Short communication

Eu(III)-induced room-temperature fast transformation of CdTe nanocrystals into nanorods

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ABSTRACT

A fast and mild synthesis method of highly crystalline CdTe nanorods (NRs) was developed by adding europium nitrate hexahydrate to an aqueous solution of CdTe nanocrystals (NCs) at room temperature within 30 min. It was suggested that strong coordination strength of Eu(III) decreases zeta potential, thereby accelerates aggregation of NCs, and favors the transformation process from NCs to NRs. The oriented attachment of aggregated particles was suggested as a major path for the formation of highly crystalline NRs under experimental conditions. The proposed extremely fast room-temperature methodology opens up novel pathways for the synthesis of one-dimensional (1D) semiconductor nanostructures with high crystallinity, which would become potential candidates for many practical applications such as photovoltaics, circuit design and fabrication of functional architectures.

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1. Introduction

One-dimensional (1D) nanostructures, including nanowires (NWs), nanorods (NRs) and nanotablets (NTs), have become a focus of interdisciplinary research in recent years. Because of the 1D quantum confinement effects, they have potential applications in the fields of nanosensors [1], photovoltaic devices [2], electronics as well as photonics [3]. Naturally, the synthesis methods of these 1D nanostructures are the prerequisite. The synthetic methods of NWs and NRs, mostly based on point-initiated uniaxial growth of the crystal, such as the use of hard (alumina membrane) [4] and soft (rodlike micelle) [5] templates, seed-mediated growth in solution [6], etc. These solution-based strategies are particularly of preference due to the synthetic flexibility and possibility of controlling the surface chemistry. However, the weakness of the strategies is that they demand drastic reaction conditions such as high temperature.

An alternative approach to obtain NRs or NWs is the assembly of zero-dimensional (0D) nanoparticles (NPs) preformed from colloidal suspensions [7–12]. Due to its simplicity, versatility, and low cost, self-assembly is an important fabrication method in nanochemistry and nanotechnology [13]. Kotov et al. [10] showed that the feasibility of the spontaneous organization of CdTe nanocrystals (NCs) into crystalline NWs can be realized during several-day aging process at room temperature. In a very recent publication [12], George Thomas and co-authors reported highly crystalline CdTe NWs with hexagonal wurtzite structure were obtained at higher concentrations of hydrazine $(2.0 \, \text{mol L}^{-1})$ through the recrystallization of linearly assembled aggregated CdTe NPs with a zinc blend structure after 36 h at room temperature. Rogach and collaborators [11] have observed that standard physiological phosphate buffer solution could further reduce the electrostatic repulsion between the NCs, thereby the NWs were observed after 6–8 h of incubation. Zhang et al. [14,15] reported that 1D wurtzite CdTe nanostructures can be prepared in aqueous media by storing CdTe precursor solution in the presence of TGA for 2 h, yet the temperature must be increased to 80 °C. Although these authors have reported the transformation process from CdTe 0D to 1D, there are still some open issues such as long-time consuming and harsh reaction conditions, etc. Herein, we report a fast, mild synthesis method of CdTe NRs by adding europium nitrate hexahydrate to an aqueous solution of CdTe NCs at room temperature within 30 min. Using the optical and microscopic studies, the transformation of CdTe NCs to NRs has been investigated, and the intermediate steps of the transformation process were recorded. The oriented attachment of the aggregated particles was suggested as a major path for the formation of highly crystalline CdTe NRs. It was proposed that strong coordination strength of Eu(III) decreases zeta potential, thereby accelerates aggregation of NCs substantially, and favors the transformation process from NCs to NRs. The high crystallinity NRs would become potential candidates for many practical applications such as photovoltaics, circuit design and fabrication of functional architectures, etc.

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2. Experimental

2.1. Apparatus

All steady-state fluorescence measurements were made with a Hitachi F-4500 fluorescence spectrophotometer (Tokyo, Japan) equipped with a R3896 red-sensitive multiplier and a 1 cm quartz cell. Ultraviolet–visible (UV–vis) absorption spectra were recorded with a Hitachi U-3010 spectrophotometer (Tokyo, Japan). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were recorded using JEOL 2010 operating at an acceleration voltage of 200 kV. The CdTe NCs and NRs dilute solutions were deposited onto copper grids with carbon support by slowly evaporating the solvent in air at room temperature. X-ray powder diffraction (XRD) patterns were taken on a Japan Rigaku D/max γ_A X-ray diffractometer (XRD-6000) equipped with graphite monochromatized Cu-Kα radiation ($\lambda = 1.54060$ Å). X-ray photoelectron spectroscopy (XPS) was measured on a thermoelectron instrument (Thermo-VG Scientific ESCALAB 250). The fluorescence lifetime and fluorescence polarization (FP) signals were measured with the time correlated single photo counting technique on the combined steady-state and lifetime spectrometer (Edinburgh Analytical Instruments, FLS920). All pH values were measured with a model PHS-3C meter (Hangzhou, China). Fluorescence lifetime and FP signals were measured.

2.2. Materials

All chemicals used were of analytical grade or the highest purity available. All solutions were prepared with double deionized water (DDW). Te powder (-60 mesh, 99.999%), thioglycolic acid (TGA, 99%), L-cysteine hydrochloride monohydrate (L-cys, 98%) and europium nitrate hexahydrate (Eu(NO$_3$)$_3 \cdot$ 6H$_2$O, abbreviated as Eu(III), 99.99%) were purchased from Alfa Aesar (Karlsruhe, Germany), cadmium chloride hemi (pentahydrate) (CdCl$_2 \cdot$ 2.5H$_2$O), NaBH$_4$ and other routine chemicals were acquired from Guoyao Chemical Reagent Company (Shanghai, China) and used as received without further purification.

2.3. Synthesis of CdTe NCs

The CdTe NCs were synthesized by refluxing an aqueous solution of CdCl$_2 \cdot$ 2.5H$_2$O and freshly prepared sodium hydrogen telluride (NaHTe) in the presence of TGA and L-cys as the stabilizers, basing on the reported method [16] with some slight modifications. In a typical process, CdCl$_2 \cdot$ 2.5H$_2$O (0.0444 g, 0.194 mmol) was dissolved in 100 mL of DDW, then TGA (20 μL, 0.28 mmol) and L-cys (0.0152 g, 0.0865 mmol) were added with vigorous stirring. The pH of the solution was adjusted to 11.00 by adding 1 mol L^{-1} NaOH solution. The reaction mixtures were deaerated with argon for 30 min. Then, 0.5 ml of oxygen-free 0.16 mol L^{-1} NaHTe solution, which was freshly prepared from Te powder and NaBH$_4$ in water, was injected into the above solution under vigorous stirring. The reaction mixture was refluxed in an oil-bath at ∼100 °C for 5 min. The CdTe NCs were arrested by reducing the reaction temperature.

2.4. Transformation procedure of CdTe NCs into NRs

It is known that one of the important steps in the transformation of NCs to NRs was the removal of excess stabilizer [10]. To accomplish this step, acetone was added dropwise until turbidity occurred. The precipitate and supernatant were separated through centrifugation. The resultant CdTe NCs were precipitated and washed for one time with acetone. Then the treated NCs were dried at room temperature in vacuum, and the purified CdTe NCs powder was redissolved in pH 11.00 NaOH solution. The pH of 8.20 was measured. Subsequently the solution of Eu (NO$_3$)$_3 \cdot$ 6H$_2$O was added into the purified NCs to induce the transformation from CdTe NCs to NRs. Here the element of Eu was presented in the form of trivalent ion (K_{sp} of Eu (OH)$_3 = 8.9 \times 10^{-24}$). All the experiments were performed under ambient conditions.

3. Results and discussion

3.1. Characterization of CdTe NCs

The typical UV–vis absorption spectra and fluorescence emission spectra of the CdTe NCs are shown in Fig. 1. The UV–vis absorption spectrum of the NCs (Fig. 1, curve a) shows a broad band with a characteristic first excitonic peak at 461 nm. On the other hand, the fluorescence spectrum shows a strong and narrow emission band centered at about 520 nm (Fig. 1, curve b), suggesting a narrow size distribution of as-prepared CdTe NCs hydrosols. The particles of the CdTe NCs were depicted in the TEM image in Fig. 2A. The average size was approximately 4 nm, and the facetted crystalline surfaces were already present. Scherrer line width analysis [17] of all shown peaks yields particle diameters around 4 nm, which is consistent with the TEM image. The corresponding powder XRD pattern was depicted in Fig. 3 (curve a). It exhibits the typical size-broadened reflections of blende-type CdTe, in good agreement with the previous report [18].

3.2. Characterization of CdTe NRs

After Eu(III) was added to the purified CdTe NCs within 30 min, highly crystalline CdTe NRs with average width of ca. 15 nm were observed (Fig. 2B). HRTEM images of crystalline CdTe NRs are shown in Fig. 2C and D. The lattice fringe spacing is 0.372 nm, which corresponds to the (111) lattice planes of cubic CdTe. These planes are aligned perpendicular to the NRs' long axis. The inset shows a Selected Area Electron Diffraction (SAED) pattern of these NRs. The XRD pattern of the NRs (Fig. 3, curve b) displays a typical zinc blende CdTe character (JCPDS file, no. 75-2086), which illustrates that the 1D nanostructure formation has no apparent impact on the crystallinity of the primary CdTe NCs. Moreover, the (111) reflection has strongly sharpened up which indicates that the NRs would form along the (111) lattice planes of CdTe. As seen in Fig. 1 of curve a′ and b′, the position of the first excitonic peak of 1D nanostructure in the UV–vis absorption spectrum shifts to longer wavelengths and the fluorescence maximum also
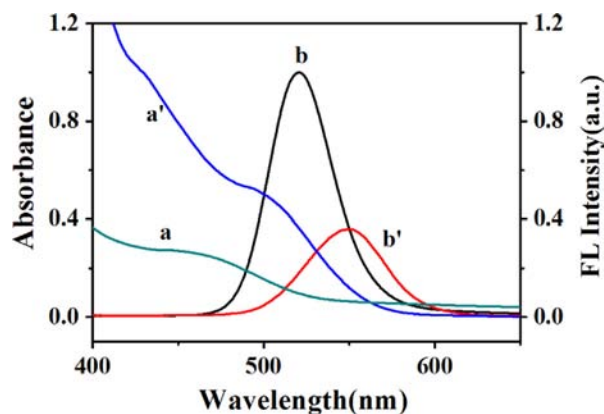

Fig. 1. UV–vis absorption and fluorescence spectra of CdTe NCs in the (a, b) absence and (a′,b′) presence of 1.0×10^{-7} mol L^{-1} Eu (III). The excitation wavelength was set at 380 nm.
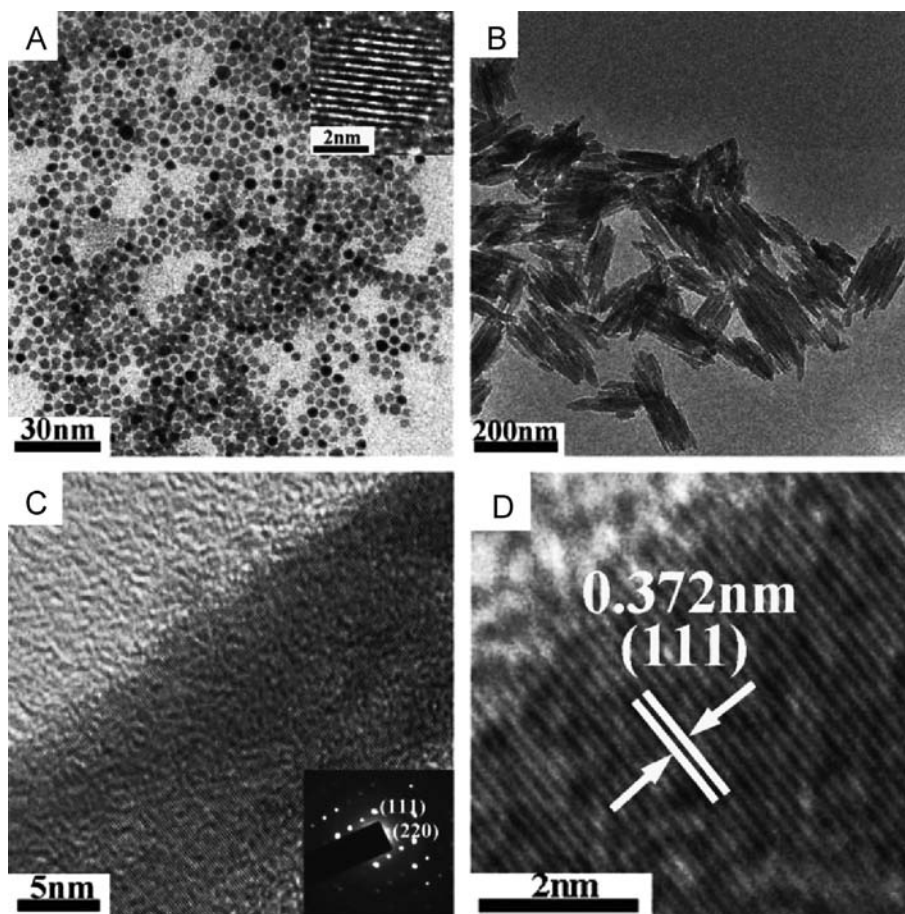
Fig. 2. (A) TEM image of CdTe NCs and HRTEM image of a single CdTe NC in the inset; (B) TEM image of CdTe NRs obtained after adding 1.0×10^{-7} mol L^{-1} Eu(III) into CdTe NCs for 30 min; (C, D) HRTEM images of a single CdTe NR and SAED pattern of the same CdTe NR in the inset of (C).
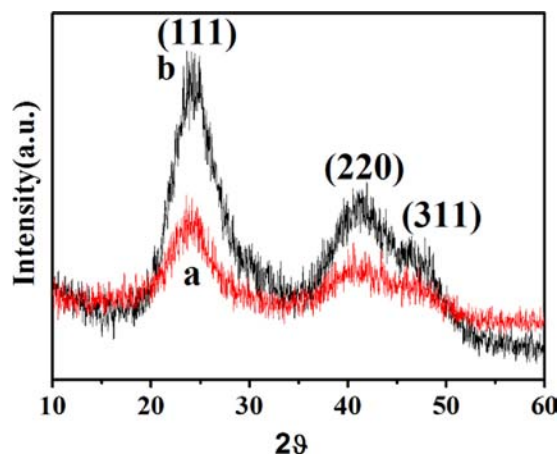

Fig. 3. XRD patterns of CdTe NCs in the (a) absence and (b) presence of 1.0×10^{-7} mol L^{-1} Eu (III).

undergoes a bathochromic shift with a dramatic decrease in intensity. The red shifts of the both absorption and emission spectra indicate an increase in the overall size of NPs. The NRs exhibit a weak fluorescence owing to the weaker quantum confinement of 1D nanostructures relative to that of 0D nanostructures [19]. Fig. S1 showed the decrease of fluorescence lifetime (from 35 ns to 27 ns) upon addition of Eu(III), the decline in the average lifetime once again indicated a increase in aspect ratio of CdTe nanostructures [20]. The bare CdTe NRs with a fluorescence emission peak at 550 nm were also synthesized, whose emission

peak position was in agreement with that of europium doped NRs (Fig. S2). The results of their fluorescence emission spectra show that fluorescence intensity of bare CdTe NRs is higher than that of europium doped NRs (Fig. S3(A)), possibly because the latter has strong structural defects and act as exciton drains or "black holes". Exciton can flow to such "black holes" and recombine without photon emission [21]. As shown in Fig. S3(B), fluorescence lifetime of the bare CdTe NRs was estimated to be 30 ns. In comparison with the fluorescence lifetime of 27 ns for Eu doped NRs, the enhancement in the average lifetime clearly indicates reduction in the rate of nonradiative charge recombination [12].

3.3. Intermediate steps from CdTe NCs to NRs

In order to reveal the intermediate steps, the transformation process of NCs into NRs in the presence of Eu(III) was detected by TEM. In the absence of Eu(III), only well-dispersed CdTe NCs were presented (0 min, Fig. 4). In the presence of Eu(III), during the initial period (lower-panel of Fig. 4, 5–10 min), the diameter of the NCs increased to about 15 nm, which is essentially equal to that of the resulted NRs. After 20 min, the NRs were basically formed. Subsequently, Cd^{2+} and Te^{2-} ions were dissociated from smaller NPs within or surrounding agglomerates, and diffused into the linear assembly of NPs, finally filled in the gaps between them [12]. This process resulted in the formation of uniform NRs with high crystallization (lower-panel of Fig. 4, 30 min). The lengths and diameters of the CdTe NRs remained invariable on prolonging the incubation time to 60 min (lower-panel of Fig. 4). HRTEM images of a series of aggregated particles were shown in Fig. S4. It can be seen that the lattice planes of the depicted particles were almost
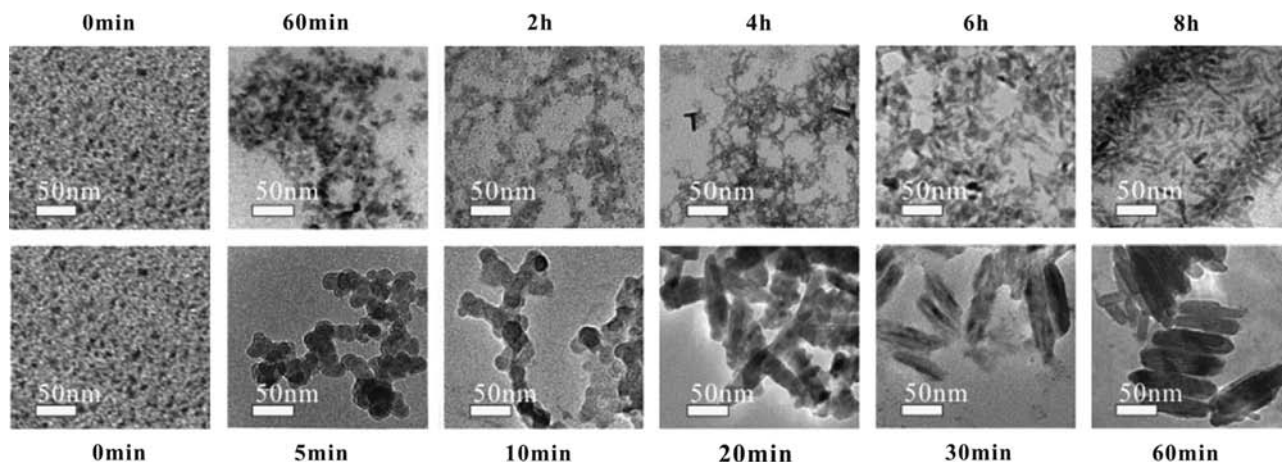
Fig. 4. (Upper panel) TEM images of CdTe NCs in the absence of Eu(III) after incubating different times. From left to right: 0 min, 60 min, 2 h, 4 h, 6 h, 8 h, respectively; (Lower panel) TEM images of CdTe NCs upon addition of 5.0×10^{-8} mol L^{-1} Eu(III) after incubating different times. From left to right: 0, 5, 10, 20, 30, 60 min, respectively.

perfectly aligned (Fig. S4(A)). Moreover, one recognizes that the lattice planes go straight through the contact areas, where the particles are epitaxially fused together. In addition, particle attachment took place preferentially along (111) direction, because the surface energy on the (111) plane is higher than other crystallographic planes such as (100) and (110) due to the high atomic density [22]. Fig. S4(B) shows that the particle growth also involves attachment characterized by a small misorientation in the interface. Thus, the presented experiments provide strong evidence that oriented attachment of aggregated particles is a major path during the formation of highly crystalline NRs under the described conditions. The bottlenecks between the adjacent particles must have been filled up and the surfaces must have been smoothened by conventional Ostwald ripening mechanism, which could also result in an overall growth of the NRs [9].

3.4. The role of Eu(III)

Above, we have been demonstrated the NCs to NRs transformation process can be rapidly realized. However, this process becomes quite slow in the absence of Eu(III). Generally, rodlike structures were observed after 6 h of incubation, and the uniform NRs with average width of ca. 5 nm and average length of ca. 40 nm were formed after a period of up to 8 h (upper-panel of Fig. 4). Without doubt, Eu(III) can accelerate the transformation process of 0D NCs to 1D NRs. At the same time, we noticed that an overall increase in the diameter when CdTe NCs were transformed into NRs in the presence of Eu(III). Due to the increase in the diameter of the NRs, the possibility of individual NCs organizing to NRs can be ruled out. These results indicated that CdTe NRs were formed through the organization of aggregated NCs. Nevertheless, what role does Eu(III) play concretely? Since surface charge and colloidal stability play major roles in the transformation of NPs to other shapes [23], zeta potential (ζ) measurements can provide valuable information. The surface charge density of CdTe NCs in the absence and presence of Eu(III) was investigated by determining the ζ. It was observed that the NCs possess a large negative ζ value (-46.6 mV) due to the presence of carboxylic and amino groups on the surface of the NCs. The strong repulsive force between the NCs prevents them from aggregation in solution. After partial removal of stabilizing ligands, ζ become less negative (~ -28.7 mV). Interestingly, a large change in ζ was observed upon addition of Eu(III) (~ -16.1 mV after 10 min). These results indicate that interaction between Eu(III) and the surface of CdTe NCs reduces the surface charge density of NCs greatly, leading to weak interaction between NCs. Importantly, strong coordination

effect between Eu(III) and ligands on the surface of the NCs reduced interparticle repulsion substantially, and gave rise to the NCs rapid aggregation, which is the rate-determining step of oriented attachment [24,25]. The XPS results showed that the NRs contain Cd, Te, Eu, and the amout of Eu is about 0.94% (wt%) (Fig. S5). It's worth noting that the 1D NRs were disaggregated to 0D NCs within 30 min upon addition of PO_4^{3-} (Fig. S6).These experiment facts further confirm the coordination effect of Eu(III) in above transformation process. Thus, we suggest that strong coordination strength of Eu(III) is the primary reason of fast transformation from CdTe NCs into NRs.

3.5. Crystalline phase of NRs

We noticed that, in previous reports [10,12,14,15], the lattice structure of TGA-capped CdTe NCs underwent reorganization from cubic zinc blende to hexagonal wurtzite in the process of 0D to 1D. At variance, here we only obtained zinc blende-type CdTe NRs. The reason can be ascribed to the following. First of all, According to the formula proposed by Yu et al. [26], the concentration of CdTe NCs in our experiments is calculated to be 1.9×10^{-5} mol L^{-1}, which is much lower than the literatures [10,12,14,15]. At lower concentration, the growth along the cubic (111) direction is dominant [27] in that the density of stacking faults is not high enough to induce the epitaxial growth of the wurtzite structure [28]. Secondly, as mentioned in Section 3.4, the NC–NC interaction was weakened after Eu(III) addition, leading to the accelerated growth speed of NRs. According to Ref. [28], this acceleration induces the preferential growth of zinc blende structure. Thirdly, according to the document [29], although the activation energy for phase transition from zinc blende to wurtzite for CdTe is low enough to allow the process to occur at room temperature, in our experiment the hexagonal wurtzite NRs were not observed after 12 h incubation because the coordination effect of Eu(III) could increase the activation energy for phase transition, and thus rupture and reformation of interatomic bonds can not be proceeded at room temperature.

3.6. Analytical applications

The FP signals of CdTe NCs were recorded with different concentrations of Eu(III). The FP signals measurements and parameter determinations are described in the supplementary materials. The FP signals of CdTe NCs are significantly increased with increasing Eu(III) concentration, and reach maximum at a concentration of 1.45×10^{-7} mol L^{-1}. A good linear relationship
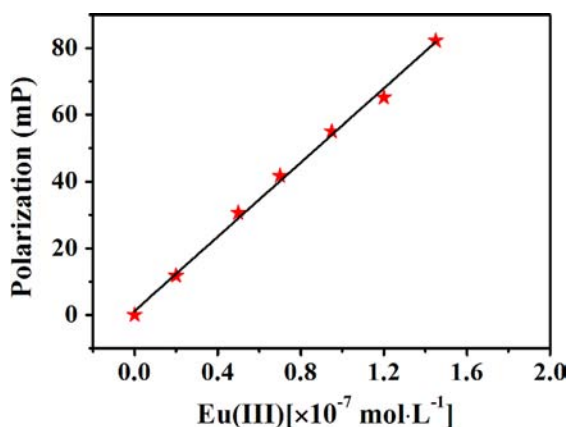
Fig. 5. The fluorescence polarization of the CdTe NCs vs. Eu(III).

($R^2 = 0.996$) was found between the FP signals and the concentrations of Eu(III) (Fig. 5). Then, we carefully compared the response of the CdTe NCs to Eu(III) ions with their responses to other metal cations. From Fig. S7, it can be seen that only Eu(III) ions effectively increase FP signals, showing a high selectivity of the probes to Eu (III). The proposed method was then applied for the determination of Eu(III) in synthetic samples, and the results of recovery were satisfactory (Table S1).

4. Conclusion

To recap, we have developed a fast and elegant room-temperature methodology for synthesizing uniform, highly crystalline and cubic zinc blende CdTe NRs. The highlight of this method is that the transformation of CdTe NCs to NRs can be quickly realized within 30 min, which is not only much faster than the previous reported method [11] of at least 6–8 h, but also decreases the reaction conditions to room-temperature. We suggest that strong coordination effect of Eu(III) decreases zeta potential, thereby accelerates aggregation of NCs, and favors the transformation process from NCs to NRs. The oriented attachment of the aggregated particles was suggested as a major path for the formation of highly crystalline CdTe NRs. Our proposed strategy opens up novel pathways for the synthesis of 1D semiconductor nanostructures with high crystallinity at room temperature, which would become potential candidates for many practical applications such as photovoltaics, circuit design and fabrication of functional architectures. Further experiments will be performed to investigate in detail the transformation mechanism of 0D/1D and the critical factors involved in the process. Meanwhile, it is expected that a direct FP sensing model will be developed based on the change in FP signals during rapid transformation between CdTe 0D NCs and 1D NRs.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2014.01.042.

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