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Temperature effect on the growth of colloidal CdTe nanotetrapods

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The colloidal CdTe nanotetrapod growth from oleic acid based precursor was studied and the effect of the synthesis temperature on the tetrapod morphology was shown.

Colloidal semiconductor nanocrystals are interesting for the development of light-emitting diodes, solar cells and lasers because of their unique size-dependent optical properties.[1–4] The colloidal synthesis of nanocrystals with the size of a few nanometers is a complex process, in which nucleation and growth play an important role. These processes have a crucial impact not only on reproducible synthesis of nanocrystals with desired size and narrow size distribution but also on nanocrystal morphology control.[5] Recently, nanocrystals of II–VI semiconductors with a complicated shape like rods, tetrapods and hyperbranched structures have been grown by varying the initial precursor concentrations, the nature of surfactants and precursors.[6–9] Perfect CdTe tetrapods were synthesized with a high yield using alkyl phosphonic[10,11] and fatty acids[12] based cadmium precursors. The main parameter to vary the length and diameter of tetrapod arms is the precursor concentration or activity.[10,12]

In this work, the temperature dependence of the growth of colloidal CdTe tetrapod-shaped nanocrystals from oleic acid based precursor was studied. The evolution of the tetrapod size was systematically studied by transmission electron microscopy (TEM), and optical characteristics were studied by optical absorption. The precursor concentration was held constant in all syntheses; the only parameter changed was the growth temperature.

CdTe tetrapods were prepared by the modified method proposed by Peng[12] using oleic acid as a surfactant. Nanocrystals were grown out in a noncoordinating solvent (diphenyl ether) under an inert atmosphere. The [Cd]:[Te] molar ratio was 1:1, and the [Cd]:[oleic acid] molar ratio was 1:3. In a typical synthesis, a mixture of cadmium acetate dihydrate (0.1333 g, 0.5 mmol), oleic acid (0.5 ml, 0.15 mmol) and Ph_2O (5 ml) was heated at 140 °C for 60 min under argon flow to remove acetic acid and water. Then, the solution was heated up to a desired temperature and 0.5 ml of a 1 M solution of tellurium in trioctylphosphine was injected quickly. Precursor injection temperature T_i was 160–240 °C, so that growth temperature T_g was less by 5–10 °C because of fast temperature drop after injection (Table 1). Overall synthesis duration was 5 min.

The kinetics of growth was studied by optical absorption. Aliquots of 50 μl were taken from the reaction solution at growth time t. Aliquots were diluted with hexane up to 1 ml for absorption measurements. Optical absorption study was performed on a Cary50 (Varian) spectrometer at 300–700 nm and room temperature. Optical density A and wavelength of the lowest excitonic maximum λ were analyzed. TEM measurements were performed using an LEO912 AB Omega microscope. CdTe tetrapod samples for TEM were purified by precipitation with acetone and redispersion in hexane.

Table 1 Growth conditions and corresponding characteristics of tetrapods: mean diameter D and length L of arms, and excitonic wavelength λ.

T_i/°C	T_g/°C	t/s	D/Å	L/Å	L:D	λ/nm
160	154	300	29±4	83±13	2.9:1	565
180	173	300	25±4	86±12	3.4:1	598
200	192	22	21±3	57±14	2.7:1	560
		300	27±4	77±19	2.9:1	615
233	225	16	24±3	55±8	2.3:1	604
		65	34±3	67±8	2.0:1	632
		300	34±4	72±10	2.1:1	652
240	235	300	38±4	60±9	1.6:1	653

The growth of tetrapod-shaped nanocrystals was observed for all synthesis temperatures as confirmed by TEM (Figure 1). With increasing the synthesis temperature the tetrapod arm length L decreased while the arm diameter D increased (Table 1). Observed aspect (L:D) ratio decreased from 3.4:1 to 1.6:1 when the growth temperature increased from 180 to 240 °C.

Tetrapod absorption spectra had a pronounced excitonic peak with a full width at half-maximum in the range of 30–40 nm (Figure 2, insert). The modification of absorption spectra during the growth at T_i = 160 °C is shown in Figure 2. Low temperature allowed us to investigate the growth process at reduced rates of nanocrystal formation. Analysis of absorption spectra showed that the tetrapod growth passes through a stage of formation of an intermediate. In addition to excitonic peak, a new absorption peak with a maximum at 450 nm was detected in absorption spectra and its wavelength was invariable during the growth. At higher temperatures of growth, this absorption maximum was

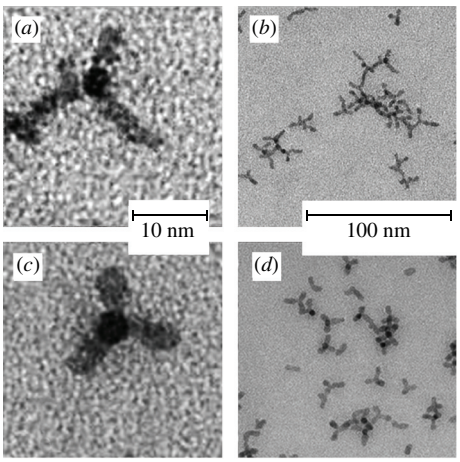

Figure 1 Individual CdTe tetrapod TEM image and image of ensemble of tetrapods grown at (*a*), (*b*) T_i = 180 °C and (*c*), (*d*) T_i = 240 °C.

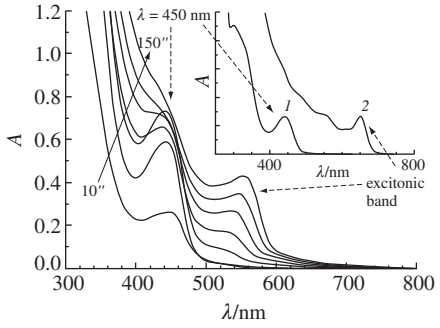

Figure 2 Modification of absorption spectra during growth of CdTe tetrapods at T_i = 160 °C. Insert: absorption spectra of (*1*) purified intermediate and (*2*) CdTe tetrapods grown at T_i = 240 °C. All spectra were taken at room temperature.

also observed at the same wavelength but at earlier times. The compound (intermediate) with the same absorption maximum (Figure 2, insert) was prepared by aging a precursor mixture at room temperature. The optical density of the intermediate at 450 nm passed through a maximum during tetrapod growth (Figure 3). This indicates the intermediate transformation to CdTe tetrapods. We suppose that the nature of the intermediate may be CdTe clusters. The magic-sized cluster formation during the growth of aggregated[13] or spherical[14] CdTe nanocrystals was already demonstrated. An absorption band at 450 nm corresponds to CdTe cluster of 2.4 nm in size with zinc-blend structure.[13] The role of magic clusters in formation of CdSe tetrapods was mentioned by Peng.[15]

The temporal variation of lowest excitonic wavelength and optical density for samples synthesized at different temperatures are shown in Figure 3. Two distinct stages of optical density variation were observed. Optical density increases at the initial stage that may be attributed to either nanocrystal concentration rise due to nucleation or nanocrystal extinction rise due to increase of arm length. The tetrapod anisotropy results from fast growth,[10] and the growth rate is defined by supersaturation. Therefore, the first stage in Figure 3 may correspond to the high initial supersaturation. The duration of the first stage is about 60 s excepting T_i = 160 °C, for which the

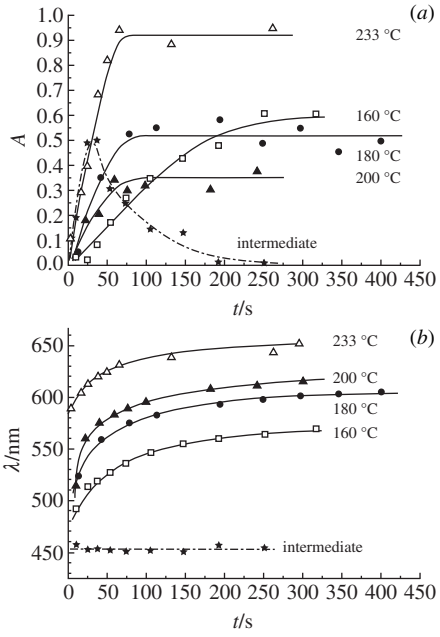

Figure 3 Temporal variation of (*a*) optical density *A* and (*b*) wavelength λ at the excitonic peak for tetrapods grown at different temperatures T_i. Data for intermediate given for the sample grown at T_i = 160 °C. The optical density of intermediate was corrected for tetrapods absorption background.

optical density increases during all the time. We think that this temperature is low to produce a considerable quantity of tetrapods and supersaturation keeps over a long period of time. This fact is in agreement with exceptional aspect ratio for tetrapods grown at 160 °C. After finishing of first stage, the optical density remains nearly constant (the growth stage). Maximal optical density was observed for the nanocrystals grown at the highest temperature T_i = 240 °C. At the same time, the excitonic transition wavelength monotonically increases during the synthesis for all temperatures, which indicates the increase of tetrapod size. TEM data (Table 1) confirm the increase of the tetrapod arms in length and diameter by 20–30% during the growth stage. The aspect ratio of tetrapod arms mainly depends on the synthesis temperature. An increase in the temperature results in a higher initial supersaturation and rapid nucleation. Cadmium precursor depletion on the nucleation results in decreasing of the growth rate. Hence, fast anisotropic growth of the tetrapod arms takes place during a shorter time and aspect ratio decreases. L. Manna *et al.*[10] reported on the effect of cadmium concentration on the tetrapod aspect ratio. Higher Cd/Te ratios keep the reaction in the anisotropic growth regime for a longer time, leading to longer arms.

In conclusion, the temperature dependence of the growth of CdTe tetrapods with oleic acid as a surfactant was studied by optical absorption and TEM. The growth of tetrapod-shaped nanocrystals was observed at 160–240 °C. The tetrapod growth passes through the stage of formation of an intermediate, which has a characteristic absorption band at 450 nm. At fixed precursor concentrations, the synthesis temperature mainly affects the tetrapod arm aspect ratio, as confirmed by TEM. Higher temperature results in shorter arms with larger diameter; therefore, the aspect ratio decreases from 3.4 to 1.6 as the temperature varies from 180 to 240 °C.

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