CdTe nanoclusters with different sizes.

CONCLUSIONS

We report on a recently developed method for the synthesis, and on the structural and optical properties of thiol–stabilized CdSe and CdTe nanoclusters in the size–quantization regime. Powder X-ray diffraction, HRTEM and EXAFS measurements provide valuable tools for the structural characterization of nanosized samples. The size–dependent photophysical properties of CdTe nanoclusters make them promising candidates for application in photovoltaic devices.

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